VOLUMETRIC ANALYSIS.

COBLENTZ.

A MANUAL

OF

VOLUMETRIC ANALYSIS

TREATING ON THE SUBJECTS OF
INDICATORS, TEST-PAPERS, ALKALIMETRY, ACIDIMETRY, ANALYSIS BY
OXIDATION AND REDUCTION, IODOMETRY, ASSAY PROCESSES
FOR DRUGS WITH THE TITRIMETRIC ESTIMATION OF
ALKALOIDS, ESTIMATION OF PHENOL, SUGAR,
TABLES OF ATOMIC AND MOLECULAR
WEIGHTS

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PREFACE.

This manual is intended to serve as a systematic introduction to the principles of volumetric analysis based on modern theories. Especial attention has been devoted to the theory of ionization and its application to indicators, also the necessary precautions as to dilution, temperature, and influence of disturbing elements—factors frequently overlooked in volumetric analysis.

As a guide for the selection of a proper indicator, the detailed descriptions are followed by a table which should be consulted by the beginner before carrying out a saturation titration.

The most important factor in volumetric analysis is the preparation and accurate standardization of the reagent solutions; in view of this, several different methods of standardization, with practical examples, are given in each case in order that the operator may learn to properly check his work.

Each different titration method is illustrated by one or more practical exercises which serve as aid to the student in the calculation of the various problems which present themselves.

In order to avoid possible confusion to the beginner direct percentage estimations are treated under a separate heading after the general principles have been thoroughly considered.

The readiness with which many standard solutions lose their titer on standing, the loss of time entailed in re-standardizing, also the convenience with which these empirical solutions may be prepared and utilized in titrating, led the author to devote a special section to this subject, which is continued throughout the text in the form of practical examples.

Under the titrimetric methods of alkaloid estimation, it has been the endeavor to impress upon the operator the necessity of accurately observing such important conditions as the careful selection and application of indicators, the nature and volume of the solvent, the precautions necessary in handling the very dilute standard solutions, etc., for unless all these are fully complied with no reliance can be placed upon results.

The didactic system (H = 1.000) of atomic weights has been adopted on the consideration that it is the oldest, most familiar and comprehensive to the student of chemistry.

NEW YORK CITY, *October, 1901.*

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VOLUMETRIC ANALYSIS.

CHAPTER I.

INTRODUCTORY.

The object of quantitative analysis is to ascertain the quantities by weight of the various constituents which enter into the composition of a compound. The methods employed in carrying out such an analysis may be divided into two classes: namely, gravimetric and volumetric.

In *gravimetric* analysis the chemist, through the addition of various reagents, converts the different constituents of the substance to be analyzed into insoluble compounds; these, after collecting, are accurately weighed, and through a knowledge of their composition it is a matter of calculation to determine the quantity of the several constituents present in the original compound. The operations of gravimetric analysis are necessarily slow, frequently complicated, and require great care and skill. These difficulties are largely overcome in volumetric analysis, which, wherever applicable, admits of great accuracy, with rapidity, and requires but simple apparatus.

In *volumetric* analysis a reagent is selected which gives with the substance to be determined certain characteristic reactions; the strength of this reagent is accurately fixed, and from the volume employed to bring about such a reaction the weight of the substance is readily determined by aid of the laws of chemical equivalence.

Standard Solutions.—These are aqueous solutions of the reagents, the strengths of which have been accurately set.

Titration.—This is the operation involved in adding the standard solution, from graduated vessels, to the solution of the substance to be examined.

Titer.—This term indicates the strength of one standard solution as compared with that of another, or its ratio to the latter.

The reagent (standard solution) employed should be one that readily reacts with the body examined; this reaction should be of such a nature that its termination can be readily distinguished by means of the eye alone or aided by means of a special class of substances, known as

Indicators.—These are solutions of certain sensitive compounds which, when added to the reacting fluids, produce either distinct changes of color or precipitates, as the case may be; such changes indicate the termination of the reaction.

APPARATUS.

Since all of the reagents employed in volumetric analysis are measured by volume, it is of the greatest importance that the measuring vessels be accurately graduated and the purity of the chemicals be beyond all question.

The Balance.

A short-arm, quick-weighing balance capable of carrying 200 Gm. and sensitive to $\frac{1}{5}$ of a milligramme is necessary. This is used for weighing the substances to be analyzed and also such chemicals as are employed in making the standard solutions. Also a balance is indispensable in testing the accuracy of pipettes, burettes, and measuring glasses.

Calibration.

Too much stress cannot be laid upon the care to be exercised in the selection of accurately graduated measuring vessels, for should there be any discrepancies among these, no reliance can be placed upon the results obtained. Not only should the graduations of each separate vessel be accurate, but they should correspond exactly one with another; for example, the ten cubic centimeters of an accurately calibrated pipette should be identical in volume with 10 cubic centimeters measured from each of the various burettes and graduated cylinders; also 250 or 500 Cc. measured from any one of the burettes should exactly fill the ¼ or ½ liter measuring flask.

If the accuracy of the calibrations cannot be guaranteed by a reputable supply house, it is advisable to verify them. This may be carried out by drawing off measured volumes of distilled water, at 15° C., into tared vessels and accurately weighing; any discrepancies may then be corrected by a new calibration by means of a diamond scratch. For testing the volume capacity of the ½ and 1 liter flasks and cylinders, which is very necessary, a balance of the capacity of one kilo, sensitive to five milligrammes, should be at hand.

It is the general custom (unless in special cases) to calibrate all measuring vessels, such as pipettes, burettes, measuring cylinders, etc., at the standard temperature of 15° C. The standard liter employed is the volume of a kilogramme of distilled water, at 15° C., weighed in air with brass weights. This modified standard * was adopted as a matter of convenience, owing to the numerous calculations, such as those involving the expansion of the solution, the container, and weighing in air, which form the necessary corrections in fixing the *true* volume of a liter at this temperature. The temperature at which the measuring vessels are calibrated is immaterial as long as they agree among themselves in their graduations. For example, a liter flask will not hold 1000 grammes of water at 25° C. if it was calibrated at 15° C., because of the expansion of the fluid; yet if 58.06 Gm. of sodium chloride were dissolved in sufficient water and made up to 1000 Cc. at 25° C., each cubic centimeter measured off *at this temperature* will contain exactly $\frac{58.06}{1000}$ part, or 0.05806 Gm.; hence vessels graduated at 15° C. can be used at any other temperature, provided the solutions are employed at a temperature not materially varying from that at which they were prepared. Therefore if our standard volumetric solutions are prepared at a temperature of either 20° or 25° or 30° C., then, when titrating, we should aim to maintain whichever standard we have selected.

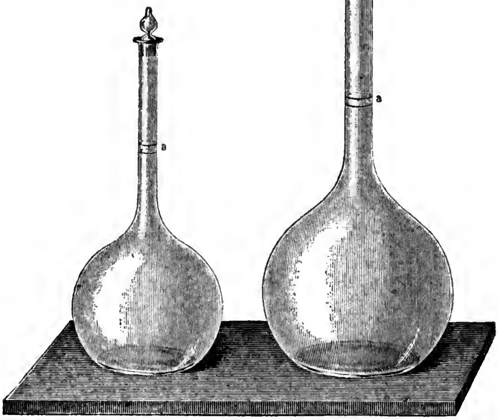

FIG. 1.—MEASURING FLASKS.

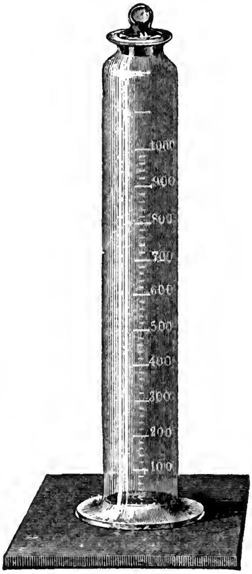

FIG. 2.—MEASURING CYLINDER.

Measuring Flasks and Cylinders.

The flasks (Fig. 1) which are employed in preparing the standard

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* The *true* standard liter of the metric system is the volume of a kilogramme of distilled water at 4° C., weighed *in vacuo*.

solutions are provided with long necks and accurately fitted glass stoppers; near the middle of the neck is a graduating line, which indicates the height to which the vessel is to be filled. These flasks are made in various sizes, being usually graduated to *contain* either 50, 100, 250, 500, or 1000 cubic centimeters at 15° C. If it is desired to *deliver* these volumes, then a second graduating line is placed slightly above the first; this allowance is necessary owing to the fluid which remains inside wetting the sides of the flask after draining off. Graduated measuring cylinders (Fig. 2) are frequently employed in place of flasks; they do not present the advantage of the latter in being tempered, so that if necessary their contents can be heated. The operator should never fail to allow the warm fluid to cool down to the temperature of the room or the selected standard temperature before diluting up to the proper volume.

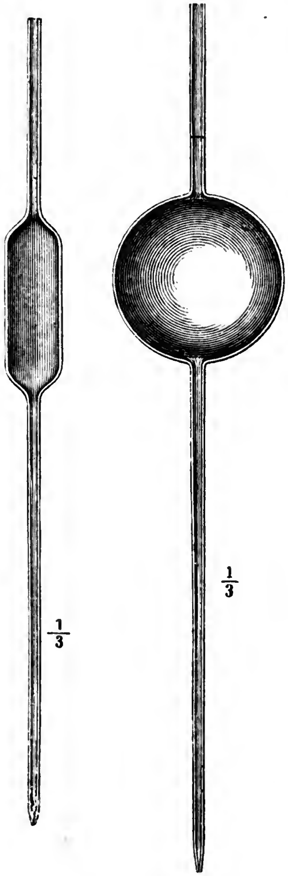

Fig. 3.—Pipettes.

Pipettes.

These useful instruments (Fig. 3) are graduated to *deliver* definite volumes of fluids at 15° C. Their measuring capacity is either 5, 10, 15, 20, 25, or 50 cubic centimeters. For measuring very small volumes, the one cubic centimeter pipette is employed; this consists of a long tube graduated to deliver tenths and hundredths of a cubic centimeter. All pipettes should be tested as to their accuracy; also the volumes which they deliver should correspond *exactly* with those of the burettes and cylinders; that is, the 5, 10, or 25 Cc. of a pipette should be identical in volume with the 5, 10, or 25 Cc. of the other graduated vessels. When emptying a pipette, the outside, if wet, should be quickly dried; the tip is then held against the inner side of the vessel into which it drains in order to hasten the flow and complete draining.

Burettes.

These are graduated vessels which are employed for the accurate delivery of the standard solutions. They consist of long glass tubes of uniform calibre, usually of a capacity of 25, 30, 50, or 100 cubic centimeters, graduated into divisions of 1 cubic centimeter and fractions thereof, which are either tenths or fifths. The calibrations extend between two points, the upper one (0) beginning a short distance below the top, and the lower one (25, 30, 50, or 100 Cc.) is placed slightly above the point where the tube begins to narrow toward the outlet. The fluid can be measured only between these extreme points.

The usual form of burette employed is that known as Mohr's (Fig. 4), which is fitted below with a short piece of heavy-walled rubber tubing, which is slipped over the narrowed extremity (*a*, Fig. 5), and if necessary tied (*b*). Into the other end of the tube is slipped a short piece of glass tubing (*d*) of small calibre drawn to a fine orifice; between the extremities of the rubber, a pinch-cock (*c*) is placed, and by pressing the tips it is caused to open and permit the flow of liquid from the burette. The pinch-cock may be replaced by inserting a glass bead or a short, rounded piece of glass rod inside of the tube; this should be of sufficient size to retain its position and not permit the liquid to pass through. It is operated by pressing the rubber tube slightly together at this point, forming a narrow channel, which permits the fluid to flow out at any rate desired. Burettes with the rubber attachment should not be employed in titrating with such sensitive solutions as potassium permanganate or silver nitrate. In such cases burettes provided with glass stop-cocks (Fig. 6) should be used; in fact, most operators

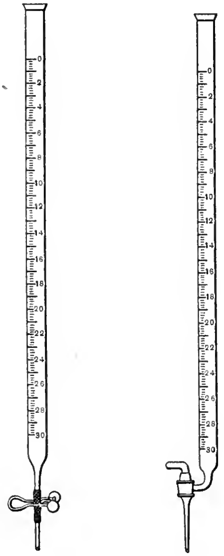

FIG. 4.—MOHR BURETTES.

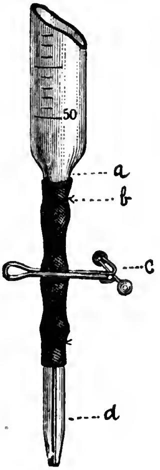

FIG. 5.—BURETTE OPERATED WITH PINCH-COCK.

prefer this form in all kinds of titrations. These, like all glass stoppers, have a tendency to stick if not properly lubricated; for this purpose petrolatum is best adapted.

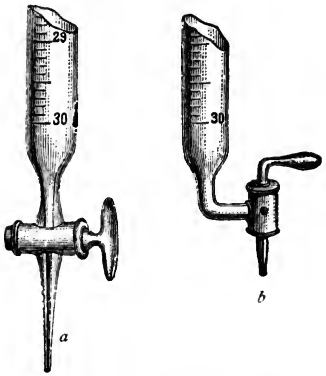

Fig. 6.—Burettes with Glass Stop-cocks.

Another form of burette is that shown in figure 7, in which the solution is allowed to drop from the rounded beak at the top of the burette. To accomplish this the instrument is slightly tipped, placing the thumb over the side tubulure; then, to regulate the dropping, the thumb is slightly raised and depressed. Among the older forms of burettes are those of Gay-Lussac (Fig. 8), which when used are inclined so that the solution drops from the beak of the smaller tube, which extends nearly to the top of the instrument. A stopper with a glass tube may be fitted into the open top of the burette, and by gently blowing into this, the rapidity of flow may be greatly increased.

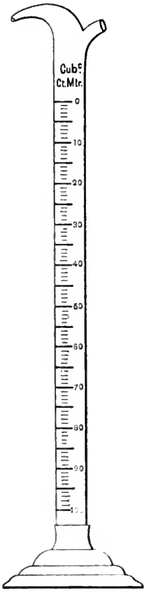

Fig. 7.—Modified Gay-Lussac Burette.

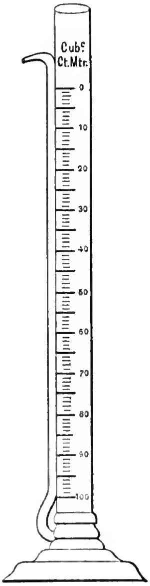

Fig. 8.—Gay-Lussac Burette.

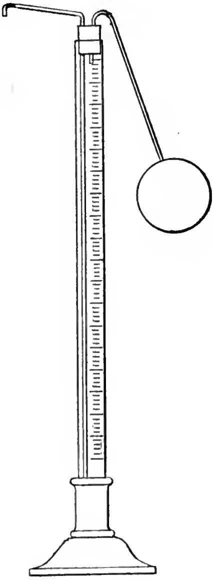

Fig. 9.—Mohr Upright Burette.

Figure 9 illustrates the Mohr upright burette, in which the rate of flow is controlled by pressing a rubber bulb which exerts an air pressure upon the fluid, forcing it upward and out of the delivery tube.

Reading off Burettes.—Beginners frequently find difficulty in making accurate readings of the height of the fluid column in the burette, owing to the peculiar appearance of its surface, as shown in figure 10, which is called the *meniscus.* There is a difference in volume if the height of the meniscus is read off on a line parallel with the upper edge, *o*, or the lower one, at *u*. But if we begin a titration by reading off from the lower edge of the meniscus, then all subsequent readings must be made from the same position. When the volumes are read off, the burettes must hang or stand perfectly perpendicular, as shown in figure 11, while the eye of the operator should be in a direct line with the surface of the fluid in the burette.

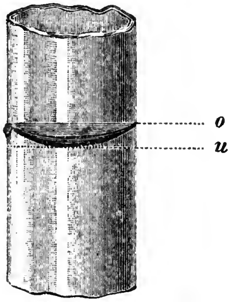

FIG. 10.—MENISCUS.

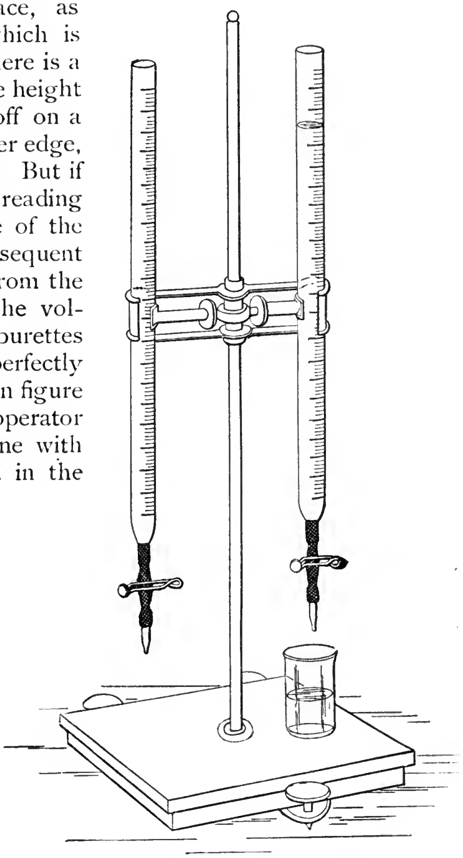

FIG. 11.—MOHR BURETTES WITH STAND.

To facilitate accuracy in reading, various devices have been proposed; one of the simplest (for colorless liquids) is that shown in figure 12, in which a piece of paper half black and half white is held against the back of the burette, the upper edge of the black portion being held a few millimeters below the level of the liquid; the lower concave curve of the meniscus then appears as a sharp black line which enables the operator to readily and accurately note the height of the fluid. Some burettes are specially constructed for the purpose of facilitating reading, being provided with white enameled sides and dark blue background (Fig. 13); the reflection of the dark band in the background with the meniscus produces an appearance as shown in figure 14. The point of the narrowest portion corresponds to the middle of the meniscus, thus enabling the operator to make very accurate readings. A convenient instrument, which avoids meniscus reading altogether, and can be employed for all kinds of fluids, is the Erdman float (Fig. 15). This consists of a small, cylindrical, closed tube, sufficiently weighted so that it will float upright, around the middle of which a line is scratched; this is placed in the fluid in the burette, and the height read off by comparing the ring (scratch) on the float with the divisions on the burette. Kreitling,* after an extended series

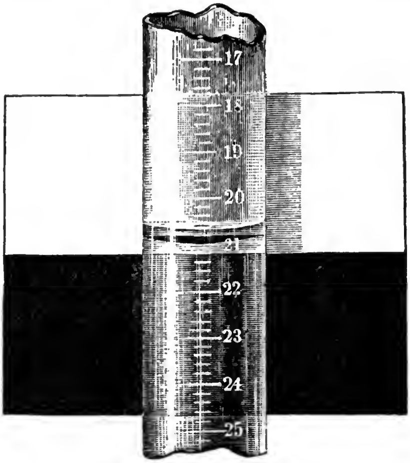

FIG. 12.—READING OF MENISCUS.

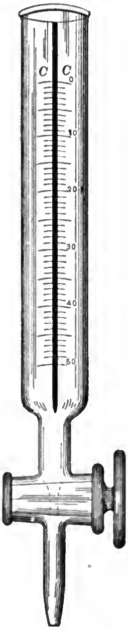

FIG. 13.—BURETTE (ENAMELED SIDES).

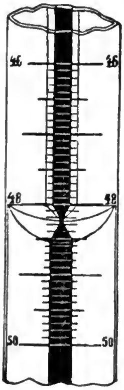

FIG. 14.—EFFECTS PRODUCED BY MENISCUS.

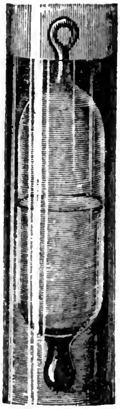

FIG. 15.—ERDMAN FLOAT.

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* Zeits. f. angew. Chemie, 1900 (34), 829; also Jour. Soc. Chem. Ind., 1900, 929.

of observations, advises against the employment of these floats as being fruitful sources of errors.

STANDARD SOLUTIONS.

The volumetric or standard solutions are the reagents employed in volumetric analysis. They are all of a definite strength, and are prepared by dissolving a given weight (in grammes) of the active reagent in a definite volume (in cubic centimeters) of distilled water.

Usually *the molecular weight of the reagent, expressed in grammes or a fraction thereof, is dissolved in sufficient water to make 1000 cubic centimeters* (*one liter*).

According to their set strength, these solutions are classified as follows:

Normal Solutions.—Expressed as **N** or $\frac{N}{1}$ **V. S.**

Volumetric solutions are designated as *normal* ($\frac{N}{1}$) when they contain in one liter (1000 Cc.) a quantity representing the molecular weight of the active reagent expressed in grammes and reduced to the valency corresponding to one atom of replaceable hydrogen or its equivalent.

Thus, in *monovalent* compounds the equivalent and molecular weights are identical; hence a normal standard solution of hydrochloric acid would contain its molecular weight, 36.18 grammes, of gaseous HCl in 1000 cubic centimeters. A normal standard solution of potassium hydroxide should contain 55.70 grammes of absolute KOH; or that of sodium hydroxide, 39.76 grammes of absolute NaOH.

In *bivalent* compounds, since they correspond in valency to two replaceable hydrogens, the equivalent would be one-half of the molecular weight; hence a normal solution of the bivalent sulphuric acid would contain $\frac{97.35}{2}$ or 48.675 grammes of absolute H_2SO_4 in 1000 cubic centimeters.

A normal solution of the bivalent oxalic acid would contain $\frac{125.08}{2}$ or 62.54 grammes of $H_2C_2O_4 + 2H_2O$ in 1000 cubic centimeters.

It will be seen from the following that 1000 Cc. of a $\frac{N}{1}$ V. S. of an acid (containing one molecule of a monovalent or one-half of a molecule of a bivalent compound) would be equivalent in neutralizing power to one molecule of sodium or potassium hydroxides or of ammonia or one-half of a molecule of calcium, strontium, or barium hydroxides or carbonates. On the same line of reasoning one liter of a $\frac{N}{1}$ V. S. of sodium, potassium, or barium hydroxides would be equivalent to one molecule of any monad acid or one-half of a molecule of a dyad or one-third of a molecule of a triad acid. One cubic centimeter (which represents the $\frac{1}{1000}$ part of the molecular weight) of a standard normal acid or alkali will be equivalent to $\frac{1}{1000}$ part of the molecular weight of a monad or $\frac{1}{2000}$ of a dyad alkali or acid.*

	MONAD $\frac{N}{1}$ V. S.		DYAD $\frac{N}{1}$ V. S.		DYAD $\frac{N}{1}$ V. S.		MONAD $\frac{N}{1}$ V. S.	
1000 Cc.,	36.18	Gm. HCl =	48.675	Gm. H_2SO_4 =	85.08	Gm. $Ba(OH)_2$ =	39.76	Gm. NaOH
100 Cc.,	3.618	" " =	4.867	" " =	8.508	" " =	3.976	" "
10 Cc.,	0.3618	" " =	0.4867	" " =	0.8508	" " =	0.3976	" "
1 Cc.,	0.03618	" " =	0.04867	" " =	0.08508	" " =	0.03976	" "

The value of a reagent expressed by its equivalent hydrogen-weight is only observed in the estimation of acids and alkalies. In such standard solutions as potassium dichromate, and permanganate, which are employed in oxidation analyses, also iodine and sodium thiosulphate, used in iodometry, either the molecular weight or a fractional part is taken.

Decinormal Solutions.—Expressed as $\frac{N}{10}$ or $\frac{N}{10}$ **V. S.**

These standard solutions contain in one liter (1000 Cc.) *one-tenth* ($\frac{1}{10}$) of the weight of the active reagent employed in the normal solution.

Thus, if a $\frac{N}{1}$ V. S. of hydrochloric acid contains 36.18 Gm. of HCl in one liter, a $\frac{N}{10}$ V. S. should contain 3.618 Gm. in the liter. A decinormal solution of silver nitrate ($AgNO_3 = 168.68$) would contain one-tenth of its molecular weight or 16.868 Gm. in 1000 Cc. Ten cubic centimeters of a decinormal ($\frac{N}{10}$) solution correspond to 1 cubic centimeter of a normal ($\frac{N}{1}$) solution.

Centinormal Solutions.—Expressed as $\frac{N}{100}$ or $\frac{N}{100}$ **V. S.**

The centinormal solution contains in one liter (1000 Cc.) *one-hundredth* ($\frac{1}{100}$) of the weight of the active reagent employed in the normal solution.

Thus, if a normal solution of potassium hydroxide contains 55.70 Gm. of dry KOH in one liter, a centinormal solution would contain $\frac{55.70}{100}$ or 0.557 Gm. in one liter, each cubic centimeter representing 0.000557 Gm.

One cubic centimeter of a $\frac{N}{1}$ V. S. is equivalent in strength to 10 Cc. of a $\frac{N}{10}$ V. S., which, in turn, is equivalent to 100 Cc. of a $\frac{N}{100}$ V. S. For example:

	1 Cc. $\frac{N}{1}$ V. S.	Will neutralize or is equivalent to	10 Cc. $\frac{N}{10}$ V. S.	Will neutralize or are equivalent to	100 Cc. $\frac{N}{100}$ V. S.	
KOH	= 0.0557	Gm.	0.00557	Gm. × 10	0.000557	Gm. × 100
NaOH	= 0.03976	"	0.003976	" × 10	0.0003976	" × 100
HCl	= 0.03618	"	0.003618	" × 10	0.0003618	" × 100
H_2SO_4	= 0.048675	"	0.0048675	" × 10	0.00048675	" × 100

Deci- and centi-normal solutions are employed in such estimations where the quantity of the substance to be determined is very

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* Compare Alkalimetry, page 44, and Acidimetry, page 64.

small; hence a high degree of accuracy is necessarily desirable. Such highly diluted volumetric solutions as $\frac{N}{20}$, $\frac{N}{25}$, $\frac{N}{100}$, are chiefly employed in the titrimetric estimation of the alkaloids. Owing to the great dilution of these solutions we are able to measure off volumes representing exceedingly small quantities of the actual reagent, which under ordinary circumstances would be impossible with stronger solutions and a burette with the usual graduations. With the former, an error of one-tenth or two-tenths of a cubic centimeter would not materially affect the general result, while the same error with a normal solution, which is either 10 or 100 times as strong, would make a serious difference.

Preparation and Preservation of Solutions.

In the preparation of standard solutions marked changes of temperature, with a corresponding alteration in volume, frequently occur, as, for example, the diminution in temperature and consequent contraction in volume following the solution of many saline bodies, or the rise in temperature, with expansion, attending the mixing of sulphuric acid or caustic alkalies with water. In all cases the solution is allowed to stand sufficiently long until its temperature has assumed that of the room; then it is made up to the proper volume. Subsequent titrations should be made at, or as near as possible to, the temperature at which the standard solutions were prepared. Excepting those of the alkalies, all standard solutions should be preserved in glass-stoppered bottles and away from the direct sunlight; this precaution is particularly necessary with solutions of silver nitrate, iodine, and potassium permanganate. Cork stoppers should be avoided. Alkaline solutions have a tendency to become ropy, particularly so when kept in closed vessels; such should be placed in containers (Fig. 16) provided with a rubber stopper through which a drying tube, filled with soda-lime, passes; this permits the free access of air deprived of carbonic acid gas which would otherwise be absorbed by the alkaline liquid. Solutions, as those of potassium permanganate, stannous chloride, or sulphurous acid, which readily change upon exposure, are best preserved by covering their surface with a layer of refined liquid petrolatum.

FIG. 16.—CONTAINER FOR ALKALI SOLUTIONS.

In laboratories where volumetric solutions are in almost constant use a storage vessel attached to a burette with a constant filling device is very useful. This idea, as shown in figures 17 and 18, was originally proposed by Mohr. Both the reservoir and burette are provided with soda-lime tubes, to be used only with solutions of sodium, potassium, or barium hydroxides ; in other cases these tubes may be filled with cotton. In order to fill the burette, the lower pinch-cock (see *a*, Fig. 18) is securely closed while that (*b*) leading to the reservoir is opened ; then, blowing slightly through the drying-tube of the latter, the solution flows down the siphon and fills the burette, the height of the column being controlled by closing the pinch-cock (*b*) again. Since after once starting, the siphon remains filled, the subsequent charging of the burette is readily regulated at *b*.

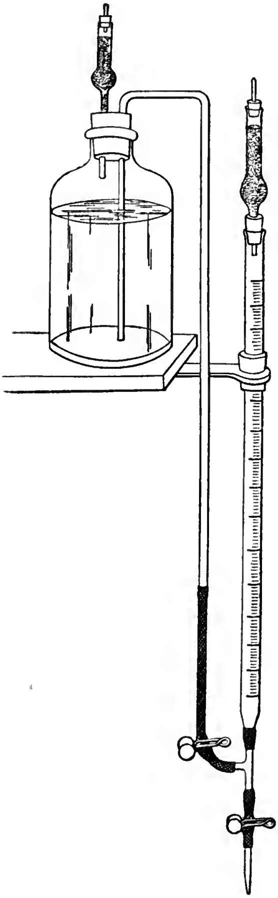

FIG. 17.—BURETTE WITH CONSTANT FILLING DEVICE.

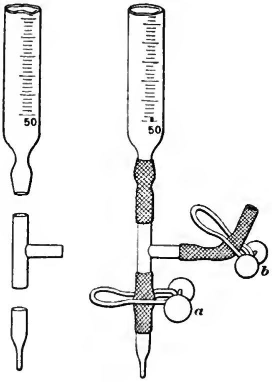

FIG. 18.—CONSTRUCTION OF BURETTE TIP.

The stability of volumetric standard solutions depends largely upon the nature of the reagent. While no general fixed period can be given, we find that such solutions as those of the standard acids, alkalies, sodium chloride, or potassium bichromate can be preserved for a year or even longer, where others, as stannous chloride, iodine, sulphurous acid, or potassium permanganate, cannot be relied upon after a period of a few weeks unless standardized immediately before using. It should be the invariable rule to examine the titer of each standard solution at frequent intervals.

According to the method of procedure, volumetric processes may be divided into the following classes :

I. *Analysis by Saturation or Alkalimetry and Acidimetry.*—These methods embrace the quantitative estimation of acids and alkalies by neutralization with standard volumetric solutions of alkalies and acids.

II. *Volumetric Analysis by Oxidation or Reduction.*—Determinations of this class are based on the oxidizing power of standard solutions of such reagents as the permanganate, dichromate, and ferricyanide of potassium, also iodine; or the reducing action of such reagents as sulphurous acid, sodium thiosulphate, arsenous oxide, stannous chloride, oxalic acid, etc.

III. *Analysis of Precipitation.*—These methods are chiefly applicable in the estimation of halogens and cyanides, which are precipitated as insoluble silver salts through the addition of a standard solution of silver nitrate. On the other hand, silver may be estimated by precipitation with a standard solution of sodium chloride.

CHAPTER II.

ANALYSIS BY SATURATION.

Analysis by saturation embraces the quantitative estimation of acids or alkalies by means of the neutralizing (saturating) power of a standard solution of an alkali or acid. To fix the exact point of neutrality or completion of the reaction, indicators are employed. Before taking up the various operations classed under this heading, a consideration of the choice, applications, and theory of indicators will be considered.

INDICATORS.

Indicators are solutions of certain substances which afford ocular evidence of the condition of the solution being examined, showing whether it is of acid, alkaline, or neutral reaction, the change from one condition to another being accompanied by a marked alteration in color. As regards their sensitiveness,—that is, the accuracy and readiness with which an indicator responds by a change of color upon the solution assuming the slightest degree of alkalinity or acidity,—there is considerable variation; thus, iodeosin will show the alkaline reaction of distilled water which has been shaken in a glass flask, while toward weak acids it is far less sensitive. For titrating such weak bases as the alkaloids, where very dilute acids and alkalies are employed, but very few indicators are available, such as congo red, lacmoid, brazilin, and iodeosin. In the selection of an indicator we must be guided by its individual peculiarities and the nature of the acid or alkali to be titrated; for instance, phenolphthalein can be used in the estimation of caustic soda or potassa, but is useless for ammonia; with oxalic acid only phenolphthalein, litmus, or rosolic acid should be used. Before entering into a classification and further consideration of indicators in general, a brief review will be devoted to the theory of their action.

Theory of Indicators.—The changes in color produced by the addition of acids and alkalies to solutions of indicators finds plausible explanation in the modern "Ionic" or "Dissociations" theory. For example, when salts, bases, and acids are dissolved in water, they dissociate (split up) more or less into their ions. Thus, potassium hydroxide (KOH) in aqueous solution dissociates into electro-positive potassium (+K) ions and electro-negative hydroxyl (—OH) ions; sulphuric acid (H_2SO_4), into electro-positive hydrogen ($+H_2$) ions and electro-negative sulphuryl ($—SO_4$) ions; the extent of this dissociation depends upon the nature of the dissolved body and the degree of dilution. Thus, strong acids and alkalies dissociate more completely than the relatively weaker ones; also the greater the dilution, the more complete is this ionization. The electrical conductivity of these solutions increases proportionately with the degree of dissociation.

A solution which contains free hydrogen ions reacts acid, while one containing hydroxyl ions is alkaline; if an acid and alkaline solution are brought together, the electro-positive hydrogen ions unite with the electro-negative hydroxyl ions, producing a neutral condition. According to the degree of ionization or the relative number of either hydrogen or hydroxyl ions in solution, an acid or a base is termed stronger or weaker.

Indicators are compounds of a comparatively feeble acid or basic character, and in consequence of this, form salts with alkalies or acids; these salts ionize (dissociate) at the instant of their formation and give rise to colors which differ from those of the non-ionized indicator itself. Any feeble acid or base is suitable as indicator provided its ions possess a color different from that of the electrically neutral substance. If the indicator be a strong acid or base, it would ionize in the free state on dilution and give no color when neutralized. On the other hand, weak acid and basic indicators fail to ionize when diluted, and only does this take place when they have been converted into salts by neutralization. Thus, phenolphthalein, a weak acid indicator, is colorless in its molecular (undissociated or non-ionized) state; but when neutralized by an alkali, its salt ionizes, liberating anions of an intense red color. On adding a few drops of this indicator to an acid solution, any tendency it may have to ionize is prevented by the acid present; if, now, an alkali is gradually added, the OH ions of the base unite with the H ions of the acid, and if the latter is very strong, sufficient H ions remain in the fluid to prevent any ionization (change of color) of the indicator until the first drop of excess of alkali unites with the phenolphthalein and forms a salt which ionizes immediately, giving rise to the characteristic red color which indicates the termination of the reaction. If the acid which is being titrated is feeble and the neutralization nears completion, the number of H ions are not present in sufficient quantity to fully prevent ionization of the indicator; in consequence of this some of the ions are liberated before the completion of the reaction; in other words, the color change lacks sharpness and the end-point is indefinite. If a feeble acid is to be titrated, then, according to the above, an indicator is selected whose tendency to ionize is much less than the acid itself, and the alkali salt of the former should ionize sufficiently to cause a distinct color change. In this case phenolphthalein would be indicated, provided a strong base is used for titrating. This indicator being itself a weak acid, is not adapted for the titration of feeble bases like ammonia, for the salt produced is too weak to withstand the hydrolytic action of the water in such diluted solutions, and, as a consequence, a large excess of the base must be added to overcome this. This accounts for the incomplete change in color and why an excess of the alkali is necessary for the production of a red color. Methyl-orange is a feeble base and with acids forms a salt which dissociates into red-colored ions; this, upon neutralization with an alkali, returns to its nondissociated condition, which is yellow. In consequence of the weak basicity of this indicator its compound with acids is readily decomposed by alkalies, while a strong acid or a relatively large volume of a feeble acid is necessary to dissociate it in its non-ionized condition, hence methyl-orange is very sensitive to alkalies and but slightly so toward acids. Litmus, an acid indicator, slightly dissociates when dissolved, its negative ions being blue and non-ionized molecules red. If added to a base (alkali), a salt is formed which at once ionizes, with the production of a blue color; the addition of an acid represses this ionization and the red color of the undissociated molecule appears.

Dilution.—The relative volume of water employed in the operations of acidimetry and alkalimetry exerts a material influence upon the results, especially in the presence of very sensitive indicators. Titrations should not be carried out in very concentrated solution because of the unfavorable conditions for dissociation which hem the reactive powers of the dissolved substances. Further dilution increases the degree of dissociation, and, up to certain limits, the reactive ability of the different ions; but if this dilution be made excessive, the latter diminishes, because, on the one hand, of the scattered condition of the ions, whereby their sphere of molecular activity is lessened, and, on the other, the water itself takes part in the reaction, in which it brings about a premature dissociation of some indicators, because of its slight hydrolytic dissociation into hydrogen ions which react like an acid, and hydroxyl ions which react alkaline. For example, methyl-violet in neutral or alkaline solution is violet, and with acids is green, requiring a relatively large amount of the latter to change its violet to green; if, however, its green solution is highly diluted with water, the OH ions of the latter are sufficiently alkaline to change this to violet. On the other hand, Porrier's blue gives blue with acids and red with alkalies, but on diluting its red alkaline solution with water, the H ions of the latter are sufficiently acid to change this acid sensitive indicator to a blue.

For like reasons on adding methyl-orange, congo red, or lacmoid to 500 Cc. of distilled water, they all show an alkali reaction, which does not disappear until from 0.2 to 0.5 Cc. of $\frac{N}{10}$ sulphuric acid V. S. has been added. With phenolphthalein or members of Group III the large volume of water reacts like an acid from the free H ions, and the solution requires the addition of 0.5 Cc. of $\frac{N}{10}$ sodium hydroxide V. S. to produce a red color.

For titrating in strong dilutions iodeosin is the best of all indicators, the volume of water exerting no material influence.

The volume of fluid to be titrated should be kept between 50 and 100 Cc. If the volume is excessive, then a separate experiment should be made to fix the titer of the standard solution under these special conditions.

Selection of Indicators.

Where any degree of accuracy is desirable the operator is warned against the indiscriminate employment of indicators, for their degree of sensitiveness toward acids and alkalies varies considerably, depending upon the relative strength of the latter and the comparative basicity and acidity of the former. In view of these properties Glaser * has divided all indicators employed in saturation analyses into three groups.

Group I.—Members of this class include such indicators as are either of a strong acid character or very feeble basicity, hence either react readily with weak bases or require a very strong acid to form a stable salt, hence this group will be found to be *very sensitive to alkalies* and much less so toward acids. The degree of sensibility toward alkalies diminishes from 1 to 6, while toward acids it increases slightly in the same order. It should be noted that indicators of Group I show the neutral point somewhat earlier toward alkalies than acids, while the reverse is true of members of Group III.

(Methyl-violet.) † *Maximum of sensitiveness toward alkalies.*

1. Iodeosin, Resazurin.
2. Tropæolin OO, Luteol.
3. Methyl- and ethyl-orange, Helianthin.

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* F. Glaser, Zeitschrift für analytische Chemie, 1899, 273–278.

† Methyl-violet is so lacking in sensitiveness toward acids, and Porrier's blue toward alkalies, that they are of but comparatively little value as indicators.

4. Congo red.
5. Cochineal.
6. Lacmoid.

Group II.—This class possesses a slight acid character and unites with bases to form salts, which, however, because of their unstable character, are decomposed by relatively feeble acids. This group is therefore *more sensitive toward acids than Group I* and less so toward bases.

1. Fluorescein, Phenacetolin.
2. Hæmatoxylin, Galleïn, Alizarin.
3. Litmus, Orseille.
4. Para-nitro-phenol.

Group III.—These indicators possess feeble acid properties, hence unite with bases to form salts which are readily decomposed by weak acids, hence the members of this group *are very sensitive toward acids* and only slightly so toward bases.

1. Rosolic acid.
2. Curcuma.
3. Phenolphthalein, Flavescin.
4. Alpha-Naptholbenzeïn
   (Porrier's Blue.) * *Maximum of sensitiveness toward acids.*

Application of Indicators.

Strong acids, as sulphuric, hydrochloric, and nitric, can be accurately titrated with indicators of all three classes. Fairly strong acids, as formic, lactic, oxalic, and tartaric, and feeble acids, as acetic, propionic, butyric, oleic, stearic, citric, benzoic, salicylic, boric, etc., are titrated with indicators of Group III.

Strong bases, as sodium, potassium, barium, and calcium hydroxides, are adapted to any indicator, but feeble bases, as ammonia or the amine bases, admit only members of Group I.

This table enables us to determine the relative strength of an acid or base, by titrating with different indicators; for example, if one acid can be readily titrated with either lacmoid or litmus, and another only with the latter, then the former must be stronger. Lacmoid is fairly good for formic acid, but litmus is better; for acetic acid (which is weaker) an indicator from group III must be used. That the acidity of organic acids increases with the number of hydroxyl groups can be demonstrated in the above manner.

In the selection of an indicator one must not only be guided by the general rules of grouping, as shown above, but also as to the possibilities of the presence of carbonates, either in the alkali examined or alkali standard solution. During the neutralization the carbonic anhydride of the carbonate or bicarbonate is liberated, which, from its acid reaction, influences some indicators, although the solution is at the same time strongly alkaline. In such cases we either resort to the method of residual titration (page 46), if the indicator is sensitive to carbonic anhydride, or, more usually, select one of several which are uninfluenced by this gas.

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* See foot-note, p. 24.

INDICATORS NOT SENSITIVE TO CARBONIC ANHYDRIDE.

Cochineal.
Congo Red.
Fluorescein.
Gallein.
Lacmoid Paper (red).
Methyl-orange.
Phenacetolin.

Quantity of Indicator.

An indicator should be sufficiently sensitive that when added to 10 Cc. of water which contains just a trace of acid or alkali, a distinctive color change should take place, and this should, upon further dilution with water, not suffer any alteration in color. The strength of indicator solutions is so adjusted that from 3 to 5 drops added to 50 Cc. of water will give a sharp color change when titrated with decinormal acid or alkali. With such indicators as methyl-orange, litmus, or lacmoid, as small a quantity as possible should be employed, owing to the formation of confusing transition colors in changing from an acid to alkaline or alkaline to acid reaction, the first-named giving an orange and the latter two a violet when too much of the indicator is present. When titrating with centinormal solutions, the smallest possible quantity of an indicator should be used, for, since the color produced depends upon its forming a salt with the alkali or acid, it will be readily seen that an unnecessarily large volume of the centinormal solution will be necessary to convert all of it into a salt or, when formed, to decompose it. For example, four drops of litmus solution added to 10 Cc. of water required 5 drops of $\frac{N}{100}$ acid or alkali V. S., to change from red to blue or blue to red, 20 drops of litmus required from 10 to 12 drops of either standard solution, while 40 drops of the indicator required from 18 to 20 drops of the latter solutions. A few indicators, such as luteol, phenolphthalein, and methyl-orange, form exceptions to this rule.*

Influence of Volatile Solvents.

See page 80.

Hot Titrations.

The titration of hot solutions is often a matter of necessity in handling slightly soluble substances or the estimation of caustic alkalies in the presence of carbonates with certain indicators (as phenolphthalein or litmus); in other cases it is a matter of convenience only. Where some indicators can under no circumstances be employed in hot solution, the majority of the others, including methyl-orange, cochineal, litmus, and phenolphthalein, are affected more or less; that is, the titer of a solution varies slightly, whether taken in the cold or boiling, so it is advisable, when a hot titration must be made, the titer of the normal standard solutions should be fixed in a separate experiment carried on under the same conditions.†

Terminating Point.—In order that we may be able to clearly

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* O. Linde, Archiv. d. Pharmazie, 1900, p. 121.

† Lunge, Pharm. Zeitung, 1887, p. 739; Dunn, Phar. Journal and Trans., VIII, p. 1030; Zeitschr. f. angew. Chemie, 1894, p. 550.

distinguish changes in color, porcelain vessels should be used as containers; these are preferable to glass because of the solvent power of distilled water or alkaline solutions upon the latter, particularly so when hot. If, however, glass beakers or flasks are preferred, they should be placed upon white paper or a porcelain pill-tile. With some indicators, also, when titrating highly diluted solutions the change of color, upon the approach of neutrality, is so gradual that it is sometimes a difficult matter to establish the terminating point with any degree of certainty.

One method of ascertaining this consists in removing a small quantity (5 or 10 Cc.) of the fluid being titrated to two small beakers or watch-glasses, each one containing a like volume; then to one add a drop of the standard solution which is being used, noting any change in color by comparison with the other sample. If neutrality has not been reached, the contents of these two trial vessels are rinsed back into the main solution, and after adding a few drops more of the standard solution with stirring, the comparison is again repeated; this is continued until the operator is satisfied that the distinctive change in color has taken place.

Another method consists in placing alongside the sample being titrated two beakers or dishes containing like volumes of water and the same number of drops of the indicator; to one is added just sufficient of the standard acid to produce a change in color, to the other a like quantity of standard alkali; with these as guides the end-reaction can be noted by comparison.

In titrating highly colored fluids either the special indicator fluorescein is used or recourse is had to the various indicator test papers (p. 34). The solution being titrated is tested from time to time by placing a drop on the moistened reagent-paper. The paper should not be dipped into nor be allowed to float in the solution while titrating. While titration by artificial light can be carried on with such indicators as methyl-orange, cochineal, congo red, galleïn, and phenolphthalein, it is not to be recommended to beginners.

Description of Indicators.

Of the vast number of indicators which have been proposed from time to time, only a comparative few have received a general adoption, chiefly owing to the fact that the majority offer but few, if any, advantages over those already in use.

To each 50 to 100 Cc. of the fluid to be titrated, from 2 to 5 drops of the indicator may be added; however, with such indicators as methyl-orange, litmus, or azolitmin, no more than just sufficient to tinge the solution should be used, owing to the production of confusing transition tints when the fluid is highly colored.

When titrating with centinormal solutions, as little of the indicator should be employed as possible.

The following list comprises a selection of the more reliable ones in common use,* arranged according to their position in the group classification :

Iodeosin. **Bases** = *Rose-red.* **Acids** = *Yellow.*

This indicator is only adapted for the estimation of very minute quantities of alkali in connection with $\frac{1}{100}$ and $\frac{1}{1000}$ normal solutions. Iodeosin solution is prepared by dissolving 2 milligrammes of the powder in one liter of pure ether,† which must be absolutely free from all traces of acid, and previous to using should be shaken with distilled water for hydration. In titrations with this indicator, from 50 to 100 Cc. of a distilled water solution of the substance are placed in a tall glass cylinder, which can be securely closed with either a glass or cork stopper. To this is added from 10 to 20 Cc. of the etherial iodeosin solution ; the mixture is then shaken and set aside ; the etherial layer, which floats, will be colorless as well as the fluid if the latter be absolutely *neutral;* if traces of alkali are present, the rose-red tint of the iodeosin passes into the aqueous fluid leaving the ether colorless ; if acid, the etherial layer becomes yellow. This indicator is chiefly employed in *alkaloidal* titrations, particularly those of weak basic character, as emetin, atropin, morphin, etc., while those of more marked basic properties can be estimated just as well with congo red, cochineal, or hæmatoxylin.

All glass utensils used should be thoroughly washed with hot water, also the distilled water should be tested for its reaction before using.

Iodeosin is a tetra-iodo-fluorescein, which occurs as a brick-red powder soluble in alcohol and slightly so in hydrated ether.

Resazurin. **Bases** = *Blue.* **Acids** = *Red.*

The solution of this indicator is prepared by dissolving 0.2 Gm. of the color in 40 Cc. of $\frac{N}{10}$ alkali V. S. and diluting to one liter. This indicator is extremely sensitive to alkalies, 2 drops being sufficient for 100 Cc. of solution to be titrated. It is not adapted to the estimation of carbonates, monobasic organic acids, or nitric acid. Resazurin results from the action of fuming nitric acid on a solution of resorcin in anhydrous ether.

Tropæolin OO. **Bases** = *Yellow.* **Acids** = *Orange to Red.*

The indicator solution is prepared by dissolving 0.05 Gm. of the dye in 100 Cc. of 50 per cent. alcohol, of which from 2 to 5 drops are sufficient for 50 Cc. of the solution to be titrated. Because of the formation of transition tints this indicator is not employed in titrations, these difficulties being largely due to the variability of the market article.

Luteol. **Bases** = *Yellow.* **Acids** = *Colorless.*

The solution is prepared by dissolving 0.1 Gm. of the color in 50 Cc. of alcohol, of which four drops are sufficient for 50 Cc. of the fluid to be titrated. When pure, this indicator is exceedingly sensitive toward alkalies, being more so toward ammonia than Nessler's solution, for 10 Cc. of a solution made by adding one drop of aqua ammonia to a liter of water will give an immediate yellow color with luteol. This indicator is employed by some in the titrimetric estimation of alkaloids.

Chemically, luteol is an oxy-chlor-diphenyl-quinoxaline.

Methyl-orange.‡ **Bases** = *Yellow.* **Acids** = *Red.*

The solution is prepared by dissolving 0.05 Gm. of the color in 100 Cc. of distilled water. The operator is especially cautioned against employing excessive quantities of this indicator. The less highly colored the solution, the sharper will be the color change ; from 1 to 2 drops are sufficient to produce a pure yellow or red in 50 to 100 Cc. of an alkaline or acid liquid, the color change being sharp and sudden even with $\frac{N}{10}$ solutions. Large quantities of the indicator stain the liquid orange which will require excessive quantities of the standard acid or alkali to produce a pure red or yellow. Methyl-orange, like the other members of Group I, is more sensitive toward alkalies than acids ; that is,

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* For a complete treatise on indicators see "Indicators and Test Papers," by A. J. Cohn. Wiley and Sons, New York.

† Commercial ether may be purified by washing with a solution of caustic soda, then several times with water, finally with distilled water, from which it is drawn off just previous to using.

‡ Otherwise known as Helianthin, Porrier's orange 3P., Tropæolin D., or Mandarin orange.

it shows a change in color earlier when titrating alkalies with acids than the reverse; hence, in standardizing our solutions this should be observed.

This indicator is not to be employed with solutions weaker than decinormal.

Methyl-orange is especially valuable in titrating alkalies because it is not influenced by the presence of such disturbing elements as carbonic acid, sulphuretted hydrogen, hydrocyanic, boric, stearic, oleic, and palmitic acids, or phenol; such titrations proceed in the cold. Methyl-orange is the sodium salt of dimethyl-anilin-azobenzene-sulphonate, and occurs as an orange powder which is moderately soluble in water and dilute alcohol.

METHYL-ORANGE USEFUL IN TITRATING.	AVOID.
Strong and feeble bases (KOH, NaOH, $Ca(OH)_2$, $Ba(OH)_2$, NH_3).	All organic acids.
Carbonates and bicarbonates (cold).	Arsenous and boric acids.
Sulphides.	Presence of large quantities of ammonia salts alkali sulphates, nitrous acid, and nitrites.
Strong acids, as HCl, H_2SO_4, HNO_3, H_2SO_3.	Hot titrations.
H_3PO_4 and H_3AsO_4 to MeH_2PO_4.	

Dimethyl-amido-azobenzene. **Bases** = *Yellow.* **Acids** = *Red.*

A solution of 0.05 Gm. in 100 Cc. of 96 per cent. alcohol. This indicator was introduced as a substitute for methyl-orange because of its sharper transition tints; it is, however, not quite as sensitive as the latter. When due care is observed in not employing excessive quantities, methyl-orange is to be preferred.

Congo Red. **Bases** = *Red.* **Acids** = *Blue.*

The solution is prepared by dissolving 0.5 Gm. of the color in 90 parts of water and adding 10 parts of alcohol; from 3 to 5 drops are usually sufficient for a titration. This indicator is especially adapted for the estimation of mineral acids, as well as their standardization, particularly the decinormal solutions. The alkali and alkali-earth hydroxides, ammonia, and their carbonates may be accurately titrated.

Congo red as well as tropœolin cannot be used as some recommend for differentiating organic from inorganic salts. The presence of sulphurous acid, sulphites, and sulphuretted hydrogen does not interfere with its accuracy.

Congo red is a sodium tetrazo-diphenyl-napthionate, and appears in red-brown lumps soluble in water and alcohol.

CONGO RED USEFUL IN TITRATIONS.	AVOID.
Inorganic Acids, also H_3PO_4.	Organic acids (not affected by).
Caustic alkalies and carbonates.	Nitrous acid and nitrites.
Alkali-earths and carbonates.	Large amounts of neutral salts of alkalies; also salts of NH_3, Ca, Mg, Ba.
Ammonia, Amine bases.	Hot titrations.

Cochineal. **Bases** = *Violet.* **Acids** = *Yellowish-red.*

This solution is best prepared by macerating (cold) for several days 3 Gm. of cochineal (whole) in 250 Cc. of 25 per cent. alcohol. This tincture may also be prepared by dissolving its color principle, carminic acid, in 25 per cent. alcohol (1 part in 100). Color changes of this indicator are more readily observed by artificial yellow light. When titrating acids with alkalies, the indicator, which is acid, should be neutralized by the addition of a minute quantity of dilute ammonia, whereby a violet tint is produced.

COCHINEAL USEFUL IN TITRATING.	AVOID.
Alkali hydroxides and carbonates.	Organic acids.
Alkali-earth hydroxides and carbonates.	Presence of Fe, Al, and Cu salts.
Ammonia.	
Mineral acids.	
Alkaloids.	

Lacmoid. **Bases** = *Blue.* **Acids** = *Red.*

Of the *purified** indicator 0.2 Gm. are dissolved in 100 Cc. of alcohol. Should the lacmoid, after purification, still show a disturbing violet tinge, then 0.3 Gm. of it is

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*Commercial lacmoid varies in quality; the greater its degree of purity, the more readily should it dissolve in water, yielding an intense pure blue solution. Samples dissolved with 0.5 Gm. of beta-napthol green in a mixture of 70 Cc. of water and 30 Cc. of alcohol. From its position in the table, lacmoid is less sensitive toward bases than any of the preceding indicators; however, on the other hand, it is far more sensitive toward acids. Although this indicator is classed as not being sensitive to carbonic anhydride, yet it is not as sharp as congo red or methyl-orange in the titration of carbonates. The color change in hot titrations is not as sharp as when the solutions are cold. Lacmoid, like litmus, is a popular and very sensitive indicator. It appears either as a brown or dark violet powder or blue-black scales resulting from the action of sodium nitrite on resorcin. The indicator solution should be kept away from the light.

LACMOID USEFUL IN TITRATING.	AVOID.
Mineral acids (HCl, H_2SO_4, HNO_3).	Organic acids.
Strong bases [NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, NH_3].	Nitrous acid.
Alkali or alkali-earth carbonates (residual or hot titration).	Sulphides.
Borates.	

Fluorescein. **Bases** = *Yellowish-green Fluorescence.* **Acids** = *Non-fluorescent Yellow.*

The solution is prepared by dissolving 0.05 Gm. of the color in 50 Cc. of alcohol and adding 50 Cc. of water; from 3 to 5 drops are sufficient for a titration. Fluorescein is exceedingly sensitive to alkalies, particularly so in *alcoholic* or *etherial* solution; one drop of $\frac{N}{100}$ KOH V. S. is sufficient to produce an intense fluorescence. Carbonic acid gas does not influence this indicator. Fluorescence does not cease entirely upon neutralization; however, the change in intensity is so marked that no one can mistake the end-reaction. Titration by artificial light is preferable, owing to the disappearance of the disturbing yellow tinge. This indicator is adapted to the titration of colored fluids, which must, however, be clear and free from any precipitate. Fluorescein is a tetra-oxy-phthalophenon and is a product of the condensation of phthalic anhydride and resorcin; it appears as dark yellow crystals, which are only slightly soluble in water and alcohol.

The fluid being titrated should be viewed by *reflected* light only, for by transmitted light its alkaline solutions are red.

FLUORESCEIN USEFUL IN TITRATING.	AVOID.
Mineral acids (HCl, H_2SO_4, HNO_3).	Ca and Ba Hydroxides; also their salts.
Caustic alkalies (KOH, NaOH, NH_3 only).	Acetic acid.
Alkaloids.	
Hot titrations are admissible.	

Phenacetolin. **Carbonates** = *Red;* **Hydroxides** = *Yellow.* **Acids** = *Yellow.*

About two drops of a solution of 1 Gm. in 100 of alcohol are sufficient for titrating 50 to 60 Cc. of fluid. The carbonates, bicarbonates, and sulphides of the alkalies and alkali-earths, as well as ammonia, produce a red color, while caustic alkalies (hydroxides) and acids change this to a yellow.

This indicator is especially adapted to the estimation of commercial caustic alkalies, which usually contain carbonates as impurity. To the yellow-colored solution of the caustic alkali, the standard acid is added until it changes to a red; this moment indicates the point at which the alkali hydroxides have become neutralized. Further addition of acid serves to intensify the red until the carbonates have been neutralized, when a yellowish-red gives way to a pure golden-yellow. These titrations will show a slight deficiency in the amount of hydroxide and slight excess in the carbonate, due to extreme sensitiveness of this indicator toward carbonic anhydride. The proportion of alkali hydroxide must always be far in excess of the carbonate present. In this same manner calcium hydroxide may be estimated in the presence of calcium carbonate. Organic acids

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which are only slightly soluble in water should be rejected. Purification, with the removal of a reddish fluorescent substance, may be carried out by precipitating its filtered, cold aqueous solution through acidulation with an acid. The precipitate is collected, washed with cold water, dried at a low temperature, and dissolved in alcohol while on the filter; the filtrate is evaporated to dryness on a water-bath.

cannot be estimated with this indicator. Phenacetolin is obtained by heating molecular quantities of phenol, concentrated sulphuric and acetic acids; it forms a yellowish-brown powder soluble in alcohol.

PHENACETOLIN USEFUL IN TITRATING.	AVOID.
Mineral acids (HCl, H_2SO_4, HNO_3).	Organic acids.
Caustic alkalies and alkali-earths (KOH, $NaOH$, $Ca(OH)_2$, $Ba(OH)_2$).	Excessive quantities of ammonia salts.
Hot titrations.	

Hæmatoxylin. **Bases** = *Blue.* **Acids** = *Red.*

For this indicator solution 0.5 Gm. of hæmatoxylin are dissolved in 100 Cc. of alcohol. A tincture may be prepared from the logwood (Campeachy wood) by digesting one part of the shavings from the *inner part* of the billet with 20 parts of alcohol for a day, then filtering, and preserving in well-stoppered vials. Hæmatoxylin can only be used with strong acids and caustic alkalies; carbonates cannot be titrated cold.

Color changes are readily distinguished by artificial light.

This indicator is recommended in the titration of alkaloids. Hæmatoxylin, the color principle of logwood, appears as pale yellow crystals, which readily change upon exposure to the light and air.

Galleïn. **Bases** = *Bright Red.* **Acids** = *Pale Brown.*

This indicator is prepared by dissolving 0.5 Gm. of galleïn in 50 Cc. of alcohol, which is then diluted with water to 100 Cc. In neutral solution this indicator gives a yellow, while a slight excess of alkali changes it to a bright red; a large excess produces a violet, which finally changes to a brownish-yellow. Carbonates produce a violet, while bicarbonates change this to a bright red. The sensitiveness of this indicator is materially increased in the presence of alcohol and ether. If an acid is titrated in presence of salts of ammonia or the alkali-earths, the neutral point will be indicated by a pure blue; ammonia imparts a violet, while caustic alkalies give a blue color. The presence of carbonates should be avoided.

Galleïn is applicable to the estimation of strong acids, bases, ammonia, and organic acids.

Color changes soon alter on standing, hence readings should be made at once.

Galleïn is a condensation product of phthalic anhydride and pyrogallol; phenolphthalein and fluorescein are likewise condensation products in which the pyro has been replaced by either phenol or resorcin. This indicator appears either as a red-brown powder or in greenish, shining crystals, which are soluble in alcohol and almost insoluble in water.

GALLEÏN USEFUL IN TITRATING.	AVOID.
Mineral acids (HCl, H_2SO_4, HNO_3).	Carbonates.
Alkali and alkali-earth hydroxides.	
Ammonia.	
Organic acids.	
Alkaloids.	

Alizarin. **Bases** = *Red.* **Acids** = *Yellow.*

A solution of 0.5 Gm. of alizarin in 100 Cc. of alcohol is usually employed. Color changes of this indicator are very sharp and may be readily distinguished by artificial light.

Litmus. **Bases** = *Blue.* **Acids** = *Red.*

Litmus is a pigment obtained by the fermentation of certain lichens, as the *Rocella tinctoria*, *R. fuciformis*, etc., and appears commercially in the form of small friable cakes or cubes of a violet-blue color. This varies considerably in quality, because of the presence of added chalk or gypsum, also certain other color principles which detract from the sensitiveness of the substance as an indicator. The real value of litmus depends on the presence of a color principle known as *azolitmin*, which is sometimes used in pure condition; however, owing to its extremely high cost, most operators prefer to prepare a purified tincture from the commercial cubes. Of the many methods offered, the following, of Mohr, is generally preferred: The powdered litmus cubes are first extracted three times by digestion with warm alcohol (96 per cent.) and filtered; this serves to remove the undesirable colors (but not azolitmin). The residue remaining on the filter, after draining is extracted with hot distilled water, which is allowed to stand for a day in a tall cylinder in order to permit a subsidence of the insoluble suspended matter; the clear supernatant layer is then drawn off, evaporated to about one-third its volume, and sufficient acetic acid added to impart a strong acid reaction. This fluid is further concentrated to the consistence of a thick syrup, when a large excess of alcohol (90 per cent.) is added, with constant stirring, whereby the blue color principle is precipitated and the objectionable impurities remain in solution. The blue precipitate is collected, washed with alcohol, and dissolved in sufficient water, to which afterward about an equal volume of alcohol is added; the strength of this is so regulated that three drops will be sufficient to impart a distinct color to 50 Cc. of water. The addition of one drop of a $\frac{N}{10}$ acid or alkali V. S. to 50 Cc. of water tinted with the indicator should change the violet to either a distinct red or blue. Litmus tincture, because of the readiness with which it becomes ropy and changes color, should be kept in vials the necks of which are stopped with a wad of cotton in order to keep out dust and anaërobic bacteria while air is admitted.

If a purified litmus is available, the solution may be prepared by dissolving 1 Gm. in 100 Cc. of distilled water. Neutral antiseptics, as thymol and phenol, may be used for the preservation of the solution.

Litmus is a very sensitive indicator for mineral acids and the hydroxides of the alkalies and alkali-earths. Carbonates and bicarbonates may be titrated by boiling or by the residual method when the indicator is added after the carbonic anhydride has been expelled by boiling.

LITMUS USEFUL IN TITRATING.	AVOID.
Mineral acids (HCl, H_2SO_4 . HNO_3).	Organic acids except oxalic and benzoic.
Akali and alkali-earth hydroxides [$NaOH$, KOH, $Ca(OH)_2$, $Ba(OH)_2$. NH_3].	Phosphoric acid.
Carbonates and bicarbonates boiling.	Sulphurous acid.
Oxalic acid.	

Azolitmin.

Owing to the extreme high price of this color principle most operators prefer to employ the purified litmus tincture. The solution of azolitmin is prepared by dissolving 1 Gm. of the substance in 100 Cc. of distilled water to which just sufficient of $\frac{N}{10}$ KOH V. S. is added to produce a blue tone. On adding 0.5 Cc. of this indicator to 100 Cc. of distilled water, not more than 1.2 Cc. of $\frac{N}{100}$ acid V. S. or 3 Cc. of $\frac{N}{100}$ alkali V. S. should be required to change the solution to either a distinct red or blue. Azolitmin solution, as well as the paper, is sometimes used in alkaloidal titrations.

Rosolic Acid.* **Bases** = *Rose-red.* **Acids** = *Yellow.*

As indicator, a solution of 1 Gm. in 100 Cc. of 60 per cent. alcohol is employed. When added to pure water, this indicator gives a feeble yellow; with alkalies, a rose-red; while with acids the color remains unchanged. The sharpness of color change is diminished by the presence of ammonium salts, hence only *weak* ammoniacal solutions can be titrated with accuracy. Strong bases, and strong inorganic acids, also organic acids, especially weak ones, excepting acetic, can be accurately estimated with this indicator.

Rosolic acid is a dye, belonging to the rosanilin derivatives, obtained by boiling the diazo compound of rosanilin with water. The commercial salt is a mixture of several derivatives, and appears as a yellow powder soluble in alcohol and insoluble in water.

ROSOLIC ACID USEFUL IN TITRATING.	AVOID.
Strong and *weak inorganic* and *organic* acids.	Phosphoric acid.
Alkali and alkali-earth hydroxides.	Sulphites.
Weak ammoniacal solutions.	Acetic acid.
Sulphurous acid.	

Phenolphthalein. **Bases** = *Red.* **Acids** = *Colorless.*

The solution is prepared by dissolving 1 Gm. of pure phenolphthalein in 100 Cc. of 96 per cent. alcohol.

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* Synonyms: Aurin; Corallin; Para-rosolic acid.

Normal solutions which have been standardized with methyl-orange or congo red will show the same titer with phenolphthalein only when titrated in concentrated solution. This indicator should not be added to concentrated alkali solutions, for they destroy its color, and it is not adapted for the titration of ammonia. Hot titrations may be carried out with this indicator, as in the estimation of alkali carbonates or bicarbonates, but the titer of the standard acid and alkali must have been set likewise in hot solution, as it differs from the cold. Titrations may be carried out by artificial light. Alkali sulphides may be estimated with this indicator in cold solution, the red color being discharged when just half of the alkali has been neutralized ($K_2S + HCl = KCl + KHS$). On boiling the solution the entire alkali is replaced ($KHS + HCl = KCl + H_2S$). Phenolphthalein has been recommended for titrating free fatty acids in alcoholic solution ; however, according to Linde,* titers with this indicator are unreliable in strong alcoholic solutions. This difficulty may be avoided by first ascertaining how many cubic centimeters of the standard alkali are required to produce a red color with the indicator in a like volume of alcohol or ether which should be deducted in the titration proper. In the determination of the saponification number of fats, a blank experiment must also be made to determine the volume of standard acid necessary to decolorize the measured quantity of alcoholic potassium hydroxide used. When volatile fatty acids are to be estimated in a large volume of water (250 to 500 Cc.), a blank experiment should be made to determine the volume of standard alkali necessary to produce a red coloration in the same quantity of water used ; this should be deducted from the results obtained in the regular estimation. Phenolphthalein is a yellowish-white powder soluble in dilute alcohol, insoluble in water, and melts at 150° C. It is prepared by fusing phenol with phthalic anhydride in the presence of a dehydrating agent.

Phenolphthalein is exceedingly sensitive toward acids, strong or weak, organic or inorganic. Phosphoric acid indicates alkalinity with the formation of its secondary salt, Me_2HPO_4.

PHENOLPHTHALEIN USEFUL IN TITRATING.

Mineral acids, strong and weak.
Organic acids (all).
Fatty acids.
Alkali and alkali-earth hydroxides.
Carbonates or bicarbonates (boiling).
Phosphoric acid (to Me_2HPO_4).

AVOID.

Ammonia and salts.
Boric acid except with glycerin.†

Guide to Selection of Indicators.

CAUSTIC ALKALIES AND ALKALI-EARTH HYDROXIDES
(CONTAINING SMALL AMOUNTS OF CARBONATES).

TITRATED COLD.

Indicator not Affected by CO_2.

Methyl-orange.
Galleïn.
Fluorescein.
Phenacetolin.
Congo Red.
Cochineal.
Iodeosin (minute quantities only).

TITRATED HOT.‡

Indicator Acid by CO_2. Dispelled on Boiling.

Lacmoid.
Litmus or Azolitmin.
Phenolphthalein.
Luteol.
Resazurin.
Rosolic Acid.

ALKALI AND ALKALI-EARTH CARBONATES.

TITRATED COLD.

Indicator not Affected by CO_2.

Methyl-orange (alkalies only).
Congo Red.
Fluorescein (avoid Ca and Ba hydroxides).
Phenacetolin.
Cochineal.

TITRATED HOT.

Litmus or Azolitmin.
Lacmoid (residual titration).
Phenolphthalein.
Cochineal.
Luteol.
Rosolic Acid.

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* O. Linde, Archiv. d. Pharmazie, 1900, 238, p. 126.

† Zeitschr. f. angew. Chemie, 1896, 551, and 1897, 5.

‡ Consult, "Influence of Temperature," p. 26.

AMMONIA (NH_3).

Luteol.
Litmus or Azolitmin.
Cochineal.
Galleïn.
Methyl-orange (large amount of NH_3 salts absent).
Rosolic Acid (large amount of NH_3 salts absent).
Congo Red.

ALKALOIDS (SEE PAGE 78).

Luteol.
Iodeosin.
Lacmoid.
Brazilin.
Hæmatoxylin.
Cochineal.
Azolitmin.
Fluorescein.

INORGANIC ACIDS.

Phenolphthalein.
Congo Red.
Litmus or Azolitmin.
Lacmoid.
Fluorescein.
Resazurin.
Luteol.
Methyl-orange.
Rosolic Acid.
Cochineal.
Galleïn.

PHOSPHORIC ACID.

Methyl-orange (⅓ of acid).
Phenolphthalein (⅔ of acid).
Congo Red.

ORGANIC ACIDS.

Galleïn.
Phenolphthalein.
Rosolic Acid (avoid acetic acid).

OXALIC ACID.

Rosolic Acid.
Litmus or Azolitmin.
Phenolphthalein.

ACETIC ACID.

Congo Red.
Phenolphthalein.

TEST PAPERS (Acidimetric and Alkalimetric).

Test papers serve in general as a convenient method for testing the reaction of solutions. In titrimetric operations they offer no advantages over the fluid indicators, except in the titration of colored solutions or such which destroy the color through the action of oxidizing or reducing agents; in addition, they are of value in such titrations where precipitates containing iron or alumina, also calcium phosphate, are produced in neutral or alkaline solution, since indicator colors are carried down with these precipitates.

For preparing these test papers, either the "Swedish quantitative" or Schleicher and Schüll's filter-paper, No. 595, answer best; otherwise, commercial white filter-paper, free from starch, is selected; this is immersed for several hours in diluted hydrochloric acid; then, after washing in warm water, a second maceration in very dilute aqua ammonia follows; finally the washings are completed in successive portions of distilled water; the paper is then dried preparatory to impregnation. This purified paper is immersed in the indicator solution sufficiently long to become thoroughly saturated; then it is removed by drawing over the edge of a glass plate in order to drain off all excess of fluid, after which it is dried either on clean glass plates or is suspended from stretched cords, reversing their position in order that the fluid may dry while evenly distributed over the surface. Precautions must be observed to carry this on in a room free from acid or ammoniacal vapors. The sheets of paper are now cut into suitable sized strips and placed in clean dry vials, securely corked.

When used, a drop of the fluid is applied to the paper by means of a glass rod. The paper should not be thrown into the solution while titrating.

The advantage of these papers in testing colored fluids or such as contain precipitates will be seen upon adding a drop to the dry test paper, when, owing to capillarity, the fluid rapidly spreads, forming a ring outside of and separate from the spot of coloring-matter or salt retained by the paper fibre. The color of the *edges* of this ring will indicate accurately the reaction of the fluid.

The number of indicators which can be thus employed is somewhat limited, owing in some cases to their instability under these conditions, while in the others only such as are sensitive to either acids or alkalies can be prepared.

Litmus Paper. *Bases = Blue. Neutral = Violet.*
Acids = Red.

This most popular of all test papers, which is sensitive to both acids and bases, may be prepared either from azolitmin or litmus tincture. The azolitmin solution is prepared by dissolving 0.1 Gm. of the color in 100 Cc. of distilled water, adding just sufficient alkali for solution. This may be made *feebly* acid or alkaline or tinted violet according to the kind of paper desired. Many operators prefer the violet-tinted paper, which answers for the detection of both acids and alkalies, owing to the readiness with which it turns either red or blue. In place of the azolitmin solution the tincture prepared as directed on page 32 may be employed.

Lacmoid Paper. *Bases = Blue. Acids = Red.*

The *blue* lacmoid paper is made by impregnating the prepared filter-paper with lacmoid solution; this is used for detecting acids. The color of this paper is more readily retained when in contact with water than litmus. The *red* paper is made by first treating the prepared filter with diluted sulphuric acid and drying, taking care to avoid excess, otherwise the sensitiveness of the paper toward alkalies will be impaired; it is then dipped into the lacmoid solution and dried. The dried paper should retain a rose-red color. The presence of carbonic acid gas does not interfere with the indication of alkalinity.

Methyl-orange Paper. *Bases = Yellow.*
Acids = Brownish-yellow.

Where this is to be employed for detecting acids, the plain purified filter-paper is dipped in a solution of methyl-orange and dried as directed. When neutralizing an alkali with an acid, the end-point is determined by the formation of a yellowish-red ring in which the red color remains permanent for at least a minute. To avoid unnecessary frequent testing, some indicator may be added to the solution and titration carried on till the liquid assumes a feeble orange tint, when recourse may be had to the test paper. The *red* methyl-orange paper, owing to the necessity of first strongly impregnating the paper with an acid, loses much in sensitiveness, hence is not employed.

Congo-red Paper. *Bases = Red. Acids = Blue.*
The *red* paper is prepared by impregnating purified filter-paper with a solution of 1 part of congo red in 1000 parts of 30 per cent. alcohol and drying. This serves admirably for the estimation of mineral acids in the presence of acetic acid or the salts of zinc and aluminum. The neutral point is indicated by the appearance of a blue-black ring. The *blue* paper is made by dipping the red paper in an acid bath sufficiently strong to produce a color change, then drying. Owing to the presence of some free acid, this paper is necessarily less sensitive toward alkalies.

Phenolphthalein Paper. *Bases = Red.*
This paper, prepared by impregnating purified filter-paper with phenolphthalein solution, is not so sensitive toward alkalies as a good quality of litmus, while the red paper loses its color rapidly on exposure to the air.

Hæmatoxylin and Brazilin Paper.
Because of the difficulties of preservation, these papers are rarely used.

Cochineal Paper. *Bases = Violet. Acids = Red.*
This is prepared by immersing the special filter-paper in the test solution of cochineal. According to Dieterich, its sensitiveness is such as to indicate one part of sulphuric acid in 8000 and one of hydrochloric in 10,000 parts of water.

PREPARATION OF STANDARD NORMAL ACID AND ALKALI SOLUTIONS.

The greatest care and accuracy are necessary in the preparation of these standard solutions, for the slightest inaccuracies in strength will give rise to corresponding errors in our results. It is customary to prepare one standard and verify its accuracy, then from this the various others may be adjusted; for example, a standard normal hydrochloric acid is prepared, and by means of this a standard alkali, from which, in turn, other standard acids may be adjusted. It will then be evident that if an error is committed in the preparation of the original standard, all other standards prepared by means of this will err to a corresponding degree.

Normal Hydrochloric Acid.

$HCl = 36.18$.

$\frac{N}{1}$ HCl V. S. = 36.18 Gm. absolute HCl in 1 Liter (1000 Cc.).

This standard is preferred by many because when added to solutions of the alkali-earths soluble salts result, where in case of the standard sulphuric acid precipitation ensues which is annoying to the operator. This standard has the disadvantage of incurring a slight loss in hydrochloric acid, through volatilization when boiled; hence should only be employed in *cold* titrations.

The first step in the preparation of this standard is to prepare a diluted acid which is somewhat stronger than that desired; then, after accurately establishing its strength, it can be diluted accordingly. For example, 130 Cc. of pure hydrochloric acid (U. S. P.) of specific gravity 1.163 (31.9 per cent. HCl) are diluted with sufficient water to make it measure about one liter.

The next operation is to establish the strength of this solution in absolute HCl; which may be accomplished either by means of Iceland spar or sodium carbonate or by precipitation (with silver nitrate) or iodometrically. Where great accuracy is desirable, the standard should be re-standardized by a second different method.

(*a*) *Standardization of Hydrochloric Acid by Iceland Spar.*

This method is considered as one of the most accurate and satisfactory of all thus far proposed.* The operation of standardization consists in dissolving an accurately weighed quantity of Iceland spar (crystalline $CaCO_3$) in a measured excess of the hydrochloric acid solution which is to be standardized; the uncombined excess of this is then ascertained by titrating back with a solution of an alkali; the difference represents the volume (which can be calculated into weight of absolute HCl) of the acid required to dissolve the Iceland spar; the equivalence of the latter two being known, the strength of the acid may be readily calculated.

The first step in the operation consists in filling two burettes, one with the sample of hydrochloric acid to be standardized, prepared as above directed, and the other with a solution of about 10 Gm. of potassium hydroxide in 100 Cc. of water. The relationship between these is next established by drawing off exactly 10 Cc. of the acid, about an equal volume of water is added, followed by sufficient of methyl-orange solution † to impart a faint but distinct red color, after which the alkali solution is added slowly from its burette, stirring constantly until the solution changes to a yellow. This operation is repeated with fresh portions until uniform results are obtained.

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* For a slight modification of the method here given see article by O. Masson, Druggists' Circular, 1900, p. 14, from Chemical News.

† Congo red, if available, is to be preferred because of greater sensitiveness toward acids.

We will assume that 8 Cc. of the alkali solution were required to neutralize the 10 Cc. of the hydrochloric acid: To neutralize exactly one liter (1000 Cc.) of standard normal hydrochloric acid, containing 36.18 Gm. of absolute HCl, it will require exactly 49.67 Gm. of Iceland spar ($CaCO_3$).* Conversely, 0.4967 Gm. of the latter will be required to neutralize 0.3618 Gm. of absolute HCl, which is equivalent to 10 Cc. of the normal volumetric solution. A portion of powdered Iceland spar dried at 100° C., weighing exactly 0.4967 Gm., is placed in a beaker (about 200 Cc. capacity), and to this are added about 20 Cc. of distilled water, followed by 20 Cc. of the sample of acid to be standardized, accurately measured from the burette. The beaker should be immediately covered with a clock-glass in order to avoid any loss of acid through violent effervescence; this is allowed to stand until the evolution of gas has ceased, and no undissolved particles can be distinguished. Should any of the powder remain undissolved, it will be necessary to prepare a fresh stronger acid solution. To the solution in the beaker is now added sufficient methyl-orange indicator to impart a faint but distinct red color; then the excess of hydrochloric acid is ascertained by titrating back with the previously mentioned potassium hydroxide solution, until the mixture changes to a yellow. To accomplish this, 9.96 Cc. of the alkali were required, which correspond to 12.45 Cc. of the hydrochloric acid solution; for

$$\frac{\text{Cc. KOH Sol.}}{8} : \frac{\text{Cc. HCl Sol.}}{10} :: \frac{\text{Cc. KOH Sol.}}{9.96} : \frac{\text{Cc. HCl. Sol.}}{x}$$
$$8x = 10 \times 9.96$$
$$x = 12.45$$

If 20 Cc. of the sample acid were added to the Iceland spar and the uncombined excess was equivalent to 12.45 Cc., the difference (20—12.45), 7.55 Cc., would represent the volume of acid solution which is equivalent to 0.496 Gm. of the pure calcium carbonate, and would therefore contain 0.3618 Gm. of absolute acid. Since each 10 Cc. of standard normal hydrochloric acid should contain 0.3618 Gm. of absolute acid, it will then be necessary to dilute each 7.5 Cc. of the prepared sample to 10 Cc., or 755 Cc. to 1000 Cc., in order to convert it into the normal product.

(*b*) *Standardization of Hydrochloric Acid by Sodium Carbonate.*

The sample of anhydrous sodium carbonate used for this purpose must be very pure, and is best prepared from the commercial pure bicarbonate ($NaHCO_3$) by placing a quantity on a plain filter and washing with cold distilled water until the filtrate ceases to show (after acidulating with HNO_3) any traces of sulphates or chlorides. The residue is then dried

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* One-half of the molecular weight is taken because *one* molecule of $CaCO_3$ requires *two* of hydrochloric acid; thus, $\frac{CaCO_3}{99.34} + \frac{2HCl}{2 \times 36.18} = CaCl_2 + CO_2 + H_2O$. Therefore, for one molecule of HCl (36.18 parts) one-half of a molecule of $CaCO_3$ (49.67 parts) is necessary.

and heated to dull redness for a least ten minutes in a platinum crucible, after which it is allowed to cool in a desiccator; 100 Gm. of the bicarbonate will yield about 63 Gm. of neutral carbonate ($2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$). The operation of standardization proceeds in exactly the same manner as with Iceland spar, with only a change in the equivalents, 52.65 Gm. of Na_2CO_3 being equivalent to 36.18 Gm. of absolute HCl, or 0.5265 Gm. of the former corresponds to 0.3618 Gm. of the latter.

(*c*) *Standardization of Hydrochloric Acid with Borax.*

After once recrystallizing commercial crystalline borax, the crystals are pulverized and shaken with water at 25° to 30° C., until a saturated solution has been obtained; this is then filtered and set aside in a cold place to crystallize. After well draining, the crystals are spread out between several folds of clean filter-paper, pressing in order to remove all traces of moisture; this operation is repeated, allowing the crystals to remain covered several days until all traces of adhering moisture have been removed. Neither heat nor the exsiccator should be used. Since, according to the equation,

$$\underset{379.32}{Na_2B_4O_7 10H_2O} + \underset{2 \times 36.18}{2HCl} = 2NaCl + 4H_3BO_3 + 5H_2O$$

379.32 parts of borax require 2 × 36.18 parts of absolute hydrochloric acid for neutralization, 36.18 parts of the latter will be equivalent to 189.66 ($\frac{379.32}{2}$) parts of borax, or 1.897 Gm. will correspond to 0.3618 Gm. HCl or 10 Cc. of $\frac{N}{1}$ HCl V. S. Hence, 1.897 Gm. of the purified crystals of borax are accurately weighed and dissolved in about 50 Cc. of distilled water; then two drops of *methyl-orange* are added, followed by the sample of hydrochloric acid to be standardized, which is added from a burette until the yellow of the solution just changes to a red. If, for example, 9.2 Cc. of the acid were required, then this must be diluted to 10 Cc., because it contains 0.3618 Gm. of absolute HCl; or 92 Cc. are diluted to 100 Cc., or 920 Cc. to 1000 Cc. If more than 10 Cc. of the trial acid are required to neutralize the 1.897 Gm. of borax, the former is too dilute, hence a stronger solution must be prepared. After diluting the acid, a second trial should be made, when exactly 10 Cc. of the standard acid should neutralize 1.897 Gm. of the borax.

(*d*) *Standardization of Hydrochloric Acid with Silver Nitrate.*

This may be carried out either *volumetrically*, by means of a decinormal silver nitrate V. S., in which each cubic centimeter is equivalent to 0.003618 Gm. of absolute HCl (see p. 140); or gravimetrically, in which 10 Cc. of the trial standard solution, after diluting, is heated to boiling and the chlorine estimated by precipitating with a solution of silver nitrate. The precipitate of silver chloride is collected, washed, dried, fused, and weighed; its weight, multiplied by the factor 0.25427, gives the weight of the absolute HCl contained in the 10 Cc. of the trial acid, which is then diluted accordingly, so that each 10 Cc. will contain 0.3618 Gm. of absolute hydrogen chloride.

(*e*) *Iodometric Standardization of Hydrochloric Acid.*

This very accurate method is based on the fact that diluted inorganic acids (as HCl or H_2SO_4) liberate an equivalent amount of iodine from a solution which contains a mixture of potassium iodide and iodate; thus,

$$\underset{6 \times 36.18}{6HCl} + 5KI + KIO3 = \underset{6 \times 125.89}{6I} + 6KCl + 3H_2O$$

The quantity of iodine liberated is estimated by means of a standard $\frac{N}{10}$ solution of sodium thiosulphate.

Of the sample of diluted hydrochloric acid to be standardized, exactly 5 Cc. are measured into a beaker, and diluted with about 50 Cc. of water; from 1.5 to 2 Gm. of potassium iodide and 10 Cc. of a 3 per cent. neutral solution of potassium iodate are added. The quantity of liberated iodine is then estimated by slowly adding (stirring constantly) a decinormal solution of sodium thiosulphate until the solution assumes a pale brown color, when a few drops of starch paste are added and the addition of thiosulphate solution continued until the blue color of the starch iodide disappears. Titration can be completed without the use of starch by noting the disappearance of brown color. The volume of $\frac{N}{10}$ thiosulphate V. S. is converted into cubic centimeters of $\frac{N}{1}$ V. S. by dividing by 10. The sample hydrochloric acid is then diluted until its volume corresponds to that of a $\frac{N}{1}$ thiosulphate V. S.

1 molecule of sodium thiosulphate = 1 molecule of iodine = 1 molecule of absolute HCl.
1000 Cc. of $\frac{N}{10}$ V. S. sodium thiosulphate = 1000 Cc. $\frac{N}{10}$ V. S. iodine = 100 Cc. of $\frac{N}{1}$ HCl. V. S.
1000 Cc. of $\frac{N}{1}$ V. S. " " = 1000 Cc. $\frac{N}{1}$ V. S. " = 1000 Cc. of $\frac{N}{1}$ HCl. V. S.

Example: 5 Cc. of the hydrochloric acid were measured off. Of the $\frac{N}{10}$ thiosulphate solution, 60.5 Cc. were required, which are equivalent to 6.05 Cc. of a $\frac{N}{1}$ solution.* To make these equal, we dilute 5 Cc. of our acid to 6.05 Cc., or 826.4 Cc. of the acid are measured into a cylinder and distilled water added (at 15°C.) till the volume measures exactly 1000 Cc.

II. Normal Sulphuric Acid.

$H_2SO_4 = 97.35$.

$\frac{N}{1}$ H_2SO_4 V. S. = 48.675 Gm. of absolute acid in 1 liter (1000 Cc.).

Sulphuric acid being bivalent, a quantity representing one-half of its molecular weight in absolute acid (in grammes) is taken for one liter of standard solution. (Compare Normal Solutions, page 17.)

As has already been stated, standard sulphuric acid should not be used in estimating solutions of the alkali-earths, owing to the precipitation of insoluble salts. It is adapted for hot titrations, and is preferred by many as being the best all-round standard.

A dilution is first made by mixing about 30 Cc. of pure concentrated U. S. P. sulphuric acid (sp. gr. 1.835 and 92.5 per cent. H_2SO_4) with sufficient water to make about 1050 Cc., and after cooling to 15° C., or any other chosen standard temperature, a portion is transferred to a burette. This solution may be standardized either volumetrically, gravimetrically, or through its specific gravity.

Volumetric standardization is carried out by filling two burettes, one with accurately standardized normal potassium hydroxide (page 43), and the other with the diluted sulphuric acid to be standardized; 10 Cc. of the former solution are then accurately measured off into a porcelain dish, and after diluting with water (about 50 Cc.) and adding about 2 drops of methyl-orange† solution, or sufficient to impart a distinct yellow color to the solution, the sulphuric acid is added slowly from the other burette, stirring constantly, until the solution is exactly neutral, as shown by a change from yellow to red. Note the

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* The quantity of *deci*normal thiosulphate is calculated into *normal* because our *normal* hydrochloric acid is made to conform to a *normal* thiosulphate.

† If available, congo red is to be preferred because of greater sensitiveness toward acids.

number of cubic centimeters of sulphuric acid solution added; then dilute this with sufficient water that equal volumes of the standard acid and alkali exactly neutralize eath other. For example, to neutralize the 10 Cc. of $\frac{N}{1}$ KOH V. S. it requiréd 9.8 Cc. of the sample of sulphuric acid; the latter must then be diluted to the extent of 0.2 Cc., or 980 Cc. are measured off and water added until it measures 1000 Cc.; both solutions will then be of like titer.

Gravimetric standardization is effected by accurately measuring 10 Cc. of the above-prepared acid solution into a beaker of about 200 Cc. capacity; then after diluting with about 100 Cc. of water, the beaker is covered with a clock-glass and its contents brought to a boil. To this boiling solution is slowly added a solution of barium chloride until precipitation ceases, which may be ascertained by allowing the fluid to stand sufficiently long to permit a portion of the supernatant fluid to clear, when more of the reagent is added. The clock-glass is now rinsed off into the beaker, and while still hot the fluid, with precipitate, is transferred to a quantitative ashless filter, rinsing the beaker thoroughly with boiling water to remove every trace of adhering precipitate. This latter is then washed with boiling water until all traces of barium chloride have been removed; if a platinum crucible is at hand, the still wet precipitate with filter may be ignited at once, otherwise it should be dried, then transferred to an accurately tared porcelain crucible, and ignited until a white ash results. The weight of the precipitate, multiplied by the factor 0.4201, gives the weight of absolute H_2SO_4 contained in the 10 Cc. of the solution. Two or three determinations should be made as control. *Example:* 10 Cc. of the acid solution yielded 1.211 Gm. of $BaSO_4$, which corresponds to 0.5087 Gm. of absolute H_2SO_4 (1.211×0.42006) in 10 Cc., or 50.87 Gm. in 1000 Cc. This is stronger than desired, for the standard solution should contain 48.675 Gm. of absolute sulphuric acid in 1000 Cc. ∴ We then measure off 4867.5 Cc. or volumes of our solution and add water until it measures 5087 Cc. or volumes, which will yield a normal solution.

FOR ASCERTAINING THE PERCENTAGE STRENGTH OF SULPHURIC ACID SOLUTIONS FROM THE SPECIFIC GRAVITIES AT 18° C. (WATER AT 18° C. = 1).

SPECIFIC GRAVITY.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
1.60	68.89	68.97	69.06	69.15	69.23	69.32	69.40	69.49	69.58	69.66
1.61	69.75	69.83	69.92	70.01	70.09	70.18	70.26	70.35	70.43	70.52
1.62	70.61	70.69	70.78	70.86	70.95	71.03	71.12	71.20	71.29	71.37
1.63	71.46	71.55	71.63	71.72	71.80	71.89	71.97	72.06	72.14	72.23
1.64	72.31	72.40	72.48	72.57	72.65	72.74	72.82	72.91	72.99	73.08
1.65	73.16	73.25	73.33	73.42	73.50	73.59	73.67	73.76	73.84	73.93
1.66	74.01	74.10	74.18	74.27	74.35	74.44	74.52	74.61	74.69	74.78
1.67	74.86	74.95	75.03	75.12	75.20	75.29	75.37	75.46	75.54	75.63
1.68	75.71	75.80	75.88	75.97	76.05	76.14	76.22	76.31	76.40	76.48
1.69	76.57	76.65	76.74	76.82	76.91	76.99	77.08	77.17	77.25	77.34
1.70	77.42	77.51	77.59	77.68	77.77	77.85	77.94	78.03	78.11	78.20
1.71	78.29	78.37	78.46	78.55	78.63	78.72	78.81	78.90	78.98	79.07
1.72	79.16	79.24	79.33	79.42	79.51	79.59	79.68	79.77	79.85	79.94
1.73	80.03	80.12	80.21	80.30	80.39	80.48	80.57	80.66	80.75	80.84
1.74	80.93	81.02	81.12	81.21	81.30	81.40	81.49	81.58	81.67	81.76
1.75	81.86	81.95	82.04	82.14	82.24	82.34	82.44	82.53	82.63	82.72
1.76	82.82	82.92	83.02	83.13	83.23	83.32	83.42	83.52	83 62	83.72
1.77	83.82	84.92	84.02	84.12	84.22	84.33	84.43	84.54	84.65	84.77

Standardization Through Specific Gravity.—By means of Pickering's figures, Marshall* has adapted this method to the standard-

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* Jour. Soc. Chem. Industry, 1899, p. 5.

[illegible]

ization of sulphuric acid. A sample of very pure sulphuric acid is diluted with water (30 Cc. to 1000 Cc.) and cooled to either 15°C. or 18°C.; the temperature must be known within 0.5°C. The specific gravity is then determined with great accuracy, preferably with a Sprengel tube; the weighings must be correct within 0.01 Gm., and the specific gravity must be known within 0.0005; under these conditions the standard solutions will be correct within 0.1 per cent.

III. Normal Oxalic Acid.

$H_2C_2O_4 + 2H_2O = 125.08.$

$\frac{N}{1}$ $H_2C_2O_4$ **V. S.** $= 62.54$ **Gm. of** $H_2C_2O_4 + 2H_2O$ **in 1 liter (1000 Cc.).**

Oxalic acid being a dyad, one-half of the molecular weight is taken. If an absolutely pure sample of this acid free from all traces of adhering moisture is available, this is the most convenient standard solution to prepare, for nothing further is necessary than to accurately weigh off 62.54 Gm. of the crystals, and after dissolving in a sufficient quantity of distilled water the volume is made up to 1000 Cc. Such an ideal sample is difficult to obtain owing to the great variations in the degree of purity as well as the uncertain hydration of commercial or even the chemically pure oxalic acid. A sample of the purest obtainable should be tested and then recrystallized according to the directions of the Pharmacopœia.*

Owing to the concentration of this normal solution, it has a tendency to crystallize at the point of the burette on standing, in consequence of which particles of the solid matter are liable to drop into the solution undergoing assay, hence the weaker decinormal solution is generally preferred. When titrating with oxalic acid, only phenolphthalein, litmus, or rosolic acid should be employed.

Decinormal Oxalic Acid.

$\frac{N}{10}$ $H_2C_2O_4$ **V. S.** $= 6.254$ **Gm. in 1 liter (1000 Cc.).**

This decinormal solution is prepared as above directed, employing 6.254 Gm. of the acid with sufficient distilled water to make 1000 Cc. of the solution.

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* "*Pure oxalic acid*, crystallized, is in form of colorless, transparent crystals, which, on ignition upon platinum-foil leave no residue." "To 1 part of the acid add 10 parts of cold water, and shake until the latter is saturated. Filter off the solution from the undissolved crystals, evaporate the filtrate to about three-fourths of its volume, and set it aside so that the fixed salts which it contains may crystallize out. Carefully decant the liquid from the crystals, concentrate it by evaporation, and set it aside to crystallize, stirring occasionally to prevent the formation of large crystals, which might inclose moisture." After having drained the crystalline mass in a funnel, it should be spread out in a thin layer between several folds of clean white filter-paper, pressing in order to remove all traces of moisture; this operation should be repeated with fresh paper until all traces

IV. Normal Potassium Hydroxide.

$KOH = 55.70$.

$\frac{N}{1}$ KOH V. S. = 55.70 Gm. KOH in 1 liter (1000 Cc.).

This standard is not prepared by weighing off the potassium hydroxide direct, for the commercial pure chemical is too impure, and the absolutely pure article made from metallic potassium, like the commercial article, absorbs moisture and carbonic acid gas so rapidly from the air that an accurate weighing is practically impossible. For this purpose a concentrated solution is first prepared by dissolving between 75 and 80 Gm. of potassium hydroxide (by alcohol) in sufficient distilled water to make about 1000 Cc. A burette is filled with this solution. From a second burette containing an accurately prepared standard normal acid, draw exactly 10 Cc. off into a porcelain dish, diluting with about 30 Cc. of water, and after adding one or two drops of methyl-orange solution,* the potassium hydroxide is slowly run in, stirring constantly, until the color changes from yellow to red; that is, the acid has been exactly neutralized by the alkali. Note the number of cubic centimeters of potassium hydroxide added, then dilute this with sufficient water so that equal volumes of the standard and acid alkali exactly neutralize one another.

Example.—The average of three estimations indicated that 8.5 Cc. of the potassium hydroxide solution were necessary for the neutralization of 10 Cc. of the standard hydrochloric acid; then, in order to dilute the former to the strength of the latter, either 8.5 Cc., or 85 Cc., or 850 Cc. of the alkali solution are accurately measured off and distilled water added until the total volume measures either 10 Cc., or 100 Cc., or 1000 Cc., as the case may be. The resulting potassium hydroxide solution will be a "standard normal," because it exactly corresponds in neutralizing power to our standard hydrochloric acid.

V. Normal Sodium Hydroxide.

$NaOH = 39.76$

$\frac{N}{1}$ NaOH V. S. = 39.76 Gm. NaOH in 1 liter (1000 Cc.).

This standard solution is prepared in exactly the same manner as the above potassium hydroxide. A very pure caustic soda prepared

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of adhering moisture have been removed. The crystals should *not* be dried in a desiccator or by heat.

Another method consists in preparing an *anhydrous* oxalic acid by first crystallizing from a concentrated hot dilute hydrochloric acid (1 part acid to 1 part water). After draining each time, it is repeatedly recrystallized from hot aqueous solutions until the crystals, when dissolved in water and acidulated with nitric acid, cease to react with silver nitrate solution. Each recrystallization should be carried out by placing the hot concentrated solution in a vessel of cold water, stirring constantly, in order that the oxalic acid may separate as a granular mass. This is then heated at between 60° and 70°C., until it ceases to lose weight; usually seven hours is sufficient. Of this, 4.966 Gm. are taken for 1000 Cc. of a $\frac{N}{10}$ V. S.

* Owing to the possible presence of carbonates in potassium and sodium hydroxides, an indicator which is not sensitive to carbonates should be employed, as, for example, methyl-orange, gallein, phenacetolin, congo red, or cochineal. Phenolphthalein may be used if the titration is carried on in boiling solution or the preferable residual method is employed. See pages 51 and 46.

from the metal may be obtained in the market at a moderate price, which is to be preferred to the less pure "sodium hydroxide (by alcohol)." Owing to the readiness with which solutions of this alkali attack the burettes and glass containers, preference is usually given to the standard potassium hydroxide.

VI. Decinormal Barium Hydroxide.

$Ba(OH)_2 = 170.16.$

$\frac{N}{10}$ $Ba(OH)_2$ V. S. = 8.508 Gm. $Ba(OH)_2$ in 1 liter (1000 Cc.).

A solution of pure barium hydroxide is prepared which is somewhat stronger than above directed; this is then titrated and standardized as directed under normal potassium hydroxide.

Owing to the readiness with which the above alkali solutions (especially the latter) absorb carbonic acid gas from the air, they should be kept in containers provided with rubber stoppers, through which pass drying tubes containing soda-lime (Fig. 16, p. 19) *; these same tubes should be attached to the top of the burette while using.*

VII. Decinormal Solutions.

$\frac{N}{10}$

Take of any *normal* standard solution exactly 100 Cc. and dilute with distilled water at 15° C., or any other temperature which may have been selected as standard (see page 11), to make 1000 Cc.

VIII. Centinormal Solutions.

$\frac{N}{100}$

Take of any *normal* standard solution exactly 10 Cc. and dilute with distilled water at 15° C., or any other temperature which may have been selected as standard (see page 19), to make 1000 Cc. (Compare Dilution of Indicators, page 23.)

ALKALIMETRY.

This embraces the estimation of alkalies by means of the neutralizing power of standard acids.

The neutralizing equivalent of all the standard normal acids is exactly the same, for, as already explained, they contain in one liter the molecular weight (in grammes) of the acid, if it is a univalent compound. If the acid be bivalent, then one-half of the molecular weight is taken, which, of course, reduces its valency to one atom of replaceable hydrogen. *Examples:* From the equation:

HCl	+	$NaOH$	=	$NaCl$	+	H_2O
Hydrochloric Acid		Sodium Hydroxide		Sodium Chloride		Water
36.18		39.76				

we learn that—

36.18 Gm. HCl are equivalent to 39.76 Gm. NaOH.
1000 Cc. $\frac{N}{1}$ HCl containing 36.18 Gm. HCl are " " 39.76 Gm. NaOH.
1 Cc. $\frac{N}{1}$ HCl " 0.03618 Gm. HCl is " " 0.03976 Gm. NaOH.

In case of the bivalent acids we have an equation like the following:

$$\underset{\substack{\text{Sulphuric Acid}\\ 97.35}}{H_2SO_4} + \underset{\substack{\text{Sodium Hydroxide}\\ 2 \times 39.76}}{2NaOH} = Na_2SO_4 + 2H_2O.$$

One molecule (97.35 p.) of sulphuric acid is equivalent to *two* molecules (2 × 39.76 p.) of sodium hydroxide, or *one-half* of a molecule (48.675 p.) of the acid is equivalent to *one* molecule (39.76 p.) of the alkali.

48.675 Gm. H_2SO_4 are equivalent to 39.76 Gm. NaOH.
1000 Cc. $\frac{N}{1}$ H_2SO_4 containing 48.675 Gm. H_2SO_4 " " " 39.76 Gm. NaOH.
1 Cc. $\frac{N}{1}$ H_2SO_4 " 0.048675 Gm. H_2SO_4 is " " 0.03976 Gm. NaOH.

The equivalence of the standard *decinormal* acids would be *one-tenth less*, since they contain only one-tenth as much of the acid as the normal; thus:

1000 Cc. $\frac{N}{10}$ HCl containing 3.618 Gm. HCl are equivalent to 3.976 Gm. NaOH.
1 Cc. $\frac{N}{10}$ HCl " 0.003618 Gm. HCl is " " 0.003976 Gm. NaOH.
1000 Cc. $\frac{N}{10}$ H_2SO_4 containing 4.8675 Gm. H_2SO_4 are equivalent to 3.976 Gm. NaOH.
1 Cc. $\frac{N}{10}$ H_2SO_4 " 0.0048675 Gm. H_2SO_4 is " " 0.003976 Gm. NaOH.

From this it will be seen that the neutralizing equivalents of the different standard acids of the same class are exactly the same, so that, in the estimation of an alkali, it makes no difference (in neutralizing power) whether a standard normal hydrochloric, sulphuric, or oxalic acid has been employed, for one cubic centimeter of any one is equivalent to $\frac{1}{1000}$ part of the molecular weight of a univalent alkali-metal or $\frac{1}{2000}$ part of a bivalent alkali-earth. If decinormal acids are used, their equivalence would be one-tenth less.

ESTIMATION OF CAUSTIC ALKALIES.

1. Alkalies Containing but Little More than Traces of Carbonates.

ALKALI.	1 Cc. $\frac{N}{1}$ ACID V. S. IS EQUIVALENT TO	1 Cc. $\frac{N}{10}$ ACID V. S. IS EQUIVALENT TO
Potassium hydroxide, KOH, . .	0.0557 Gm.	0.00557 Gm.
Sodium hydroxide, NaOH, . .	0.03976 Gm.	0.003676 Gm.

Since nearly all samples of refined caustic potassa and soda contain but small quantities of carbonates, it is usually customary (although not strictly accurate) to ascertain the total alkalinity and calculate the carbonates as hydroxides; the result of the titration indicating, in this case, the percentage of total alkali, while the remainder represents such foreign impurities as lime, silica, alumina, sulphates, chlorides, etc.

Of the sample to be assayed, any definite quantity not exceeding 1 Gm. or an equivalent volume of a solution is selected. Owing to the very hygroscopic nature of the caustic alkalies, they cannot be weighed direct with any degree of accuracy; hence it is best to quickly break up the sample in a warm mortar, transferring immediately to a stoppered weighing bottle, when it, with its contents, are accurately weighed; then a small piece is selected for analysis and the weight again determined; the difference represents the weight of the sample selected. This is then dissolved in about 50 Cc. of water contained in a porcelain dish or a flask or beaker placed on a white surface. After adding two or three drops of methyl-orange or phenolphthalein,* or any other appropriate indicator, the normal acid (sulphuric or hydrochloric) is slowly added from a burette, stirring constantly, until a change of color takes place. The operator is cautioned against adding the standard acid too rapidly and overreaching the neutral point.

Example: A piece of caustic soda weighing 0.895 Gm. was dissolved in about 50 Cc. of water; two drops of methyl-orange were added, followed by normal sulphuric solution until the yellow color changed to a red. Having employed 21.5 Cc. of the standard acid, how much real alkali was present or what was the degree of purity of the sample? Referring to our equivalents (page 45), we see that each cubic centimeter of standard normal acid is equivalent to 0.03976 Gm. of absolute sodium hydroxide; 21.5 Cc. of the acid would then be equivalent to $21.5 \times 0.03976 = 0.85484$ Gm. of the alkali. If 0.895 Gm. of the sample contains 0.85484 Gm. of pure hydroxide, then

$$\begin{array}{cccc} \text{Weight of sample used} & \text{Weight of NaOH found} & & \\ 0.895\text{ Gm.} & : 0.85484\text{ Gm.} & :: & 100 : x \end{array}$$

$$0.895\,x = 85.484$$

$$x = 95.5+ \text{ per cent.}$$

The sample contains, therefore, 95.5+ per cent. of true sodium hydroxide.

For direct percentage estimation see pages 71, 75.

Residual Titration.

The method of residual titration is of general application in volumetric analysis, and consists in adding to the solution of the substance to be examined a measured excess of the standard volumetric reagent; and as soon as the reaction is complete, the excess, or that volume of the added reagent which has not entered into the reaction, is estimated by titrating back with another equivalent volumetric solution; the volume of the latter, deducted from that of the former, gives the volume of the standard solution consumed. To the estimation of caustic alkalies containing carbonates, this method is well adapted, since it relieves the solution of the interfering car-

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* The U. S. P. directs the employment of phenolphthalein, thereby disregarding the slight error caused by using this in cold solution in presence of carbonates. Methyl-orange, fluorescein, congo red, or cochineal are to be recommended in preference, since these indicators are not affected by the presence of carbonates. See page 26.

bonic acid gas in one short boiling. An accurately measured excess of standard normal sulphuric acid is added to the solution of the alkali; this is then boiled until all traces of carbonic acid gas have been driven off. The presence of this gas (disengaged during neutralization), owing to its acid reaction, tends to confuse the end-point of such indicators as litmus or phenolphthalein. After having become nearly cold, two drops of phenolphthalein or any other special indicator are added and the excess of acid titrated back by a standard alkali. The number of cubic centimeters of the normal alkali added, deducted from the total of acid, gives the volume of normal acid required to neutralize the sample.

Example: A piece of dry potassium hydroxide weighing 5.1 Gm. was dissolved in water and the volume made up to exactly 100 Cc.; 10 Cc. of this (containing 0.51 Gm.) were measured off into a flask for estimation. After diluting with about 50 Cc. of water, 15 Cc. of standard normal sulphuric acid were added; and to be certain that the acid was in excess one drop of phenolphthalein (or any other special indicator), when dropped in, should show an acid reaction; the mixture was then boiled and shaken until all carbonic acid gas had been expelled; then one or two drops more of the indicator were added. To neutralize the excess of acid present, 6.9 Cc. of standard normal alkali were required. Since each cubic centimeter of standard normal acid is equivalent to a cubic centimeter of standard normal alkali, then

15.0 Cc. excess of normal acid originally added.
6.9 Cc. alkali required for uncombined excess of acid.
8.1 Cc. acid consumed by the 0.51 Gm. of KOH.

If 1 Cc. $\frac{N}{1}$ H_2SO_4 is equivalent to 0.0557 Gm. of absolute KOH,
8.1 Cc. " " " " " 8.1 × 0.0557 = 0.45117 Gm. absolute KOH.

That is, 0.510 Gm. of the potassium hydroxide taken contains 0.45117 Gm. of true hydroxide; hence:

KOH taken		True KOH present	
0.510 Gm.	:	0.45117 gm.	: : 100 : x

$$0.510\,x = 0.45117 \times 100$$
$$x = 88.45 \text{ per cent.}$$

The sample is therefore 88.45 per cent. pure.

2. Estimation of Alkali Hydroxides in Presence of Carbonate.

The following method of Lunge * will yield accurate results with sodium, potassium, and calcium hydroxides in the presence of carbonates, ammonia being absent. In order to accustom the eye to the color changes, a few trial assays should be made with solutions of known composition. To the solution of the weighed sample add just sufficient phenacetolin test solution to impart a faint yellow tinge; then a standard normal acid is run in until the yellow changes to a pale rose tint. This change indicates the point at which all of the caustic alkali has been neutralized; the volume of standard acid added should therefore be noted. The further addition of acid is continued, which intensifies the red color until the moment the alkali carbonate has been neutralized, when a clear golden yellow results.

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* Journal Soc. Chem. Industry, Vol. 1, 56.

Example: A piece of caustic soda weighing 1.139 Gm. required 25.5 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. to produce a rose tint; the further addition of 2.3 Cc. of the same standard changed this to a yellow.

If 1 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. is equivalent to 0.03976 Gm. NaOH,
25.5 Cc. " " " " are " " $25 \times 0.03976 = 0.9940$ Gm. NaOH.
If 1 Cc. " " " " is " " 0.05265 Gm. Na_2CO_3,
2.3 Cc. " " " " are " " $2.3 \times 0.05265 = 0.1211$ Gm. Na_2CO_3.

Therefore the sample contains 0.9940 Gm., or 87.27 per cent. of sodium hydroxide, and 0.1211 Gm., or 10.63 per cent., of sodium carbonate.

Phenolphthalein may be employed in this class of estimations, proceeding as follows: To a well-diluted solution of the alkali sufficient of the indicator is added to impart a red color; then the normal acid solution is added slowly, keeping the tip of the burette below the surface of the liquid in order to prevent the escape of carbonic acid gas. As soon as the color is discharged, which indicates the neutralization of the caustic alkali and conversion of the neutral carbonate into bicarbonate, the volume of the acid consumed is noted. The solution is now boiled, adding acid until the red color, produced by the decomposition of the bicarbonate, ceases to return. The first added volume corresponds to alkali hydroxide, while the latter volume added is calculated as alkali carbonate.

3. Determination of Mixed Caustic and Carbonated Alkalies.

Commercial refined caustic soda and potash, also the alkaline lyes which are employed in the various industries, come under this head. The sample is first powdered in a warm mortar, and after weighing off exactly 10 Gm. in a crucible, which should be done as quickly as possible, it is ignited gently and allowed to cool in an exsiccator. A second weighing is made; the difference represents the amount of moisture; the contents of the crucible are then washed* into a beaker, filtering if necessary, and finally diluting until the volume measures exactly 500 Cc. Of this solution, aliquot portions are taken for assay.

The quantitative estimation of a mixture of soluble alkali carbonate and hydroxide may be carried out by converting both into their corresponding barium compounds through the addition of barium chloride; thus,

$$Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3 \text{ (insoluble).}$$
$$2NaOH + BaCl_2 = 2NaCl + Ba(OH)_2.$$

The quantity of barium hydroxide in the filtrate and barium carbonate in the precipitate are estimated by residual titration; the number of cubic centimeters of acid employed in each case is multiplied by the equivalents of sodium hydroxide and sodium carbonate.

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*This being quantitative work, the operator is particularly cautioned to thoroughly wash all containers and filter, if used, to avoid the loss of even a trace of the alkali.

Of the solution prepared as directed, 50 Cc., representing 1 Gm. of the dry sample, are accurately measured off, and, after diluting to about 250 Cc., the solution is brought to a boil and solution of barium chloride is added until precipitation ceases.* The filtration should be carried out as rapidly as possible, collecting the precipitate of barium carbonate on a plain filter, washing with boiling water until a drop of the wash-water fails to redden phenolphthalein.† To the filtrate is added a measured excess of normal hydrochloric acid V. S.; the solution is then boiled and agitated to remove all traces of carbonic acid, and, after adding phenolphthalein or litmus, the excess of normal acid is titrated back by means of normal alkali V. S. The difference, representing the number of cubic centimeters of normal acid required, is then multiplied by the factor for sodium hydroxide (0.03976).‡ The precipitate of barium carbonate remaining in the filter represents the alkali carbonate by an equivalent quantity. The estimation of this is carried out by piercing the bottom of the filter, and by means of boiling water every particle of the precipitate is washed down into the same beaker which was employed for the precipitation. A measured excess of normal hydrochloric acid V. S. is added in sufficient quantity to dissolve the entire precipitate with such traces as might have adhered to the sides of the beaker from the first operation of precipitation. The excess of standard hydrochloric acid, over and above that which has been neutralized by the barium carbonate, is now estimated by titrating back with a normal standard alkali, using methyl-orange as indicator. Phenolphthalein or litmus may be employed as indicator, provided the acid solution is first boiled and shaken to remove all traces of carbonic acid gas. The number of cubic centimeters of the normal standard acid V. S. required to neutralize the barium carbonate is then multiplied by the factor for sodium carbonate (0.05265).§

Example: 10 Cc. of a solution of commercial caustic soda, prepared as directed above, representing 1 Gm. of the sample, were diluted, heated to boiling, precipitated with barium chloride, filtered, and the precipitate washed. The filtrate and precipitate were separately estimated.

(*a*) To the filtrate containing the barium hydroxide (representing the sodium hydroxide) two or three drops or sufficient of methyl-orange were added to impart a faint yellow tint; this was followed by standard $\frac{N}{1}$ HCl V. S, of which 17.5 Cc. were required for

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* The beaker in which the precipitation takes place should be kept covered with a clock-glass, which serves to keep the upper sides of the beaker moist from condensation, thereby preventing the precipitate from drying on the glass.

† This filtrate containing barium hydroxide readily absorbs carbonic acid gas from the air, hence filtration and washing should proceed rapidly.

‡ 1 Cc. $\frac{N}{1}$ HCl V. S. = 0.08508 Gm. $Ba(OH)_2$ = 0.03976 Gm. NaOH or 0.05570 Gm. KOH.

§ 1 Cc. $\frac{N}{1}$ HCl V. S. = 0.09797 Gm. $BaCO_3$ = 0.05265 Gm. Na_2CO_3 or 0.06859 Gm. K_2CO_3.

neutralization (production of rose tint). Since 1 Cc. of $\frac{N}{1}$ HCl V. S. = $\left(0.08508 \text{ Gm. } Ba(OH)_2\right)$ 0.03976 Gm. of NaOH, then 17.5 Cc. are equivalent to 0.6958 Gm. (17.5 × 0.03976) of NaOH, or 69.58 per cent.

(*b*) To the precipitate of barium carbonate (representing the sodium carbonate), suspended in a little water, a measured excess consisting of 20 Cc. of $\frac{N}{1}$ HCl V. S. was run in, and as soon as solution had taken place methyl-orange was added. The excess of standard acid was then determined by titrating back with $\frac{N}{1}$ KOH V. S.; for this purpose 14.8 Cc. were required, which left 5.2 Cc. of $\frac{N}{1}$ HCl V. S. (20 — 14.8 = 5.2) for the neutralization of the carbonate. Then if 1 Cc. of $\frac{N}{1}$ HCl V. S. = (0.09797 Gm. $BaCO_3$) 0.05265 Gm. of Na_2CO_3, 5.2 Cc. are equivalent to 0.2737+ Gm. (5.2 × 0.05265) of Na_2CO_3, or 27.37 per cent.

The sample contains, therefore, 69.58 per cent. of NaOH and 27.37 per cent. of Na_2CO_3, making a total of 96.95 per cent. of total soda, the remainder consisting of various impurities.

4. Estimation of Alkali Carbonates and Bicarbonates.

SUBSTANCES TITRATED.	1 CC. OF NORMAL ACID IS EQUIVALENT TO:	
Ammonium carbonate, normal, $(NH_4)_2CO_3$,	0.04770	Gm.
Ammonium carbonate (U. S. P.), $NH_4HCO_3.NH_4.NH_2CO_2$,	0.051997	"
Lithium carbonate, Li_2CO_3,	0.036740	"
Potassium bicarbonate, $KHCO_3$,	0.099360	"
Potassium carbonate, K_2CO_3,	0.068590	"
Sodium bicarbonate, $NaHCO_3$,	0.083420	"
Sodium carbonate, Na_2CO_3 (anhydrous),	0.052650	"
Sodium carbonate, $Na_2CO_3 + 10H_2O$,	0.142050	"

For the titrimetric estimation of alkali carbonates two methods are available—namely, the hot and the cold.

Cold Process.—To the solution of 1 Gm. or less of the accurately weighed sample, in about 25 Cc. of water, two drops of methyl-orange solution are added; then the normal acid V. S. is slowly run in until the yellow just changes to a red. Should any difficulty be experienced in distinguishing the neutral point (the change from yellow to red), it is advisable to have two sample solutions, one acid and the other alkaline, tinted with the indicator, for assisting comparisons. The operator is cautioned against employing too much of the indicator.

Example: 0.850 Gm. of sodium bicarbonate, dissolved in about 25 Cc. of water, required, after the addition of 2 drops of methyl-orange, 10 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. for neutralization. Then, in accordance with the equation,

$$\begin{array}{ccccccccc} H_2SO_4 & + & 2NaHCO_3 & = & Na_2SO_4 & + & 2CO_2 & + & 2H_2O \\ \text{Sulphuric Acid} & & \text{Sodium Bicarbonate} & & \text{Sodium Sulphate} & & \text{Carbonic} & & \\ 97.35 & & 2 \times 83.42 & & & & \text{Acid Gas} & & \end{array}$$

1000 Cc. $\frac{N}{1}$ H_2SO_4 V. S. containing 48.675 Gm. of sulphuric acid are equivalent to 83.42 Gm. of sodium bicarbonate.

1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. containing 0.048675 Gm. H_2SO_4 = 0.08342 Gm. $NaHCO_3$.

10 Cc. of normal sulphuric acid V. S. = 10 × 0.08342 = 0.8342 Gm. of pure sodium bicarbonate. That is, the 0.850 Gm. of sample taken contains 0.8342 Gm., or 98.14+ per cent. of pure substance.

$$\begin{array}{ccccccc} \text{NaHCO}_3\text{ taken} & & \text{NaHCO}_3\text{ found} & & & & \\ 0.850 & : & 0.8342 & :: & 100 & : & x. \end{array}$$

$$0.850\,x = 0.8342 \times 100$$

$$x = 98.14+$$

Hot Process.—The indicators phenolphthalein, litmus, or lacmoid are available here; methyl-orange cannot be used. Boiling is necessary in order to expel the carbonic acid gas, as the presence of this, owing to its acid reaction, interferes with the end-reaction of these indicators. We may proceed in either of two ways, the first method (*a*) being preferable because of greater accuracy and rapidity.

(*a*) This is the method of *residual titration*, in which an excess (accurately measured) of standard acid is added to the solution of weighed alkali contained in a Florence flask. This mixture is then boiled, shaking at frequent intervals in order to remove all traces of carbonic acid gas, after which the indicator is added in sufficient quantity to tinge the acid solution; then the excess of acid is ascertained by titrating back with a standard alkali. The number of cubic centimeters of alkali solution used is deducted from the total number of cubic centimeters of acid added; the difference represents the quantity of standard acid required to neutralize the carbonated alkali.

Example: 1.235 Gm. of dry salts of tartar (K_2CO_3) were dissolved in about 50 Cc. of water, 20 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. added, and the solution boiled as above directed. After adding two drops of phenolphthalein, 3.5 Cc. of $\frac{N}{1}$ KOH V. S. were required to produce a distinct red. Then 20 Cc. — 3.5 Cc. = 16.5 Cc. If 1 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. = 0.06859 Gm. of K_2CO_3, 16.5 Cc. are equivalent to $16.5 \times 0.06859 = 1.131735$ Gm. of true potassium carbonate (K_2CO_3) contained in the 1.235 Gm. of sample, which must then be 91.63+ per cent. pure.

(*b*) This method consists in slowly adding the standard acid directly to the solution of weighed alkali contained in a porcelain dish, to which phenolphthalein has already been added. During the titration the solution is kept in constant ebullition in order to remove the carbonic acid gas as fast as it is liberated by the addition of acid. The addition of the standard acid is continued as long as the red color of the solution reappears, and if after three minutes' boiling the liquid fails to assume a rose tint, the titration is considered complete. The loss in volume sustained by the liquid while boiling should be repleted by the frequent addition of hot water.

For direct percentage estimation see page 71.

Estimation of Alkali Bicarbonates in Presence of Normal Carbonates (Thompson).

An accurately weighed quantity of sodium or potassium bicarbonate (containing normal carbonate) is dissolved in a measured volume of water; of this, an aliquot portion is drawn off, a measured excess of $\frac{N}{1}$ alkali V. S. (free from carbonate) added, and then a neutral solution of barium chloride in sufficient excess to precipitate all of the CO_2.* To the cold mixture of precipitate ($BaCO_3$) and fluid two drops of phenolphthalein are added and the excess of standard alkali estimated by adding $\frac{N}{1}$ HCl V. S., slowly, with constant stirring, until the pink color is discharged. The precipitate of barium carbonate does not affect the indicator or normal acid in the cold. The total excess volume of standard alkali added, *less* that of the standard acid employed for titrating back, represents the number of cubic centimeters of the former required for converting the acid or bicarbonate into mono or neutral carbonate. Thus,

NaOH	+	$NaHCO_3$	=	Na_2CO_3	+	H_2O
Sodium Hydroxide 39.76		Sodium Acid Carbonate 83.42		Neutral Sodium Carbonate		
NaOH	=	$KHCO_3$	=	$KNaCO_3$	+	H_2O
Sodium Hydroxide 39.76		Potassium Acid Carbonate 99.36		Potassium Sodium Carbonate		

If 39.76 Gm. of sodium hydroxide (1000 Cc. $\frac{N}{1}$ V. S.) are equivalent to 83.41 Gm. of sodium bicarbonate or 99.36 Gm. of potassium bicarbonate,

Then 1 Cc. $\frac{N}{1}$ NaOH V. S. (containing 0.03976 Gm. NaOH) is equivalent to 0.08342 Gm. of sodium bicarbonate or 0.09936 Gm. of potassium bicarbonate.

Example: A sample of commercial sodium bicarbonate weighing 2 Gm. was dissolved in 100 Cc. of distilled water; 50 Cc. (representing 1 Gm.) were drawn off into a flask and 20 Cc. of $\frac{N}{1}$ NaOH V. S. added; a neutral solution of barium chloride was then slowly run in (shaking constantly) until in excess; this was followed by two drops of phenolphthalein solution and $\frac{N}{1}$ HCl V. S. until the pink color of the mixture was discharged, 8.8 Cc. being required.

Then 20 Cc. — 8.8 Cc. = 11.2 Cc. $\frac{N}{1}$ NaOH V. S.
If 1 Cc. $\frac{N}{1}$ NaOH V. S. = 0.08342 Gm. $NaHCO_3$,
11.2 Cc. " " " = 11.2 × 0.08342 or 0.9343 Gm. of $NaHCO_3$.

The sample contains, therefore, 93.43 per cent. of pure bicarbonate of sodium.

The remaining 50 Cc. of the solution required 12.3 Cc. of $\frac{N}{1}$ HCl V. S., with methyl-orange as indicator, for complete neutralization; then 12.3 Cc. — 11.2 Cc. = 1.1 Cc. $\frac{N}{1}$ HCl V. S. required for the neutral sodium carbonate (Na_2CO_3) present.

Since 1 Cc. $\frac{N}{1}$ HCl is equivalent to 0.05625 Gm. Na_2CO_3, 1.1 Cc. are equivalent to 1.1 × 0.05625 Gm. = 0.0618+ Gm. of sodium carbonate, or 6.18+ per cent.

The sample contains, therefore, 93.43 per cent. of bicarbonate and 6.18+ per cent of neutral carbonate.

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* Precipitation may be known to be complete by allowing the mixture to stand a few minutes until the precipitate settles sufficiently so as to leave a clear supernatant layer; this, upon the further addition of barium chloride, should remain clear. The addition of this reagent serves to remove the carbonic acid of the carbonates as insoluble barium carbonate ($Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3$), thus enabling us to estimate the excess of standard alkali which has not been consumed in converting the acid or bicarbonate into neutral carbonate by titrating back with normal acid.

Estimation of Ammonia and its Compounds.

The indicators best adapted for the volumetric estimation of ammonia (NH_3) are litmus, congo red, rosolic acid, and methyl-orange; the latter two should not be used when salts of ammonia are present in any quantity.

Aqua Ammonia.—Owing to the readiness with which solutions of ammonia gas lose in strength through handling, it is advisable to measure off exactly 10 Cc. from an accurately graduated pipette, delivering the same into about 10 Cc. of distilled water, holding the tip of the pipette below the surface. If the specific gravity of the solution is not known, the first 10 Cc. to be titrated are measured * into a tared and stoppered weighing flask and its weight accurately determined; supposing it to weigh 9.35 Gm., then, moving the decimal point one place to the left, the specific gravity would be 0.935. Then each 10 Cc. measured off for titration would weigh 9.35 Gm.; or if 5 Cc. were taken, $5 \times 0.935 = 4.675$ Gm.

Example: 5 Cc. of aqua ammonia weighing 4.80 Gm. were diluted with about 10 Cc. of water and two drops of litmus added; 28.4 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. were required for neutralization.

$$\underset{97.35}{H_2SO_4} + \underset{2 \times 16.93}{2NH_3.H_2O} = (NH_4)_2SO_4 + 2H_2O.$$

If 97.35 parts of sulphuric acid are equivalent to 2×16.93 parts of ammonia gas, 1000 Cc. of $\frac{N}{1}$ H_2SO_4 V. S., containing 48.675 Gm. $\left(\frac{97.35}{2}\right)$, would be equivalent to 16.93 Gm. of NH_3.

Then 1 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. (containing 0.048675 Gm.) will be equivalent to 0.01693 Gm. of NH_3.

28.4 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. $= 28.4 \times 0.01693$, or 0.480 Gm. of NH_3, which is contained in 4.80 Gm. of the solution, corresponding to 10 per cent.

$$\begin{array}{ccccccc} \text{Gm. Sample} & & \text{Gm. } NH_3 & & & & \\ 4.80 & : & 0.480 & :: & 100 & : & x \end{array}$$

$$4.80\,x = 480$$

$$x = 10$$

For direct percentage estimation see page 71.

Ammonium Carbonate.—When fresh, in the unaltered condition, this salt consists of a mixture of ammonium carbonate and acid carbonate ($NH_4NH_2CO_2.NH_4HCO_3$), and may be estimated by direct or residual titration, the solution being boiled to expel carbonic acid, while rosolic acid serves as indicator. 1 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. $= 0.051996$ Gm. of the salt. Through exposure and handling, this salt loses both in ammonia and carbonic acid, and consists of a mixture of acid (NH_4HCO_3) and neutral carbonate $(NH_4)_2(CO_3)$ in variable proportions; hence separate estimations of ammonia and carbonic acid are usually made. The percentage of real ammonia (NH_3) may be determined either by direct titration with a normal or decinormal acid and rosolic acid or methyl-orange as indicator, or by the distillation method given below. The total carbonic acid may be estimated by precipitating a weighed quantity of the salt, dissolved in hot water, by barium chloride; the precipitate of barium carbonate is collected, washed with boiling water, and dissolved in an excess of normal HCl V. S., titrating back with normal KOH V. S. The number of cubic centimeters of acid required, multiplied by 0.02183 (½ of

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* The accuracy of the pipette should be verified by weighing its capacity in distilled water at 15° C. or any other standard temperature at which it may have been graduated.

mol. wt. of CO_2) will give the weight of carbonic acid gas present, which may afterward be calculated into percentage.

Direct Estimation of Ammonia Salts and Compounds.—This method embraces the estimation of ammonia in its salts as the sulphate and chloride, also in gas liquor, ammonia alum [$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$], sulphate of copper and ammonium ($CuSO_4(NH_4)_2SO_4 + 6H_2O$), also the combined nitrogen in organic substances after oxidation according to Kjeldahl.

The apparatus employed consists of a distilling flask, A (Fig. 19), of about 500 Cc. capacity, into which from 75 to 100 Cc. of distilled water with a weighed portion of the salt are introduced, or, better, 10 Cc. of a solution of the sample (representing 0.5 or 1 Gm.), prepared by dissolving 5 or 10 Gm. in 100 Cc. of water. Through a closely fitting double perforated rubber stopper passes a pipette, B, which just before beginning the operation is filled with a 10 per cent. solution of sodium hydroxide. Through the other perforation passes a bulbed fractionating tube, C; the inside diameter of the lower tip (*k*) of this should be ⅜ of an inch. The tube C is securely connected through its lateral tube H with a well-cooled Liebig condenser, E, the lower tip of which should dip beneath the surface of an accurately measured volume of normal or seminormal standard acid contained in the receiving flask F (of about 300 Cc. capacity). Through the other

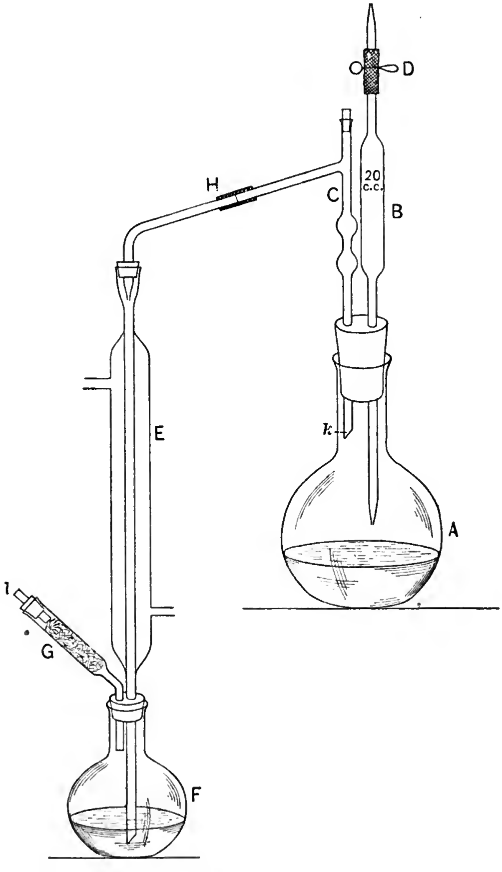

FIG. 19.—AMMONIA ESTIMATION APPARATUS.

perforation of the stopper of F passes a calcium chloride tube, G, which has been filled with glass-wool moistened (after removing the stopper, *l*) with a measured volume of the same standard acid, the purpose of which is to retain any ammoniacal vapors which might escape neutralization in F. The volume of standard acid added must be *more* than sufficient to combine with the ammonia gas evolved.

The procedure is as follows: Into F is measured from a burette from 30 to 50 Cc. of $\frac{N}{1}$ $\left(\text{or } \frac{N}{2}\right)$ HCl V. S. and two or three drops of rosolic acid solution; the stopper with G and E is introduced and securely inserted; into G, 5 Cc. of the same HCl V. S. are measured and into A is poured 75 to 100 Cc. of water and the measured volume (10 Cc.) containing the ammonium salt; the stopper with C is inserted; then into the pipette B is drawn the solution of caustic soda, noting at the same time that the pinch-cock D securely closes the rubber joint tube, preventing the premature escape of the lye; B is now inserted through the stopper into the flask (A). All the fittings of the apparatus must be air-tight. The pinch-cock D is then momentarily released, allowing about two-thirds of the caustic soda solution (15 Cc.) to run into A, after which the contents of the distilling flask are brought gradually to a boil, which is allowed to continue for from fifteen to thirty minutes. The apparatus is allowed to stand a few minutes to permit the complete absorption of the ammonia gas in F, after which the pinch-cock D is opened and air is drawn through the apparatus by means of a rubber tube attached at *l*. The inner tube of the condenser E is rinsed down inside and outside into F, also the adhering acid in G must be thoroughly washed out into F; the excess of uncombined acid in F is then ascertained by titrating back with $\frac{N}{1}$ $\left(\text{or } \frac{N}{2}\right)$ KOH V. S.

Example: 1 Gm. of commercial ammonium sulphate was dissolved in 100 Cc. water and 10 Cc. of this introduced into A, with about 100 Cc. of water, for analysis. Into F was measured 25 cc. and into G 5 Cc. of $\frac{N}{1}$ HCl V. S.; after 15 minutes' boiling 15.2 Cc. of $\frac{N}{1}$ KOH V. S. were required for the neutralization of the excess of acid; then 30 Cc. — 15.2 = 14.8 Cc. of $\frac{N}{1}$ HCl, which had combined with the liberated ammonia gas.

Since 1 Cc. $\frac{N}{1}$ HCl is equivalent to 0.0656 Gm. of ammonium sulphate, $(NH_4)_2SO_4$,*
14.8 Cc. are equivalent to $14.8 \times 0.0656 = 0.9708$ Gm.

The 1 Gm. of sample contains, therefore, 0.9708 Gm., or 97.08 per cent., of pure salt.

Since *one* molecule of ammonium sulphate yields two molecules of ammonia gas, which in turn requires two molecules of hydrochloric acid for neutralization, then *one* molecule of HCl would be equivalent to *one* molecule of NH_3, which in turn represents *one-half* of a molecule of $(NH_4)_2SO_4$:

$$\frac{2HCl}{2 \times 36.18} = \frac{2(NH_3)}{2 \times 16.93} = \frac{(NH_4)_2SO_4}{131.20}$$

36.18 Gm. HCl $\left(1000 \text{ Cc. } \frac{N}{1} \text{ HCl V.S.}\right)$ are equivalent to 65.6 Gm. $\left(\frac{131.20}{2}\right)$ $(NH_4)_2SO_4$.

1 Cc. $\frac{N}{1}$ HCl V. S. (containing 0.03618 Gm. HCl) is equivalent to 0.0656 Gm. $(NH_4)_2SO_4$.

Example: A quantity of ferric alum $(Fe_2(NH_4)_2(SO_4)_4 + 24H_2O)$ weighing 0.4821 Gm. was selected for a determination of its ammonia. For the collection of the evolved ammonia gas 25 Cc. of $\frac{N}{10}$ H_2SO_4 V. S. were employed, and after the operation 15 Cc. of $\frac{N}{10}$ KOH V. S. were required for neutralizing the excess of acid; then 25 Cc. — 15 Cc. = 10 Cc. $\frac{N}{10}$ H_2SO_4 V. S. which had combined with the liberated ammonia gas.

Since 1 Cc. $\frac{N}{10}$ H_2SO_4 V. S = 0.001693 Gm. NH_3,
10 Cc. = $10 \times 0.001693 = 0.01693$ Gm. of ammonia gas,

obtained from 0.4821 Gm. of the salt, which represents 3.51+ per cent.

The pure crystalline salt contains theoretically 3.51+ per cent. of ammonia gas; the sample is, therefore, practically pure.

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* The reaction is as follows: $\underset{\substack{\text{Ammonium}\\\text{Sulphate}}}{(NH_4)_2SO_4} + \underset{\substack{\text{Sodium}\\\text{Hydroxide}}}{2NaOH} = \underset{\substack{\text{Ammo-}\\\text{nia}}}{2NH_3} + \underset{\substack{\text{Sodium}\\\text{Sulphate}}}{Na_2SO_4} + 2H_2O.$

Indirect Estimation of Ammonium Salts by Residual Method.—Ammonium salts are estimated indirectly by first adding a measured excess of a standard alkali V. S. to a solution of the weighed substance; this then is boiled until no more ammoniacal vapors are given off—that is, until when a piece of moistened red litmus-paper held in the vapors is no longer turned blue. The operation is best carried on in a flask placed slightly at an angle in order to avoid any loss of fluid. As soon as the solution has cooled methyl-orange or rosolic acid is added and the uncombined excess of alkali estimated by means of a standard acid.

The reaction is as follows:

$$\underset{55.7}{KOH} + \underset{53.11}{NH_4Cl} = KCl + \underset{16.93}{NH_3}$$

If 55 7 Gm. of KOH are equivalent to 16.93 Gm. of NH_3, which, in turn, represents 53.11 Gm. of NH_3HCl (NH_4Cl),

Then 55.7 Gm. of KOH (1000 Cc. $\frac{N}{1}$ V. S.) = 53.11 Gm. NH_4Cl; or 1 Cc. of $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm.) is equivalent to 0.05311 Gm. of ammonium chloride.

In the case of ammonium sulphate, *one* molecule of potassium or sodium hydroxide would be equivalent to *one-half* of a molecule of the salt. Thus:

$$\underset{2\times 55.7}{2KOH} + \underset{131.21}{(NH_4)_2SO_4} = K_2SO_4 + 2H_2O + \underset{2\times 16.93}{2NH_3}$$

If 2 × 55.7 Gm. of KOH are equivalent to 2 × 16.93 Gm. of NH_3, which, in turn, represents 131.21 Gm. of $(NH_4)_2SO_4$.

Then 55.7 Gm. of KOH (1000 Cc. $\frac{N}{1}$ V. S.) = 16.93 Gm. NH_3 = 65.605 Gm. $\left(\frac{131.21}{2}\right)$ of $(NH_4)_2SO_4$.

1 Cc. of $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm.) is then equivalent to 0.065605 Gm. of ammonium sulphate.

Example: 0.5311 Gm. of ammonium chloride was weighed off and dissolved in about 100 Cc. of water and 20 Cc. of $\frac{N}{1}$ KOH V. S. added; after boiling until ammonia gas was no longer evolved, 10 Cc. of a $\frac{N}{1}$ acid V. S. were required for titrating back the excess of alkali

Then 20 Cc. the excess of $\frac{N}{1}$ alkali V. S. added.
10 Cc. the $\frac{N}{1}$ acid V. S. used for titrating back.
10 Cc. the $\frac{N}{1}$ alkali V. S. consumed.

If 1 Cc. of $\frac{N}{1}$ KOH V. S. = 0.05311 Gm. NH_4Cl,
10 Cc. " " " = 10 × 0.05311 = 0.5311 Gm.

The sample must therefore consist of absolute (100 per cent.) ammonium chloride, each 1Cc. of the $\frac{N}{1}$ alkali consumed representing 10 per cent. of absolute salt.

5. Estimation of the Organic Salts of the Alkalies and Alkali-earths.—

Such organic salts of the alkalies and alkali-earths as the acetate, salicylate, lactate, tartrate, bitartrate, and citrate yield, when strongly ignited, an equivalent amount of carbonate. Hence the quantity of such a salt or its degree of purity may be readily ascertained by igniting and titrating the amount of carbonate yielded.

Substance Examined.	1 Cc. of Normal Acid is Equivalent to:
Lithium benzoate, $LiC_7H_5O_2$,	0.12703 Gm.
“ bitartrate, $LiHC_4H_4O_6$ (dry),	0.15485 “
“ citrate, $Li_3C_6H_5O_7$,	0.06949 “
“ salicylate, $LiC_7H_5O_3$,	0.14291 “
Potassium acetate, $KC_2H_3O_2$,	0.09738 “
“ benzoate, $KC_7H_5O_2 + 3H_2O$,	0.21252 “
“ “ $KC_7H_5O_2$ (dry),	0.15888 “
“ bitartrate, $KHC_4H_4O_6$,	0.18670 “
“ citrate, $K_3C_6H_5O_7 + H_2O$,	0.10730 “
“ lactate, $KC_3H_5O_3$,	0.12716 “
“ salicylate, $KC_7H_5O_3$,	0.17476 “
“ sodium-tartrate, $KNaC_4H_4O_6 + 4H_2O$,	0.14005 “
Sodium acetate, $NaC_2H_3O_2 + 3H_2O$,	0.13508 “
“ benzoate, $NaC_7H_5O_2$,	0.14294 “
“ bitartrate, $NaHC_4H_4O_6 + H_2O$,	0.18864 “
“ citrate, $Na_3C_6H_5O_7$ (dry),	0.08540 “
“ lactate, $NaC_3H_5O_3$,	0.11122 “
“ salicylate, $NaC_7H_5O_3$,	0.15882 “
“ tartrate, $Na_2C_4H_4O_6 + 2H_2O$,	0.11420 “

The salt to be examined should be pulverized and placed in a desiccator over calcium chloride from twelve to twenty-four hours previous to analysis. Such salts as do not contain water of crystallization may be placed for several hours in a drying-oven at a temperature of from 90° to 100° C., in order to remove adhering moisture. Some crystalline salts, as the bitartrates, benzoates, and salicylates, are usually sufficiently dry to assay at once. The percentage of moisture present should be reported in the results of the analysis.

An accurately weighed quantity of the salt, usually between 1 and 2 Gm., contained in a porcelain crucible, is heated, increasing the temperature *very gradually* until redness is reached; this temperature is maintained for several minutes in order to secure a thorough decomposition of the organic matter, gases are no longer given off, and a charred mass remains. The crucible should remain uncovered during the heating, which should not take place too rapidly, otherwise loss may occur through ejection of particles of the powder by the escaping gas. After allowing the crucible to cool, its contents are treated with boiling water and carefully filtered through a very small plain wetted filter into a flask or porcelain dish. The contents of the crucible and filter are repeatedly washed until the wash-water no longer turns moistened red litmus-paper blue. Some operators transfer the cooled crucible to a beaker containing water sufficient to cover it and then titrate. The lithium salts must be titrated according to the residual method owing to the insolubility of lithium carbonate in water. From the quantity of alkali carbonate contained in the filtrate (which may be estimated by either the cold or hot process, as directed on page 50) the equivalent amount of salt may be calculated; however, the above table expresses the equivalences direct.

Direct percentage estimations may be made by weighing off molecular equivalent quantities of the substance (see pages 71, 75).

Potassium Bitartrate.—Upon ignition, two molecules of potassium bitartrate yield one molecule of potassium carbonate, or 186.7 parts of the former yield 68.59 parts $\left(\frac{137.18}{2}\right)$ of the latter, for :

*$2KHC_4H_4O_6$	=	K_2CO_3	+	$5C$	+	$2CO_2$	+	$5H_2O$
Potassium Bitartrate.		Potassium Carbonate.		Carbon.		Carbonic Acid Gas.		Water.
2 × 186.7		137.18						

The titration of the filtrate and washings of the ignited residue serves to ascertain the quantity of potassium carbonate yielded by the sample. Thus :

H_2SO_4	+	K_2CO_3	=	K_2SO_4	+	CO_2	+	H_2O
Sulphuric Acid.		Potassium Carbonate.		Potassium Sulphate.		Carbonic Acid Gas.		Water.
97.35		137.18						

1000 Cc. $\frac{N}{1}$ H_2SO_4 V. S. containing 48.675 Gm. of sulphuric acid are equivalent to 68.59 Gm. $\left(\frac{137.18}{2}\right)$ of potassium carbonate.

1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. containing 0.048675 Gm. H_2SO_4 = 0.06859 Gm. K_2CO_3.

To summarize :

If 1000 Cc. $\frac{N}{1}$ H_2SO_4 V. S. (48.675 Gm. H_2SO_4) = K_2CO_3, 68.59 Gm., = $KHC_4H_4O_6$, 186.7 Gm.,

Each 1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. (0.048675 Gm. H_2SO_4) = K_2CO_3, 0.06859 Gm., = $KHC_4H_4O_6$, 0.1867 Gm.; or

Each 1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. = 0.1867 Gm. of potassium bitartrate.

Exercise : A sample of potassium bitartrate weighing 1.88 Gm. after ignition and exhaustion of the residue with water required 9.8 Cc. of normal sulphuric acid V. S. for neutralization. If 1 Cc. of the acid is equivalent to 0.1867 Gm. of the pure salt, then 9.8 Cc. would represent 9.8 × 0.1867 = 1.829+ Gm., or 97.32+ per cent.

Sample. Real Salt.
1.88 Gm. : 1.829+ Gm. :: 100 : x
x = 97.32+ per cent.

A second but more convenient method of estimation is based on the presence of one replaceable hydrogen atom in the acid tartrate ($KHC_4H_4O_6$), which is equivalent to one molecule of potassium or sodium hydroxide. Thus :

$KHC_4H_4O_6$	+	KOH	=	$K_2C_4H_4O_6$	+	H_2O.
Potassium Acid Tartrate.		Potassium Hydroxide.		Neutral Potassium Tartrate.		Water.
186.7		55.70				

If 55.7 Gm. of KOH (1000 Cc. $\frac{N}{1}$ V. S.) are equivalent to 186.7 Gm. of the bitartrate, then 1 Cc. of $\frac{N}{1}$ KOH V. S., containing 0.0557 Gm., would represent 0.1867 Gm. of the salt.

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* The reaction may also be written thus: $2KHC_4H_4O_6 + 5O_2 = K_2CO_3 + 7CO_2 + 5H_2O$.

Example: A sample of cream of tartar weighing 1.88 Gm., after dissolving in 100 Cc. of hot water, requires 8 Cc. of $\frac{N}{1}$ KOH V. S. for neutralization, phenolphthalein having been used as indicator. Then if 1 Cc. $\frac{N}{1}$ KOH V. S. is equivalent to 0.1867 Gm. of pure bitartrate, 8 Cc. would represent $8 \times 0.1867 = 1.493+$ Gm. The 1.88 Gm. of sample contains, then, 1.493+ Gm. of absolutely pure salt, and would therefore be 79.41+ per cent. pure.

If 1.867 Gm. are taken, then each 1 Cc. of a $\frac{N}{1}$ V. S. consumed corresponds to 10 per cent. of pure salt. (Compare pages 71, 75.)

Potassium Sodium Tartrate.—The estimation of Rochelle salt is carried out after the first-mentioned method under cream of tartar, the alkali resulting from ignition being potassium sodium carbonate.

*$2(KNaC_4H_4O_6 + 4H_2O)$	=	$2KNaCO_3$	+	$5C$	+	CO_2	+	$12H_2O$
Rochelle Salt. 2 × 280.1		Potassium Sodium Carbonate. 2 × 121.24		Carbon.		Carbonic Acid Gas.		Water.

H_2SO_4	+	$KNaCO_3$	=	$KNaSO_4$	+	CO_2	+	H_2O
Sulphuric Acid. 97.35		Potassium Sodium Carbonate. 121.24		Potassium Sodium Sulphate.		Carbonic Acid Gas.		Water.

1000 Cc. ($\frac{N}{1}$ H_2SO_4 V. S.) containing 48.675 Gm. of sulphuric acid are equivalent to 60.62 Gm. $\left(\frac{121.24}{2}\right)$ of potassium sodium carbonate.

1 Cc. ($\frac{N}{1}$ H_2SO_4 V. S.) containing 0.048675 Gm. of sulphuric acid is equivalent to 0.06062 Gm. potassium sodium carbonate.

Then if,

1000 Cc. $\frac{N}{1}$ H_2SO_4 V. S. (containing 48.675 Gm. H_2SO_4) are equivalent to $KNaCO_3$, 60.62 Gm., which, in turn, represents $KNaC_4H_4O_6$, 140.05 Gm.,

1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. (0.048675 Gm.) is equivalent to 0.14005 Gm. of pure Rochelle salt.

A quantity between 1.2 and 1.5 Gm. is sufficient for an estimation. If 1.4 Gm. are taken, then each 1 Cc. of $\frac{N}{1}$ acid V. S. consumed corresponds to 10 per cent. of pure salt. (Compare pages 71, 75.)

Potassium Citrate.—Two molecules of potassium citrate when ignited yield three molecules of carbonate, which in turn requires three molecules of sulphuric acid for neutralization. Or one-half a molecule of the acid which is contained in one liter of standard solution will neutralize one-sixth of the three molecules of the carbonate which correspond to one-sixth of two molecules of the citrate, thus:

$2K_3C_6H_5O_7 + H_2O$	=	$3K_2CO_3$	+	$9C$	+	$6H_2O$
Potassium Citrate. 2 × 321.90		Potassium Carbonate. 3 × 137.18		Carbon.		Water.

$3H_2SO_4$	+	$3K_2CO_3$	=	$3K_2SO_4$	+	$3CO_2$	+	$3H_2O$
Sulphuric Acid. 3 × 97.35		Potassium Carbonate. 3 × 137.18		Potassium Sulphate.		Carbonic Acid Gas.		Water.

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*The reaction may also be written thus:

$$2KNaC_4H_4O_6.4H_2O + 5O_2 = 2KNaCO_3 + 6CO_2 + 12H_2O.$$

$$\begin{array}{lccccc} & 3H_2SO_4 & = & 3K_2CO_3 & = & 2K_3C_6H_5O_7 + H_2O \\ & 3 \times 97.35 & & 3 \times 137.18 & & 2 \times 321.90 \\ & 292.05 & & 411.54 & & 643.80 \\ 1\text{ L. } \frac{N}{1}\ H_2SO_4\text{ V. S.} & 48.675\text{ Gm.} & = & 68.59\text{ Gm.} & = & 107.30\text{ Gm.} \end{array}$$

Each 1 Cc. $\frac{N}{1}$ H_2SO_4 V. S. (0.048675 Gm.) is equivalent to 0.10730 Gm. of potassium citrate.

If 1.073 Gm. are taken, then each 1 Cc. of $\frac{N}{1}$ acid V. S. consumed corresponds to 10 per cent. of pure salt. (Compare pages 71, 75.)

6. Estimation of Sodium Hydroxide in Potassium Hydroxide.—

This embraces the estimation of sodium hydroxide or potassium hydroxide in mixtures of both.* This process, which has been adopted in the U. S. Pharmacopœia (p. 312), depends on the conversion of both alkalies into bitartrates, the potassium salt being almost insoluble in the solution of the sodium bitartrate.

To a weighed quantity of the mixed alkalies—for example, 1 gramme dissolved in 10 Cc. of water—two drops of phenolphthalein are added, followed by a solution (15 Gm. in 100 Cc. water) of tartaric acid, which is slowly added from a burette until the solution is accurately neutralized. Both alkalies are thereby converted into neutral tartrates.

$$\underset{\text{Potassium Hydroxide.}}{2KOH} + \underset{\text{Tartaric Acid.}}{H_2C_4H_4O_6} = \underset{\text{Potassium Tartrate.}}{K_2C_4H_4C_6} + 2H_2O$$

$$\underset{\text{Sodium Hydroxide.}}{2NaOH} + \underset{\text{Tartaric Acid.}}{H_2C_4H_4O_6} = \underset{\text{Sodium Tartrate.}}{Na_2C_4H_4O_6} + 2H_2O$$

The next step is to add to this neutral solution a volume of the tartaric acid solution equal to that first used, whereby the neutral tartrates are converted into acid tartrates (bitartrates).

$$\underset{\text{Potassium Tartrate.}}{K_2C_4H_4O_6} + \underset{\text{Tartaric Acid.}}{H_2C_4H_4O_6} = \underset{\text{Acid Potassium Tartrate.}}{2KHC_4H_4O_6}$$

$$\underset{\text{Sodium Tartrate.}}{Na_2C_4H_4O_6} + \underset{\text{Tartaric Acid.}}{H_2C_4H_4O_6} = \underset{\text{Acid Sodium Tartrate.}}{2NaHC_4H_4O_6}$$

In order to completely precipitate the acid potassium tartrate, an equal volume of alcohol is added to the solution, or absolute alcohol is added until precipitation ceases, the corresponding sodium salt being soluble in this mixture. The precipitate is then collected on a plain filter, and after the fluid has drained off, the container is rinsed with alcohol, which is poured over the precipitate, in order to remove all traces of adhering solution of sodium bitartrate. To the filtrate which contains the latter salt, phenolphthalein is added, followed by normal potassium hydroxide V. S. until the solution turns a pale red.

$$NaHC_4H_4O_6 + KOH = NaKC_4H_4O_6 + H_2O.$$

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* Commercial caustic potash frequently contains large quantities of the cheaper caustic soda, hence examination is always advisable. See Amer. Jour. Phar., page 392, 1898.

The number of cubic centimeters of $\frac{N}{1}$ KOH V. S. employed, multiplied by 0.03976, gives the amount of sodium hydroxide present in the salt. The difference represents the potassium hydroxide.

Example: 1 Gm. of commercial caustic potash, after treating with tartaric acid and filtering, the filtrate required 3.5 Cc. of $\frac{N}{1}$ KOH V. S. for neutralization.

Since 1 Cc. of $\frac{N}{1}$ KOH V. S. is the equivalent of 0.03976 Gm. of sodium hydroxide, 3.5 Cc. = 3.5 × 0.03976, or 0.13916 Gm. of sodium hydroxide, which would be 13.916 per cent.

1.00000 Gm. sample consisting of sodium and potassium hydroxide.
0.13916 Gm. of sodium hydroxide found.
0.86084 Gm. of potassium hydroxide or 86.084 per cent. by difference.

Therefore the sample contains 13.916 per cent. of sodium hydroxide and 86.084 per cent. of potassium hydroxide.

If the total amount of alkali is not known, then after determining the quantity of sodium hydroxide, the potassium hydroxide may be estimated by calculating the weight of tartaric acid required to form the bitartrate with the soda; this is deducted from the total amount added to the mixture of the two alkalies. The difference represents the quantity of tartaric acid which has combined with the potassium hydroxide to form a bitartrate; from this the weight of the alkali is readily calculated.

Example: 10 Cc. of a potash lye, when treated as above directed, required in total 24 Cc. (or 3.6 Gm.) of the tartaric acid solution (15 Gm. in 100 Cc.). The filtrate of sodium acid tartrate required 4 Cc. of $\frac{N}{1}$ KOH V. S. for neutralization.

The 4 Cc. of $\frac{N}{1}$ KOH V. S. = 4 × 0.03979 or 0.160 Gm.* NaOH.

The 0.160 Gm. NaOH required 0.6 Gm. or 4 Cc. of the tartaric acid solution.

$$\underset{2 \times 40}{2NaOH} + \underset{2 \times 150}{2H_2C_4H_4O_6} = 2NaHC_4H_4O_6 + 2H_2O$$

$$40 : 150 :: 0.160 : x$$

$$x = 0.60 \text{ Gm. tartaric acid.}$$

Then 3.6 Gm. or 24 Cc. tartaric acid, the total quantity used.
0.6 Gm. or 4 Cc. " " required for the NaOH.
3.0 Gm. of tartaric acid is required for the KOH.
3 Gm. of tartaric acid corresponds to 1.12 Gm. of KOH.

$$\underset{2 \times 56}{2KOH} + \underset{2 \times 150}{2HC_4H_4O_6} = 2KHC_4H_4O_6 + 2H_2O$$

$$150 : 56 :: 3 : x$$

$$x = 1.12 \text{ Gm. KOH.}$$

Therefore the 10 Cc. of lye contains 0.160 Gm. of NaOH and 1.12 Gm. of KOH.

Estimation of the Alkalies when Present as Neutral Chlorides.—This method of J. T. White (Chemical News, lvii, 214) consists in adding 5 Cc. of a hot saturated solution of ammonium bicarbonate to a solution of 0.2 Gm. of the mixed chlorides in 20 Cc. of water contained in a 100 Cc. flask; the mixture is cooled and alcohol added in small quantities, shaking, until it measures exactly 100 Cc. After standing about 3 hours, to

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* Rounded off from 0.1598 Gm. Also the fractions in the following equations are likewise rounded to nearest whole numbers.

allow the potassium chloride to completely precipitate, 10 Cc. of the clear fluid, containing only NaCl, are drawn off with a pipette, evaporated, and ignited; the residue is moistened with a few drops of ammonium chloride and again ignited; the sodium chloride thus obtained, representing *one-tenth* of the entire amount present, is estimated by means of a standard decinormal solution of silver nitrate. Each Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. = 0.005806 Gm. of sodium chloride; this, multiplied by 10, gives the total quantity present in the 0.2 Gm. of mixed chlorides. The potassium chloride is found by difference.

TITRATION OF ALKALI-EARTHS.

SUBSTANCE TITRATED.	1 Cc. OF $\frac{N}{1}$ HCl OR $\frac{N}{1}$ HNO_3 IS EQUIVALENT TO
Calcium hydroxide, $Ca(OH)_2$,	0.03678 Gm.
Calcium carbonate, $CaCO_3$,	0.04967 "
Calcium oxide, CaO,	0.02784 "
Barium hydroxide, $Ba(OH)_2$ (dry),	0.08508 "
Barium carbonate, $BaCO_3$,	0.09797 "
Magnesium oxide, MgO,	0.01999 "
Magnesium carbonate, $MgCO_3$ (not U. S. P.),	0.04182 "
Strontium oxide, SrO,	0.05142 "
Strontium carbonate, $SrCO_3$	0.07325 "

Standard hydrochloric or nitric acid only is admissible in the titration of the alkali-earths.

Titration is best carried on by the "residual" method, employing any of the usual indicators except methyl-orange, which should only be used in cold solution.

Example: To 50 Cc. of a solution of calcium hydroxide (lime water) an excess consisting of 30 Cc. of $\frac{N}{10}$ HCl V. S. was added, and after boiling the solution for a few minutes, two drops of phenolphthalein solution were added, followed by sufficient $\frac{N}{10}$ alkali V. S. to impart to the mixture a rose tint. Of the standard decinormal alkali solution, 10 Cc. were required for the neutralization of the excess of the added decinormal acid. What percentage of calcium hydroxide ($Ca(OH)_2$) does the solution contain?

According to the equation

$$\underset{\substack{\text{Hydrochloric}\\\text{Acid.}\\2\times36.18}}{2HCl} + \underset{\substack{\text{Calcium}\\\text{Hydroxide.}\\73.56}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{CaCl_2} + 2H_2O$$

2 × 36.18 parts of HCl are equivalent to 73.56 parts of $Ca(OH)_2$; then

3.618 Gm. of HCl (contained in 1000 Cc. $\frac{N}{10}$ HCl V. S.) = 3.678 Gm. of $Ca(OH)_2$

1 Cc. of $\frac{N}{10}$ HCl V. S. (0.003618 Gm. HCl) is equivalent to 0.003678 Gm. of $Ca(OH)_2$

20 Cc. " " " (30 Cc. — 10 Cc. = 20 Cc.) would represent 20 × 0.003678 = 0.07356 Gm. of calcium hydroxide.

Therefore 0.07356 Gm. or 0.147+ per cent. of calcium hydroxide are contained in 50 Cc. (about 50 Gm.) of lime water.

$$50 : 0.07356 :: 100 : x$$
$$x = 0.147+ \text{ per cent.*}$$

Lime water or baryta water may also be titrated direct in the cold with phenolphthalein as indicator, disregarding the small quantity

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* True percentage by weight would require that the specific gravity of the solution be taken into consideration. In this case, where it is practically identical with that of water, it may be neglected.

of carbonate present and what may be formed while operating. A decinormal acid is employed here owing to the very small percentage of calcium or barium hydroxide present in the solution.

Estimation of Mixed Hydroxides and Carbonates.

The following method is applicable to mixtures of the hydroxides and carbonates of calcium and barium: A portion of the finely powdered substance weighing one gramme or less is suspended in about 30 Cc. of water; 3 drops of phenacetolin are added, or a sufficient quantity to impart a faint yellow to the mixture; standard normal hydrochloric acid is now run in slowly, with constant stirring, until a permanent rose tint appears; this point indicates the neutralization of the hydroxide, and the volume of the standard acid added should be noted. The further addition of acid is continued until the color changes to a deep yellow; the number of cubic centimeters added represents the carbonate present. The volume of acid first added is multiplied by its equivalent in $Ba(OH)_2$ or $Ca(OH)_2$, while the latter volume is multiplied by the equivalent of $BaCO_3$ or $CaCO_3$.

Example: An old sample of barium hydroxide was finely powdered and a portion weighing 1.0508 Gm. suspended in water required 10 Cc. of $\frac{N}{1}$ HCl V. S. for the production of a pink color. A further addition of 2 Cc. was required to change this to a deep yellow.

Since 1 Cc. of $\frac{N}{1}$ HCl V. S. is equivalent to 0.08508 Gm. of $Ba(OH)_2$,* 10 Cc. would be equivalent to $10 \times 0.08508 = 0.8508$ Gm. $Ba(OH)_2$ or 80.96+ per cent.; for:

$$1.0508 \text{ Gm.} : 0.8508 \text{ Gm.} :: 100 : x;\ x = 80.96+ \text{ per cent.}$$

1000 Cc. $\frac{N}{1}$ HCl V. S. containing 36.18 Gm. HCl are equivalent to 85.08 Gm. (½ of 170.16) $Ba(OH)_2$.

1000 Cc. $\frac{N}{1}$ HCl V. S. containing 36.18 Gm. HCl are equivalent to 95.97 Gm. (½ of 195.94) $BaCO_3$.

Since 1 Cc. of $\frac{N}{1}$ HCl V. S. is equivalent to 0.09797 Gm. of $BaCO_3$,† 2 Cc. would be equivalent to $2 \times 0.09797 = 0.19594$ Gm. $BaCO_3$, or 18.64 per cent.; for:

$$1.0508 \text{ Gm.} : 0.19594 \text{ Gm.} :: 100 : x;\ x = 18.64 \text{ per cent.}$$

The sample contains, therefore, 80.96 per cent. of barium hydroxide and 18.64 per cent. of barium carbonate.

Another method whereby phenolphthalein may be employed as indicator may be carried out as follows: To about 50 Cc. of water containing the weighed sample two or three drops of phenolphthalein are added and the mixture is quickly heated to boiling; to this is cautiously added $\frac{N}{10}$ HCl V. S. until the red color is just discharged. Up to this point the hydroxides have been neutralized, while the carbonates, becoming denser on boiling, are neutral to the indicator. A measured excess of acid is now added, and after heating and

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* $$\underset{2 \times 36.18}{2HCl} + \underset{170.16}{Ba(OH)_2} = BaCl_2 + 2H_2O$$

† $$\underset{2 \times 36.18}{2HCl} + \underset{195.94}{BaCO_3} = BaCl_2 + CO_2 + H_2O$$

agitating to remove the liberated carbonic acid gas, the excess of unneutralized acid is determined by titrating back with $\frac{N}{10}$ KOH V. S.; the number of cubic centimeters of the latter, subtracted from the former, represents the equivalent of carbonate.

Example: 50 Cc. of lime water containing some calcium carbonate required, under the above conditions, 15 Cc. of $\frac{N}{10}$ HCl V. S. to discharge the red color produced by the phenolphthalein. A measured excess, consisting of 15 Cc. more of the acid, was added, and after expelling the CO_2, 10 Cc. of $\frac{N}{10}$ KOH V. S. were required to produce a red color. What is the percentage of calcium hydroxide and carbonate present?

First operation:

If 1 Cc. $\frac{N}{10}$ HCl V. S. is equivalent to 0.003678 Gm. calcium hydroxide,
15 Cc. " " " are " " $15 \times 0.003678 = 0.05517$ Gm. calcium hydroxide.

Second operation:

30 Cc. $\frac{N}{10}$ HCl V. S. = total added (15 + 15).
15 Cc. $\frac{N}{10}$ HCl V. S. = used for neutralizing the calcium hydroxide.
15 Cc.
10 Cc. $\frac{N}{10}$ KOH V. S. corresponding to an excess of 10 Cc. $\frac{N}{10}$ HCl.
5 Cc. $\frac{N}{10}$ KOH V. S. required for neutralizing the calcium carbonate.
If 1 Cc. $\frac{N}{10}$ HCl V. S. is equivalent to 0.004967 Gm. calcium carbonate,
5 Cc. " " " are " " $5 \times 0.004967 = 0.024835$ Gm. calcium carbonate.

Then the 50 Cc. (practically 50 Gm.) of lime water would contain 0.05517 Gm., or 0.1103+ per cent., of $Ca(OH)_2$ and 0.024835 Gm., or 0.0496+ per cent., of $CaCO_3$.

ACIDIMETRY.

Acidimetry, the reverse of alkalimetry, embraces the quantitative estimation of acids by means of the neutralizing power of standard alkali solutions.

The neutralizing equivalents of the standard normal, decinormal, or centinormal potassium, sodium, or barium hydroxides are exactly the same in each case, so that as far as their saturating or neutralizing powers are concerned it makes no difference which standard alkali is selected for the titrimetric estimation of an acid.

For example, one molecule of either NaOH (39.76 p.), KOH (55.7 p.), $Ba(OH)_2$ (85.08 p.), or NH_3 (16.93 p.) will exactly neutralize one molecule of a monovalent acid (as HCl, HBr, $HC_2H_3O_2$), one half of a molecule of a bivalent acid (as H_2SO_4, $H_2C_2O_4$, $H_2C_4H_4O_6$), or one-third of a molecule of a trivalent acid ($H_3C_6H_5O_7$, H_3PO_4).

Owing to the fact that solutions of the caustic alkalies readily absorb carbonic acid gas from the air, care should be taken to prevent its access into the containers. A convenient method for preserving standard solutions of the caustic alkalies and barium hydroxide is that shown in figure 16; another form, especially adapted to such cases where the standard solution is in constant use, is shown in figure 17. The chief indicators adapted to the estimation of organic acids are phenolphthalein and gallein.

Standard solutions of the alkalies readily lose their titer upon standing; a restandardization entails loss of time and is unnecessary as long as an accurately standardized acid solution is available. Titration with such empirical alkali solutions is treated under a separate chapter on page 76.

TABLE OF EQUIVALENTS.

As standard solution either sodium or potassium hydroxide is usually employed.

ACID.	1 Cc. $\frac{N}{1}$ ALKALI V. S. IS EQUIVALENT TO:	1 Cc. $\frac{N}{10}$ ALKALI V. S. IS EQUIVALENT TO:
Acetic acid, absolute, $HC_2H_3O_2$,	0.05956 Gm.	0.005956 Gm.
Citric acid, cryst., $H_3C_6H_5O_7 + H_2O$,	0.06948 "	0.006948 "
Hydriodic acid, absolute, HI,	0.12689 "	0.012689 "
Hydrobromic acid, absolute, HBr,	0.08034 "	0.008034 "
Hydrochloric acid, absolute, HCl,	0.03618 "	0.003618 "
Hypophosphorous acid, HPH_2O_2,	0.06551 "	0.006551 "
Lactic acid, absolute, $HC_3H_5O_3$,	0.08934 "	0.008934 "
Nitric acid, absolute, HNO_3,	0.06257 "	0.006257 "
Oleic acid, $HC_{18}H_{33}O_2$,	0.27996 "	0.027996 "
Oxalic acid, cryst., $H_2C_2O_4 + 2H_2O$,	0.06254 "	0.006254 "
Phosphoric acid, H_3PO_4, (To form K_2HPO_4; with phenolphthalein.)	0.048635 "	0.0048635 "
Phosphoric acid, H_3PO_4, (To form KH_2PO_4; with methyl-orange.)	0.09727 "	0.009727 "
Potassium dichromate, $K_2Cr_2O_7$,	0.1461 "	0.01461 "
Potassium bitartrate, $KHC_4H_4O_6$, (By direct titration.)	0.1867 "	0.01867 "
Sulphuric acid, absolute, H_2SO_4,	0.048675 "	0.0048675 "
Tartaric acid, cryst., $H_2C_4H_4O_6$,	0.07444 "	0.007444 "
Hydrofluoric acid, absolute, HFl,	0.0199 "	0.00199 "

The necessary amount of fluid (acid) should be weighed off in a tared and stoppered weighing flask, in order to avoid injury or corrosion of the balances. For weighing off definite amounts of an acid it is best to follow the method detailed under Hydrochloric Acid, page 72. The amount of acid selected depends upon its strength. For this purpose the Pharmacopœia tabulates a list of various acids, stating the amount to be taken. Any weight* approximately near that given may be selected. It is best to avoid taking large amounts of the acids, as this would result in the useless waste of a large volume of the standard alkali solution.

After weighing off the acid, the contents of the weighing flask are carefully rinsed out into a beaker or other flask preparatory to titrating. Then a few drops of the indicator are added, and titration carried out with normal alkali solution until the fluid turns rose-red (with phenolphthalein), or blue (with litmus), or yellow (with methyl-orange), or faint violet red (with rosolic acid), etc.

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* Compare "Direct Percentage Estimations," page 71.

1. Volumetric Assay of Monobasic Inorganic Acids.—*As* HCl, HBr, HI, HFl, HNO_3, HPH_2O_2.—

Of the concentrated acids, a quantity between 2.5 and 3.5 Gm. is sufficient; while of the diluted acids, from 5 to 10 Gm., according to the degree of dilution, are generally taken.

Example: A quantity of concentrated hydrochloric acid measured into a glass-stoppered weighing-flask was found to weigh 3.12 Gm.; this, after diluting with about 10 Cc. of water and adding two drops of methyl-orange, required 26 Cc. of standard normal potassium hydroxide for neutralization.

According to the equation:

$$\underset{55.70}{KOH} + \underset{36.18}{HCl} = KCl + H_2O$$

55.70 Gm. of potassium hydroxide (or 1000 Cc. of $\frac{N}{1}$ KOH V. S.) will neutralize exactly 36.18 Gm. of absolute hydrochloric acid (HCl).

Then 1 Cc. $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm. KOH) will be equivalent to 0.03618 Gm. of absolute HCl.

26 Cc. $\frac{N}{1}$ KOH V. S. = 26 × 0.03618, or 0.94068 Gm. of HCl.

The sample weighing 3.12 Gm. contains, therefore, 0.94068 Gm. of absolute HCl, corresponding to 30.15 per cent.; for:

$$3.12 \text{ Gm. sample} : 0.94068 \text{ Gm. HCl} :: 100 : x$$
$$3.12\,x = 0.94068 \times 100$$
$$x = 30.15 \text{ per cent.}$$

The sample contains 30.15 per cent. of absolute acid.

2. Volumetric Assay of Inorganic Dibasic Acids.—*As Sulphuric Acid* (H_2SO_4).—

The operation is precisely the same as that directed under the monobasic acids, and a quantity weighing between 0.5 and 1.5 Gm. is sufficient. In the calculation of results it must be remembered that each molecule of the alkali is equivalent to one-half of a molecule of a dibasic acid; thus:

$$\underset{2 \times 55.70}{2KOH} + \underset{97.35}{H_2SO_4} = K_2SO_4 + 2H_2O$$

If 2 × 55.70 Gm. of potassium hydroxide will neutralize exactly 97.35 Gm. of absolute sulphuric acid,

55.70 Gm. or 1000 Cc. $\frac{N}{1}$ KOH V. S. would be equivalent to 48.675 Gm. of H_2SO_4 (½ of 97.35).

Then 1 Cc. $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm. KOH) would be equivalent to 0.048675 Gm. of absolute H_2SO_4.

For like reasons one cubic centimeter of normal alkali V. S. is equivalent to $\frac{1}{2000}$ part of the molecular weight of oxalic, tartaric, or any other dibasic acid.

3. Volumetric Assay of Inorganic Tribasic Acids.—*As Phosphoric Acid* (H_3PO_4).—

Phosphoric acid is usually estimated by Thompson's method, in which both indicators, methyl-orange and phenolphthalein, are employed. The former indicating the formation of a primary salt (MeH_2PO_4), while the latter that of a secondary salt (Me_2HPO_4), the result from either can be employed as a basis for calculation.

(*a*) To an accurately weighed quantity (between 1 and 2 grammes) of the acid, diluted with about 20 Cc. of water, two drops of methyl-orange are added, followed by a standard normal alkali until the red color of the solution changes to a pale yellow. The number of cubic centimeters of the alkali solution required, multiplied by the factor 0.09727, gives the quantity of absolute H_3PO_4 contained in the sample. The reaction is as follows:

$$\underset{\substack{\text{Potassium}\\ \text{Hydroxide.}\\ 55.70}}{KOH} + \underset{\substack{\text{Phosphoric}\\ \text{Acid.}\\ 97.27}}{H_3PO_4} = \underset{\substack{\text{Primary or Mono-}\\ \text{potassic Phosphate.}}}{KH_2PO_4} + H_2O$$

55.70 parts of KOH are necessary for 97.27 parts of H_3PO_4 to produce the primary salt,

1000 Cc. $\frac{N}{1}$ KOH V. S. (containing 55.70 Gm.) = 97.27 Gm. absolute H_3PO_4

1 Cc. " " " (" 0.0557 Gm.) = 0.09727 " " "

(*b*) Phenolphthalein is now added and the addition of the standard alkali continued until a red color appears. The number of cubic centimeters of standard alkali added with that of the previous titration, multiplied by the factor 0.048635, gives the weight of absolute acid contained in the sample. This second titration serves as a check to the first. The reaction is as follows:

$$KOH + KH_2PO_4 = \underset{\substack{\text{Secondary or Di-potassic}\\ \text{Phosphate.}}}{K_2HPO_4} + H_2O$$

For the production of a secondary salt *two* molecules of the alkali have been employed; hence one molecule of $\frac{N}{1}$ KOH V. S. would be equivalent to one-half of a molecule of H_3PO_4. Thus:

$$\underset{2 \times 55.70}{2KOH} + \underset{97.27}{H_3PO_4} = K_2HPO_4 + 2H_2O.$$

If 2 × 55.70 parts of KOH are necessary for 97.27 parts of H_3PO_4 to produce the secondary salt,

1000 Cc. $\frac{N}{1}$ KOH V. S. (containing 55.70 Gm.) = 49.635 Gm. of H_3PO_4 $(\frac{97.27}{2})$

1 Cc. " " " (" 0.0557 Gm.) = 0.049635 Gm. of absolute H_3PO_4.

4. Volumetric Estimation of Organic Acids.—

Very few indicators are adapted to the estimation of organic acids, and even these vary in their degree of sensitiveness to different acids. The operator should consult the tables on page 34.

Acetic Acid.—$CH_3COOH = 59.56$.—Owing to abnormalities in the ratio of percentage strength to specific gravity, the strength of this acid is best ascertained volumetrically, employing either *phenolphthalein* or *congo red* as indicator.

Example: 6 Gm. of a sample of acetic acid, after diluting with about 10 Cc. of water and adding two drops of indicator, required 36 Cc. of $\frac{N}{1}$ KOH V. S. for neutralization. What was the strength of the sample in absolute acid?

$$\underset{\substack{\text{Potassium}\\ \text{Hydroxide.}\\ 55.70}}{KOH} + \underset{\substack{\text{Acetic Acid.}\\ 59.56}}{CH_3COOH} = \underset{\substack{\text{Potassium}\\ \text{Acetate.}}}{CH_3COOK} + H_2O$$

1000 Cc. $\frac{N}{1}$ KOH V. S. (containing 55.70 Gm. KOH) are equivalent to 59.56 Gm. of absolute acetic acid (CH_3COOH).

1 Cc. $\frac{N}{1}$ KOH V. S. (containing 0.05570 Gm. KOH) $=$ 0.05956 Gm. CH_3COOH.

36 Cc. of $\frac{N}{1}$ KOH V. S. are equivalent to 36×0.05956 or 2.144+ Gm. of absolute acid, which corresponds to 35.73+ per cent.

Gm. Acid taken: Gm. Abs. Acid:

$$6 : 2.144+ :: 100 : x$$

$$6x = 214.400$$

$$x = 35.73+$$

The sample contains 35.73+ per cent. of absolute acid.

Vinegar.—Besides acetic acid, vinegar contains variable quantities of albuminous substances, gums, glycerol, malic and other organic acids, with not less than 0.25 per cent. of ash (cider vinegar). The strength in acetic acid and quantity of total solids vary largely according to the source.

Cider vinegar contains from 3.5 to 6 per cent. of absolute acetic acid and 1.7 to 2.4 per cent. extractive.

Wine vinegar contains from 6 to 12 per cent. of absolute acetic acid and 1.5 to 1.8 per cent. extractive.

Beer and malt contain from 3 to 6 per cent. of absolute acetic acid and 5 to 6 per cent. extractive.

Glucose vinegar contains dextrin, dextrose, and calcium sulphate; and when concentrated and mixed with four times its volume of alcohol, it deposits dextrin on standing.

A good genuine vinegar should contain not less than 5 per cent. of absolute acetic acid; when less than 3 per cent., it is unfit for use. Sophistication usually consists in adding boiled cider, glucose, or extractives to a diluted acetic acid, coloring with caramel. Analysis of the ash* is usually resorted to in cases of doubtful origin.

The presence of mineral acids (HCl, H_2SO_4) may be ascertained qualitatively by adding 5 drops of methyl-violet† (0.1 Gm. to 1000 Cc. water) to 25 Cc. of the sample, which has been diluted down to 2 per cent. acid strength; these change the blue to blue-green or green.

For titration 10 Gm. of the sample, diluted to about 50 Cc., may be taken; should the color interfere with the sharpness of the end-reaction of the indicator, recourse may be had to phenolphthalein paper, which is moistened with a drop of the liquid from time to time during the titration.

	PURE CIDER VINEGAR, PER CENT.
* Calcium oxide (CaO),	3.40 to 8.20
Magnesium oxide (MgO),	1.80 to 3.50
Potassium oxide (K_2O),	46.35 to 65.65
Sodium oxide (Na_2O),	Trace.
Sulphuric anhydride (SO_3),	4.60 to 16.30
Phosphoric anhydride (P_2O_5),	3.30 to 6.60
Carbon dioxide, loss,	40.00 to 0.0

† Methyl-violet B_2, No. 56, Bayer & Co. (Elberfeld Farbenfabriken).

Alcohol is always present in genuine fermentation vinegar; this may be identified by distilling off about 10 Cc. from 100 to 200 Cc. of the sample which has been completely neutralized by the addition of powdered chalk; the presence of alcohol in this distillate may be established by the iodoform test.* If alcohol is absent, a quantity of the sample should be ignited and the ash examined quantitatively.

Acetates of Potassium and Sodium.—These salts upon ignition are converted into their respective carbonates, which may then be estimated as directed on page 56 or 71.

$$\text{Since} \quad \underset{\substack{\text{Potassium Acetate.}\\ 2 \times 97.38}}{2CH_3COOK} = \underset{\text{Potassium Carbonate.}}{K_2CO_3} = \underset{\substack{\text{Hydrochloric Acid.}\\ 2 \times 36.18}}{2HCl,}$$

then 1 Cc. $\frac{N}{1}$ HCl or H_2SO_4 V. S. is equivalent to 0.09738 Gm. potassium acetate.

1 Cc. " " " " " " " " 0.13508 Gm. sodium acetate (cryst.).

Metallic Acetates (Lead, Zinc, Copper, Iron, etc.).—To a weighed quantity of the neutral acetate,† dissolved in distilled water, a measured excess of $\frac{N}{1}$ Na_2CO_3 V. S. is added, the mixture boiled, filtered, and washed with hot water. The filtrate with washings are collected in a graduated cylinder, made up to a definite volume, and an aliquot portion taken and titrated with $\frac{N}{1}$ HCl V. S. After calculating the number of cubic centimeters required for the *entire* volume of filtrate, it is deducted from the volume of $\frac{N}{1}$ Na_2CO_3 V. S. originally added; the difference represents the number of cubic centimeters of normal alkali required for the acetic acid present. 1 Cc. $\frac{N}{1}$ Na_2CO_3 = 0.05956 Gm. acetic acid (abs.).

Tartaric Acid.—$H_2C_4H_4O_6 = 148.88$.—From 2 to 3 Gm. of the acid are sufficient for a titration, phenolphthalein only being employed as indicator. Each cubic centimeter of standard normal alkali corresponds to 0.07444 Gm. of the dry acid, as will be seen from the following equation:

$$\underset{\substack{\text{Potassium Hydroxide.}\\ 2 \times 55.70}}{2KOH} + \underset{\substack{\text{Tartaric Acid.}\\ 148.88}}{H_2C_4H_4O_6} = \underset{\text{Potassium Tartrate.}}{K_2C_4H_4O_6} + 2H_2O.$$

If 55.70 Gm. or 1000 Cc. $\frac{N}{1}$ KOH V. S. will neutralize 74.44 Gm. $\left(\frac{148.88}{2}\right)$ of tartaric acid,

1 Cc. $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm. KOH) = 0.07444 Gm. $H_2C_4H_4O_6$.

Citric Acid.—$H_3C_6H_5O_7 + H_2O = 208.44$.—From 2 to 3 Gm. of the acid are sufficient for a titration, employing phenolphthalein as indicator. Each cubic centimeter of normal standard alkali is equivalent to 0.06948 Gm. of the crystalline acid.

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* To a weak alcoholic liquid add 5 to 10 drops of Lugol's solution, followed by just sufficient of sodium hydroxide solution to leave the liquid a pale yellow after slight warming; if a complete decolorization ensues, add one or two drops more of the iodine. The minute quantity of iodoform produced may be identified by its odor.

† If free acetic or inorganic acid is present, it must first be exactly neutralized.

$$\underset{\substack{\text{Potassium Hydroxide.}\\ 3\times 55.70}}{3\mathrm{KOH}} + \underset{\substack{\text{Citric Acid}\\ 208.44}}{\mathrm{H_3C_6H_5O_7 + H_2O}} = \underset{\text{Potassium Citrate.}}{\mathrm{K_3C_6H_5O_7}} + \mathrm{4H_2O}$$

If 55.70 Gm. or 1000 Cc. $\frac{N}{1}$ KOH V. S. will neutralize 69.48 Gm. $\left(\frac{208.44}{3}\right)$ of citric acid,

1 Cc. $\frac{N}{1}$ KOH V. S. (containing 0.0557 Gm. KOH) = 0.06948 Gm. $H_3C_6H_5O_7 + H_2O$.

The presence of tartaric acid may be qualitatively detected by heating about 1 Gm. of the sample with 10 Cc. of sulphuric acid at 100° C. for forty minutes; pure citric acid yields a clear yellow solution, while the presence of 1 per cent. of tartaric acid imparts a brown color, deepening with increase in the latter.

Quantitatively, tartaric acid may be estimated in presence of citric by conversion into insoluble acid tartrate ($KHC_4H_4O_6$), in which 2 Gm. of the sample are dissolved in 45 Cc. of alcohol (0.920), 5 Cc. of a saturated alcoholic solution of potassium acetate added, and the mixture stirred for about ten minutes. The reaction proceeds as follows:

$$\underset{\substack{\text{Tartaric}\\ \text{Acid.}}}{\mathrm{H_2C_4H_4O_6}} + \underset{\substack{\text{Potassium}\\ \text{Acetate.}}}{\mathrm{KC_2H_3O_2}} = \underset{\substack{\text{Acid Potassium}\\ \text{Tartrate.}}}{\mathrm{KHC_4H_4O_6}} + \underset{\substack{\text{Acetic}\\ \text{Acid.}}}{\mathrm{HC_2H_3O_2}}$$

If the quantity of tartaric acid be very small, no well-defined precipitate forms, but white streaks will be formed on the sides of the beaker where the stirring-rod has touched; 2 per cent. of this acid may be thus detected. If a weighable quantity of precipitate forms, it is collected on a small plain filter, washed with alcohol, then rinsed from the filter into a beaker with a cold saturated aqueous solution of potassium acid tartrate; this mixture, after standing for some hours, with an occasional stirring, is again collected on a small filter and washed with alcohol; the filter with precipitate is transferred to a beaker containing from 30 to 50 Cc. of hot water, and, after adding two drops of phenolphthalein, is titrated with $\frac{N}{10}$ KOH V. S.; each 1 Cc. is equivalent to 0.007444 Gm. of tartaric acid.

Lime (Lemon or Bergamot) Juice.—These juices* contain, besides free citric acid, upon which their commercial value depends, small quantities of volatile organic acids, their salts, albuminous and mucilaginous substances.

Lime juice contains from	6.0 to	13.0 ounces free acid per gallon.
Concentrated lime juice contains from	56.0 to	72.0 ounces free acid per gallon.
Lemon juice contains from	10.6 to	13.5 ounces free acid per gallon.
Concentrated lemon juice contains from	82.0 to	112.0 ounces free acid per gallon.

The British Pharmacopœia standard is 11.9 ounces of citric acid per gallon.

After proving the absence of any free inorganic acids (HCl, H_3PO_4) or tartaric acid, the free citric acid of the sample may be estimated by titrating with $\frac{N}{2}$ KOH V. S. If it be a concentrated juice, 50 Cc. should be diluted with water to 500 Cc., measuring off 25 Cc. ($\frac{1}{20}$ part) for a titration; with the unconcentrated juice from 10 to 20 Cc. are sufficient. It is best to add the alkali in sufficient quantity to neutralize about four-fifths of the acid present; then bring to a boil, and after allowing to cool, the titration is completed. Each cubic

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* Allen's Commercial Organic Analysis, Vol. I, p. 536, 3d ed.

centimeter of $\frac{N}{2}$ KOH V. S. is equivalent to 0.03474 Gm. of the crystalline citric acid, and, multiplying the number of grammes in each cubic centimeter of juice by 160, the result gives the number of ounces per gallon.

DIRECT PERCENTAGE ESTIMATIONS.

By the aid of standard volumetric solutions the percentage purity of a substance may be obtained direct, without further calculation, by weighing off a quantity represented by *one-tenth* of the molecular weight of the compound examined when a $\frac{N}{1}$ volumetric solution is employed, and *one-hundredth* part with a $\frac{N}{10}$ volumetric solution. Compounds of higher valence—as, tartaric, citric, phosphoric, and sulphuric acids, also potassium carbonate and citrate, potassium sodium tartrate and strontium lactate, also others through their high molecular weight—would, under the above conditions, require excessive volumes of the standard solution; hence $\frac{1}{20}$, $\frac{1}{40}$, $\frac{1}{60}$, and $\frac{1}{200}$ part of their respective molecular weights is selected for analysis. A table of equivalents is given on page 75.

Examples.

Acetic Acid.—($CH_3COOH = 59.56$.)

Employing a $\frac{N}{1}$ alkali V. S., each cubic centimeter consumed in neutralization represents 1 per cent. of absolute acetic acid if 5.956 Gm. $\left(\frac{59.56}{100}\right)$ of the sample is taken. This is based on the following:

$$\underset{55.7}{KOH} + \underset{59.56}{CH_3COOH} = CH_3COOK + H_2O$$

1000 Cc. of $\frac{N}{1}$ KOH V. S. containing 55.7 Gm. KOH = 59.56 Gm. CH_3COOH
100 Cc. " " " " " 5.57 Gm. " = 5.956 Gm. "
1 Cc. " " " " " 0.0557 Gm. " = 0.05956 Gm. "

If 5.956 Gm. of acetic acid are taken for analysis, this, if absolute, would require 100 Cc. of $\frac{N}{1}$ KOH V. S. (5.57 Gm. KOH) for neutralization; hence the sample would be 100 per cent. strong. To neutralize each 0.05956 Gm. of absolute acetic acid, one cubic centimeter, which is the $\frac{1}{100}$ part (or 1 per cent.) of the $\frac{N}{1}$ V. S., will be required; hence each cubic centimeter of $\frac{N}{1}$ alkali V. S. added represents 1 per cent. of the absolute acid.

Acetic Acid, Glacial.—

Owing to the high strength of this acid, the amount taken in the above example would require an excessive volume of standard alkali V. S.; hence $\frac{1}{20}$ part of the molecular weight, or 2.978 Gm., is taken. Each cubic centimeter of $\frac{N}{1}$ alkali V. S. corresponds to 2 per cent.

of absolute acetic acid. For weighing off sample, compare with Hydrochloric Acid.

Hydrochloric Acid.—($HCl = 36.18$.)

Each cubic centimeter of a $\frac{N}{1}$ alkali V. S. represents 1 per cent. of absolute acid when 3.618 Gm. $\left(\frac{36.18}{10}\right)$ of the sample are taken, or each 1 Cc. of a $\frac{N}{10}$ alkali V. S. represents 1 per cent. of absolute acid if 0.3618 Gm. $\left(\frac{36.18}{100}\right)$ of the sample is taken. The latter case will be applied here.

A sample of acid of specific gravity 1.124 was selected, and exactly 2 Cc. (weighing 2.248 Gm.) were measured off and diluted to 100 Cc.

A quantity representing 0.3618 Gm.* of the original sample is measured off, which, on calculation, was found to be 16.09 Cc.; for:

$$\overset{\text{Diluted Solution.}}{1\text{ Cc.}} \quad : \quad \overset{\text{Acid Content.}}{0.02248\text{ Gm.}} \quad :: \quad x \quad : \quad 0.3618\text{ Gm.}$$

$$x = 16.09\text{ Cc.}$$

After diluting this with water and adding two drops of methyl-orange, 26.28 Cc. of $\frac{N}{10}$ alkali V. S. were required for neutralization. The solution contains, therefore, 26.28 per cent. of absolute acid.

$$\underset{55.7}{KOH} + \underset{36.18}{HCl} = KCl + H_2O$$

100 Cc. of a $\frac{N}{10}$ KOH V. S. containing 0.557 Gm. KOH = 0.3618 Gm. HCl.
1 Cc. " " " " " 0.00557 Gm. " = 0.003618 Gm. "

The 0.3618 Gm. of hydrochloric acid taken would require, if absolute, 100 Cc. of $\frac{N}{10}$ KOH V. S.; then each 1 Cc. of $\frac{N}{10}$ alkali V. S. will represent $\frac{1}{100}$ part or 1 per cent. (0.003618 Gm.) of absolute acid.

Nitric Acid.—($HNO_3 = 62.57$.)

For like reasons as given under Glacial Acetic Acid, $\frac{1}{20}$ part of the molecular weight, or 3.1285 Gm., is taken. Each 1 Cc. of $\frac{N}{1}$ alkali V. S. corresponds to 2 per cent. of absolute nitric acid. For weighing off sample, follow the method given under Hydrochloric Acid.

Sulphuric Acid.—($H_2SO_4 = 97.35$.)

It is advisable to select a small quantity of a dilute solution of the acid and titrate with $\frac{N}{10}$ alkali V. S. Each 1 Cc. of $\frac{N}{1}$ alkali V. S. represents 10 per cent. of absolute acid if 0.48675 Gm. $\left(\frac{97.35}{20}\right)$ of the sample is taken, or each 1 Cc. of $\frac{N}{10}$ alkali V. S. represents 1 per cent. of absolute acid with the same quantity of the sample.

An acid of specific gravity 1.835 was selected and exactly 2 Cc.

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* This is $\frac{1}{100}$ part of 36.18, which corresponds to 100 Cc. of a $\frac{N}{10}$ HCl V. S., and is equivalent to 100 Cc. of a $\frac{N}{10}$ alkali V. S.

(weighing 3.67 Gm.) were measured into a cylinder and diluted to 100 Cc., and, after cooling, an aliquot volume representing 0.48675 Gm. $\left(\frac{97.35}{20}\right)$ was taken for estimation. This is equivalent to 13.26 Cc. of the diluted solution; for:

Diluted Solution.		Acid Content.				
1 Cc.	:	0.0367 Gm.	::	x	:	0.48675 Gm.
		x	$=$	13.26 Cc.		

100 Cc. of $\frac{N}{10}$ KOH V. S. containing 0.557 Gm. KOH = 0.48675 Gm. H_2SO_4
1 Cc. " " " " " 0.00557 Gm. " = 0.0048675 Gm. "

The 0.48675 Gm. of sulphuric acid taken would require, if absolute, 100 Cc. of $\frac{N}{10}$ KOH V. S.; then each 1 Cc. of $\frac{N}{10}$ alkali V. S. will represent the $\frac{1}{100}$ part or 1 per cent. (0.0048675 Gm.) of absolute acid.

Phosphoric Acid.—($H_3PO_4 = 97.27$.)

Each 1 Cc. $\frac{N}{1}$ alkali V. S. corresponds to 5 per cent. of absolute acid when 0.9727 Gm. of the sample is taken, employing *phenolphthalein* as indicator; or each 1 Cc. of a $\frac{N}{10}$ alkali V. S. corresponds to 0.5 per cent. under the same conditions:

2KOH	+	H_3PO_4	=	K_2HPO_4	+	H_2O
2 × 55.7		97.27				
55.7	=	48.635				

100 Cc. $\frac{N}{1}$ KOH V. S. containing 5.57 Gm. KOH = 4.8635 Gm. H_3PO_4
1 Cc. " " " " 0.0557 Gm. " = 0.048635 Gm. "

If the 0.9727 Gm. of the sample taken was absolute (100 per cent.) acid, 20 Cc. of a $\frac{N}{1}$ KOH V. S. would be required for complete neutralization ($0.048635 \times 20 = 0.9727$). Each 1 Cc. of the alkali V. S. would then represent $\frac{100}{20}$ or 5 per cent. of absolute acid.

When *methyl-orange* is used as indicator and 0.9727 Gm. of the sample is taken, each 1 Cc. of $\frac{N}{1}$ alkali V. S. corresponds to 10 per cent. of absolute acid; or if $\frac{N}{10}$ alkali V. S. is employed under the same conditions, each 1 Cc. will be equivalent to 1 per cent. of acid.

KOH	+	H_3PO_4	=	KH_2PO_4	+	H_2O
55.7		97.27				

100 Cc. of $\frac{N}{1}$ KOH V. S. containing 5.57 Gm. KOH = 9.727 Gm. H_3PO_4
1 Cc. " " " " " 0.0557 Gm. " = 0.09727 Gm. "

For neutralizing 0.9727 Gm. of absolute acid 10 Cc. of a $\frac{N}{1}$ KOH V. S. would be necessary ($0.09727 \times 10 = 0.9727$); then each 1 Cc. of the alkali V. S. would represent the $\frac{1}{10}$ part, which is equivalent to 10 per cent. of absolute acid. A greater degree of accuracy may be attained by employing a $\frac{N}{10}$ alkali V. S.

The necessary quantity of acid may be measured as directed under Hydrochloric Acid.

Citric Acid.—($H_3C_6H_5O_7 + H_2O = 208.44$.)

Each 1 Cc. of $\frac{N}{1}$ alkali V. S. corresponds to 2 per cent. of absolute acid when 3.474 Gm. of the sample are taken.

$$\underset{3 \times 55.7}{3KOH} + \underset{208.44}{H_3C_6H_5O_7} = K_3C_6H_5O_7 + 3H_2O$$

If 3 × 55.7 Gm. of KOH are equivalent to 208.44 Gm. of $H_3C_6H_5O_7$,
55.7 Gm. " " " " " 69.48 Gm. " "
100 Cc. of $\frac{N}{1}$ KOH V. S. containing 5.57 Gm. KOH = 6.948 Gm. $H_3C_6H_5O_7$.

Owing to the large volume of alkali V. S. which would be required for neutralization if 6.948 Gm. of the acid were taken, a smaller quantity—usually one-half; that is, 3.474 Gm.—suffices. To saturate 3.474 Gm. of a sample of absolute acid, 50 Cc. of $\frac{N}{1}$ alkali V. S. would be required. Since this quantity represents one-half of an amount equivalent to 100 Cc. of the normal alkali, each cubic centimeter would then represent 2 per cent. of absolute acid.

Sodium Benzoate.—($NaC_7H_5O_2 = 142.94$.)

Two molecules of the salt, when ignited, yield one molecule of sodium carbonate, which, in turn, requires one molecule of sulphuric acid for neutralization. One-half a molecule of the acid (48.675 Gm. H_2SO_4) which is contained in one liter of a normal solution will neutralize one-half of a molecule of sodium carbonate (52.65 Gm.), which, in turn, corresponds to one molecule of sodium benzoate (142.94 Gm.). Thus:

$$\underset{2 \times 142.94}{2NaC_7H_5O_2} + 5O_2 = \underset{105.3}{Na_2CO_3} + 5H_2O + 3CO_2 + 5C_2$$

$$\underset{97.35}{H_2SO_4} + \underset{105.3}{Na_2CO_3} = Na_2SO_4 + H_2O + CO_2$$

$$97.35 \text{ p. } H_2SO_4 = 105.3 \text{ p. } Na_2CO_3 = 285.88 \text{ p. } NaC_7H_5O_2$$

48.675 Gm. H_2SO_4 (1000 Cc. $\frac{N}{1}$ V. S.) are equivalent to 142.94 Gm. $NaC_7H_5O_2$
4.8675 Gm. " (100 Cc. $\frac{N}{1}$ V. S.) " " " 14.294 Gm. "

If 14.294 Gm. of a sample of absolute purity (100 per cent.) were taken for analysis, 100 Cc. of $\frac{N}{1}$ H_2SO_4 V. S. (4.8675 Gm. H_2SO_4) would be required. Each 1 Cc. of the acid, which is the $\frac{1}{100}$ part, would correspond to 0.14294 Gm. or 1 per cent. of pure salt. However, to avoid the inconvenience attending the employment of excessive volumes (95 to 100 Cc.) of the normal acid, as would be the case in the above, we select *one-tenth* the quantity,—that is, 1.4294 Gm. of sodium benzoate,—when each 1 Cc. of $\frac{N}{1}$ acid V. S. consumed would correspond to 10 per cent. of absolutely pure salt present.

This same line of reasoning is applied to all of the various organic salts of inorganic bases.

Potassium and Sodium Hydroxides.

The method of measuring off molecular quantities of the dissolved alkali is identical with that employed under Hydrochloric

Acid. For example, a piece of caustic soda weighing 7.51 Gm. was dissolved in water and the volume made up to exactly 100 Cc. A volume representing 0.3976 Gm. of the dry hydroxide was measured off for assay; this quantity was found on calculation to be represented by 5.3 Cc. of the solution; for:

Diluted Solution.		Alkali Content.				
1 Cc.	:	0.0751	::	x	:	0.3976

$$x = 5.3 \text{ Cc.}$$

This volume, after diluting with a little water and adding methyl-orange, was titrated with a $\frac{N}{1}$ acid V. S., each 1 Cc. corresponding to 10 per cent. of absolute hydroxide present.

$$\underset{97.35}{H_2SO_4} + \underset{2 \times 39.76}{2NaOH} = Na_2SO_4 + H_2O$$

1000 Cc. $\frac{N}{1}$ H_2SO_4 (containing 48.675 Gm. H_2SO_4) = 39.76 Gm. of NaOH
100 Cc. " " " 4.8675 Gm. " = 3.976 Gm. " "

If the sample of 3.976 Gm. were absolutely pure, 100 Cc. of normal acid would be required, or each 1 Cc. would represent $\frac{1}{100}$ part, corresponding to 1 per cent. purity. For reasons already cited in the preceding example, one-tenth of the equivalent of alkali is taken,—namely, 0.3976 Gm.; hence each 1 Cc. of normal acid consumed would correspond to 10 per cent. of pure substance.

TABLE OF EQUIVALENTS FOR DIRECT PERCENTAGE ESTIMATIONS.

Methyl-orange is employed as indicator in all cases excepting acetic, lactic, tartaric, and citric acids, where phenolphthalein may be used. For ammonia, rosolic acid is recommended.

SUBSTANCE.	MOLECULAR WEIGHT.	QUANTITY TAKEN.	PERCENTAGE STRENGTH EQUIVALENT TO EACH 1 CC. OF $\frac{N}{1}$ ACID OR ALKALI V. S.
Acetic Acid,	59.56	5.956 Gm.	1
" " Glacial,		2.978 "	2
Aqua Ammonia,	16.93 (NH_3)	3.386 "	0.5
" " Fort.,		1.693 "	1
Citric Acid ($+H_2O$),	208.44	3.474 "	2
Hydrobromic Acid,	80.34	8.034 "	1
Hydrochloric Acid,	36.18	3.618 "	1
Lactic Acid,	89.34	4.467 "	2
Liquor Plumbi Subacetatis,		15.593 "	1
" Potassæ,		27.850 "	0.2
" Sodæ,		19.880 "	0.2
Lithium Benzoate (ignited),	127.03	1.2703 "	10
" Carbonate,	73.48	0.3674 "	10
" Citrate (ignited),	208.47	0.6949 "	10
" Salicylate,	142.91	1.4291 "	10
Nitric Acid,	62.57	3.1290 "	2
Phosphoric Acid,	97.27	0.9727 "	See text.
Potassium Hydroxide,	55.70	0.5570 "	10
" Acetate,	97.38	0.9738 "	10
" Bicarbonate,	99.36	0.9936 "	10
" Bitartrate,	186.70	1.8670 "	10
" Carbonate,	137.18	0.6859 "	10
" Citrate (H_2O) (ignited),	321.90	1.0730 "	10
" Sodium Tart. (ignited),	280.10	1.4005 "	10

Table of Equivalents for Direct Percentage Estimations.—(*Continued.*)

Substance.	Molecular Weight.	Quantity Taken.	Percentage Strength Equivalent to each 1 Cc. of $\frac{N}{1}$ Acid or Alkali V. S.
Sodium Hydroxide, ...	39.76	0.3976 Gm.	10
“ Acetate ($3H_2O$) (ignited), .	135.08	1.3508 “	10
“ Benzoate (ignited), ...	142.94	1.4294 “	10
“ Bicarbonate, ...	83.42	0.8342 “	10
“ Carbonate (dry), ...	105.30	0.5265 “	10
Strontium Lactate ($3H_2O$) (ignited), .	317.27	1.58635 “	10
Sulphuric Acid, ...	97.35	0.48675 “	$\frac{1}{10}$ Cc. = 1
Tartaric Acid, ...	148.88	3.7220 “	2

The results obtained with some of the organic salts, as the benzoates, citrates, and salicylates, are only of an approximate value owing to the slight excess of alkali possibly present in some, and acid in other samples.

Employment of Empirical Alkali Solutions in the Titration of Acids and Alkalies.

Standard solutions of the caustic alkalies, when not kept with all precautions, deteriorate readily upon standing, through absorption of carbonic acid gas from the air, also through their action upon the silica of the glass containers. To restore the titer of such an alkali solution each time it is desired for use is not only annoying, but also an unnecessary waste of time. Again, it may not be desirable, nor is it necessary, that a newly made alkali solution be standardized. As long as we are in possession of a standard acid the strength of which has been accurately fixed, we are able to carry on all neutralization titrations with alkali solutions of varying strengths. For this purpose the titer of the alkali in question is accurately fixed by measuring 10 Cc. of the standard acid V. S. from a burette into a beaker, and, after diluting with a little water and adding two or three drops of methyl-orange, the alkali solution is added until the solution changes from a red to yellow; the number of cubic centimeters required is then noted.

Either by means of the standard acid V. S. the actual alkali (NaOH or KOH) content of 1 Cc. of the empirical alkali solution is accurately ascertained, and this is converted into equivalent cubic centimeters of $\frac{N}{1}$, $\frac{N}{10}$, or $\frac{N}{100}$ V. S.;

Or the number of cubic centimeters of the alkali solution employed is, by means of the standard acid V. S., converted into their equivalent volume of standard $\frac{N}{1}$, $\frac{N}{10}$, or $\frac{N}{100}$ V. S.

Example: (*a*) To a sample of potassium carbonate weighing 0.3810 Gm. an excess consisting of 10 Cc. of $\frac{N}{1}$ acid V. S. was added, and for titrating back the uncombined excess, 4 Cc. of an empirical solution of potassium hydroxide were required.

In a trial experiment it was found that 10 Cc. of the $\frac{N}{1}$ acid V. S. required 8 Cc. of the empirical alkali solution for complete neutralization.

If 1 Cc. of $\frac{N}{1}$ acid V. S. is equivalent to 0.0557 Gm. KOH,
10 Cc. " " " are " " 0.557 Gm. KOH, which

must be present in the 8 Cc. of empirical alkali solution.

One Cc. of this solution would then contain $\frac{0.557}{8}$ or 0.069625 Gm. of KOH, which is equivalent to 1.25 Cc. of a $\frac{N}{1}$ V. S.; for:

Gm. KOH Cc. Gm. KOH
0.0557 : 1 :: 0.069625 : x
$x = 1.25$ Cc.

In the actual titration 4 Cc. of this empirical solution were employed, which, expressed in normal units, would be equivalent to $4 \times 1.25 = 5$ Cc. of $\frac{N}{1}$ KOH V. S.

Then 10 Cc. = $\frac{N}{1}$ acid V. S., the added excess
5 Cc. = volume of $\frac{N}{1}$ KOH V. S. calculated from absolute KOH present in the 12 Cc. of empirical alkali solution consumed in titrating back.
5 Cc. = $\frac{N}{1}$ acid V. S. required.

If 1 Cc. of $\frac{N}{1}$ acid V. S. = 0.06859 Gm. of potassium carbonate,
5 Cc. " " " = 0.34295 " " " "

Therefore the sample weighing 0.3810 Gm. contains 0.3429 Gm., or 90 per cent., of pure carbonate.

(*b*) To a solution of 0.212 Gm. of potassium carbonate an excess consisting of 10 Cc. of $\frac{N}{1}$ acid V. S. was added, and for titrating back the uncombined excess, 5.6 Cc. of an empirical solution of potassium hydroxide were required. In a trial experiment it was found that 10 Cc. of the $\frac{N}{1}$ acid V. S. required 8 Cc. of the alkali for complete neutralization.

Since 8 Cc. of the alkali solution are equivalent to 10 Cc. of a $\frac{N}{1}$ acid V. S., then 5.6 Cc. of the former would correspond to 7 Cc. of the normal acid; for:

Alkali Normal Acid
8 Cc. : 10 Cc. :: 5.6 : x
$x = 7$ Cc.

Then 10 Cc. — 7 Cc. = 3 Cc., the volume of $\frac{N}{1}$ acid V. S. required to neutralize the potassium carbonate present.

If 1 Cc. $\frac{N}{1}$ acid V. S. = 0.06859 Gm. K_2CO_3,
3 Cc. " " " = 0.20577 Gm. "

The sample of 0.212 Gm. contains, therefore, 0.20577 Gm., or 97.06+ per cent., of real potassium carbonate.

Example: A sample of acetic acid weighing 5.956 Gm. required for neutralization 57.6 Cc. of a weak solution of sodium hydroxide.

In a trial experiment it was found that 10 Cc. of a $\frac{N}{1}$ acid V. S. required for neutralization 16 Cc. of this empirical alkali solution.

If 1 Cc. of $\frac{N}{1}$ acid V. S. is equivalent to 0.03976 Gm. NaOH,
10 Cc. " " " are " " 0.3976 Gm. NaOH,

which must be present in the 16 Cc. of the alkali solution. 1 Cc. of this solution would then contain $\frac{0.3976}{16}$ or 0.02485 Gm. of NaOH, which is equivalent to 0.625 Cc. of a $\frac{N}{1}$ NaOH V. S.; for:

$$\begin{array}{ccccccc} \text{Gm. NaOH} & & \text{Cc.} & & & & \\ 0.03976 & : & 1 & :: & 0.02485 & : & x \end{array}$$
$$x = 0.625 \text{ Cc.}$$

In the titration of the acetic acid 57.6 Cc. of this weak solution of alkali were consumed, which, expressed in normal units, would be equivalent to 0.625 × 57.6 Cc. = 36 Cc. of $\frac{N}{1}$ NaOH V. S.

If 1 Cc. of $\frac{N}{1}$ NaOH V. S. = 0.05956 Gm. of absolute acetic acid,
36 Cc. " " " = 36 × 0.05956 or 2.14416 Gm. of absolute acetic acid.

The sample weighing 5.956 Gm. contains 2.144+ Gm., or 36 per cent., of absolute acetic acid.

Example: A residue of cocaine was dissolved in 10 Cc. of a $\frac{N}{25}$ acid V. S., and for titrating back the excess of uncombined acid 17.4 Cc. of an empirical alkali solution were required.

In a trial experiment 14.5 Cc. of the alkali solution were required to neutralize 5 Cc. of the $\frac{N}{25}$ acid V. S. Since 14.5 Cc. of the alkali solution are equivalent to 5 Cc. of the $\frac{N}{25}$ acid V. S., 17.4 Cc. of the former would represent 6 Cc. of the latter; for:

$$14.5 : 5 :: 17.4 : x$$
$$x = 6$$

Then 10 Cc. — 6 Cc. = 4 Cc., the volume of $\frac{N}{25}$ acid V. S. required for the cocaine.

If 1 Cc. $\frac{N}{25}$ acid V. S. = 0.01203 Gm. cocaine,
6 Cc. " " " = 6 × 0.01203 = 0.07218 Gm.

The residue contains, therefore, 0.07218 Gm. of pure cocaine.

Application of Volumetric Methods to the Estimation of Alkaloids.

The application of the principles of alkalimetry to the quantitative estimation of alkaloids is based on their neutralizing power toward acids.

Gravimetric methods, which consist in weighing the alkaloidal residue obtained by extraction with volatile immiscible solvents, are open to error owing to the difficulty of removing all traces of non-alkaloidal matter extracted along with the alkaloid. This error, however small, is very considerable when the quantity of residue is small; hence, as a check to these results, we resort to volumetric estimation. However, it must be borne in mind that not only the greatest care, but all necessary precautions, must be closely observed if any degree of accuracy is to be attained. In inexperienced hands these methods are fruitful sources of error. In the first place, care must be exercised to insure the greatest possible degree of accuracy in the preparation of the standard solutions; secondly, the eye must be trained, through some practice, to distinguish the terminal color-point reaction of the various indicators when employed not only in conjunction with highly diluted standard solutions, but also slightly colored alkaloidal solutions; finally, *the titer of the standard acid and alkali solutions must be fixed under conditions similar to those carried out in the actual titration employing the same indicator.*

The standard solutions[*] employed in this class of work are $\frac{N}{10}$, $\frac{N}{20}$, $\frac{N}{25}$, $\frac{N}{50}$, and $\frac{N}{100}$; stronger solutions than $\frac{N}{10}$ are not admissible because of the minute quantity of the alkaloid operated upon; also errors resulting from slight differences in the reading of the burettes, as well as those arising from overstepping the neutral-point,[†] are magnified by the high equivalence of the alkaloid. Only distilled water, free from all traces of acid or alkali, should be employed in alkaloidal titrations.[‡]

Indicators.

The usual indicators of acidimetry and alkalimetry are, with few exceptions, insufficiently sensitive toward the alkaloids. Experiments have shown that different alkaloidal indicators vary considerably in their degree of sensitiveness toward the same alkaloid;[§] in view of this, Kippenberger[||] has constructed a table for the assistance of the operator in their proper selection. *No more*

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[*] Owing to the readiness with which the weak alkali standard solutions lose their titer, it is frequently necessary to employ an empirical alkali solution in a titration; this subject is specially considered on page 76.

[†] For where one drop of a $\frac{N}{1}$ V. S. may be employed to render an acid solution neutral, the same might have been accomplished with five drops of a $\frac{N}{10}$ V. S., which represent one-half of a drop of the former. We may operate still more accurately with $\frac{N}{25}$, $\frac{N}{50}$, and $\frac{N}{100}$ standard solutions.

[‡] The neutrality of this is established by placing 100 Cc. in a stoppered cylinder (which has been previously rinsed with hydrochloric acid, afterward removing all traces of the latter with distilled water); an etherial iodeosin solution is added and the mixture well shaken; if reddening occurs, only one drop of a $\frac{N}{100}$ acid V. S. should be required to decolorize, or if the ether layer remains colorless, then only one drop of a $\frac{N}{100}$ alkali V. S. should be necessary to cause the aqueous fluid to assume a rose tint. For the preservation of the water, a flask which has been washed as above directed should always be used, because new ones always give up traces of alkali to the water. Should any appreciable quantity of $\frac{N}{100}$ acid V. S. be required to render the water neutral, this should be noted and taken into account with the final results.

[§] Variations in the deportment of the various indicators to the different alkaloids are explained in the theories of electrolytic, hydrolytic, and general dissociation which take place in the highly diluted solutions. Electrolytic dissociation refers to the dissociation of the standard alkali or acid (for example, H_2SO_4 into SO_4 and H_2 ions); hydrolytic dissociation, which is very slight, is the resolution of the molecules of water into H and OH ions; general dissociation is the breaking up of the dissolved salt molecule, as alkaloid hydrochlorid, into base and acid, which occurs more or less according to the dilution of the solution. With solution of the amorphous alkaloid in the standard acid, according to the degree of dilution a greater or lesser general dissociation liberates a greater or lesser amount of alkaloid base; if the latter is a strong base, then a feeble acid indicator may be taken; if the alkaloid is a weak base, then the indicator must possess relatively strong affinities; these conditions are necessary in order to avoid dissociation of the indicator salt of the alkaloid before neutralization of the excess of acid has taken place. The indicator as an acid should not possess a greater affinity for the alkaloidal base than the acid employed in titrating.

[||] Kippenberger, Zeitschrift für analytische Chemie, 1900, p. 201.

indicator than just sufficient to produce a faint but distinct tint should be employed, while the volume of the fluid to be titrated should be kept as low as possible.

KIPPENBERGER'S ALKALOID INDICATOR TABLE.*

ACONITINE: *Azolitmin*, Iodeosin, Hæmatoxylin, Cochineal.
ATROPINE: *Lacmoid*, *Fluorescein*, Iodeosin, Hæmatoxylin.
BRUCINE: *Cochineal*, Iodeosin, Azolitmin, Hæmatoxylin.
COCAINE: *Lacmoid*, Fluorescein, Cochineal, Hæmatoxylin.
CONIINE: *Cochineal*, *Lacmoid*, Iodeosin, Hæmatoxylin, Congo-red, Fluorescein.
CODEINE: *Iodeosin*, *Lacmoid*, Cochineal, Hæmatoxylin, Fluorescein.
EMETINE: *Iodeosin*, *Cochineal*.
MORPHINE: *Hæmatoxylin* (Co.), *Cochineal*, *Lacmoid*, Iodeosin.
PELLETIERINE: *Cochineal*, Fluorescein, Iodeosin.
PAPAVERINE: *Lacmoid*.
NARCOTINE: *Lacmoid*.
QUININE: *Hæmatoxylin*, *Azolitmin*, Fluorescein.
STRYCHNINE: *Azolitmin*, Iodeosin, Hæmatoxylin, Cochineal.
SPARTEINE: *Hæmatoxylin*, Azolitmin, Alkanin.
VERATRINE: *Lacmoid*, Iodeosin, Hæmatoxylin, Cochineal.

Influence of the Presence of Volatile Solvents.†—Some operators recommend that the alkaloidal residue be dissolved in alcohol, then diluted with water till turbid, and titration begun. The introduction of alcohol is in most cases a fruitful source of error, for although it may be neutral, it influences the indicator color changes, rendering them indistinct and unreliable.

Exception may be made with the indicators fluorescein and gallein, for the presence of alcohol (or ether) adds very materially to their degree of sensitiveness; in fact, the presence of this solvent is absolutely necessary when titrating with centinormal solutions. Ether or chloroform diminishes the sensitiveness of phenolphthalein, luteol, rosolic acid, congo red, and tropæolin. The other indicators are not affected by these two solvents.

Whenever employed, the alcohol should be tested for the presence of acid, and, if present, it must be estimated and taken into account in the calculations.

Procedure.

The total alkaloid which has been extracted by means of ether or chloroform, or a mixture of these, from a drug or its preparation, as directed on pages 84 and 87, may be subjected to volumetric assay, either direct while in solution or in the dry condition. The

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* All indicators which give doubtful reactions have been omitted from the table. The more sensitive indicators are italicized.

† Two excellent articles upon this subject are by O. Linde, Archiv d. Pharmazie, 1900, p. 124; Prof. Caspari, Amer. Jour. Phar., 1896, p. 473.

greatest care must be exercised in thoroughly removing all traces of ammonia or alkali solution which is retained by the ether or chloroform used in extracting the alkaline aqueous alkaloidal solution. This is accomplished by carefully washing the ether or chloroformic alkaloid solution several times with distilled water. Before drawing off the etherial or chloroformic solution of the alkaloids just previous to evaporating for estimation, the delivery tube of the separator should be cleansed to remove all traces of adhering saline matter which might be carried along into the final residue. The method of residual titration is invariably employed in which, to the dry alkaloidal residue contained in a beaker or short wide-necked flask, an accurately measured excess of a $\frac{N}{25}$ acid V. S.* is added; then by rotating bring about a solution of the alkaloid in the acid, disregarding any traces of resinous or oily matter which remain undissolved. It is advisable to allow at least from ten to fifteen minutes to elapse, after apparent solution of the residue, before beginning titration. Then from one to three drops or a sufficient quantity of the indicator are added to impart a faint but distinctive tint, indicating the solution to be of a strong acid reaction. The excess of standard acid is then determined by titrating back with either a $\frac{N}{50}$ or $\frac{N}{100}$ alkali V. S.; the number of cubic centimeters of the alkali consumed are, after having been converted into their equivalent † in standard acid (by dividing by 2 or 4), subtracted from the original excess volume of $\frac{N}{25}$ acid V. S. added. This gives the number of cubic centimeters of the $\frac{N}{25}$ acid V. S. required to neutralize the alkaloid, which is then multiplied by the equivalent for the latter.‡

Example: 10 Cc. of $\frac{N}{25}$ acid V. S. were employed to dissolve a residue consisting of cocaine, and 12 Cc. of a $\frac{N}{50}$ alkali V. S. were required to neutralize the uncombined excess of acid. The 12 Cc. of $\frac{N}{50}$ alkali V. S. are equivalent in titer to 6 Cc. of a $\frac{N}{25}$ V. S.; hence 10 Cc. — 6 Cc. = 4 Cc., the volume $\frac{N}{25}$ acid V. S. required. Since 1 Cc. of $\frac{N}{25}$ acid V. S. is equivalent to 0.01203 Gm. of cocaine, 4 Cc. $= 4 \times 0.01203 = 0.04812$ Gm. Therefore there is 0.04812 Gm. of cocaine present in the residue.

Residual Titration with Iodeosin.—The alkaloidal residue is dissolved in an accurately measured excess of $\frac{N}{20}$ or $\frac{N}{25}$ acid V. S. and carefully transferred to a tall (100 Cc.) glass cylinder which can be securely closed with a glass or cork stopper, the vessel being thoroughly rinsed with several small portions of distilled water,

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* If desirable, a $\frac{N}{10}$ or $\frac{N}{20}$ V. S. may be employed.

† Cc. $\frac{N}{50}$ V. S. ÷ 2 = Cc. $\frac{N}{25}$ V. S.—that is, 25 Cc. of the former are equivalent in titer to 12.5 Cc. of the latter; or Cc. $\frac{N}{100}$ V. S. ÷ 4 = $\frac{N}{25}$ V. S.—that is, 25 Cc. of the $\frac{N}{100}$ V. S. are equivalent in titer to 6.25 Cc. of a $\frac{N}{25}$ V. S.

‡ For titrating with alkali solutions which have lost their titer, see page 76.

testing the last rinsings for any traces of acid. To the acid alkaloid solution in the cylinder are added about 10 Cc. of etherial iodeosin, which, after shaking, will assume a yellow color; to this is now added a $\frac{N}{50}$ or $\frac{N}{100}$ alkali V. S., shaking after the addition of each five drops, until the aqueous solution takes on a faint rose tint and the ether layer has become colorless (see page 28). The calculations are the same as given in the preceding. Some practice is necessary before beginning titrations with this indicator.

Equivalents of the More Important Alkaloids.

Each molecule of a standard acid will neutralize an amount of alkaloid equivalent in grammes to its molecular weight, provided it is a monacid base; should it be diacid (like emetine), then one acid equivalent will neutralize a quantity equal to one-half of its molecular weight. For example:

1000 Cc. of $\frac{N}{1}$ HCl V. S. (36.18 Gm. HCl) = Strychnine ($C_{21}H_{22}N_2O_2$) 331.52 Gm.
1 Cc. “ $\frac{N}{1}$ “ “ (0.03618 “ “) = “ 0.3315 “
1 Cc. “ $\frac{N}{10}$ “ “ (0.003618 “ “) = “ 0.03315 “
1 Cc. “ $\frac{N}{20}$ “ “ (0.001809 “ “) = “ 0.01658 “
1 Cc. “ $\frac{N}{25}$ “ “ (0.0014472 “ “) = “ 0.01326 “
1 Cc. “ $\frac{N}{100}$ “ “ (0.0003618 “ “) = “ 0.003315 “

The fixing of the equivalents of such alkaloids as quinine, brucine, atropine, etc., is a simple matter, as shown in the case of strychnine above, because the composition of these bases has been accurately established. On the other hand, differences of opinion exist as to the exact composition of some others, as, for example, seven different formulæ have been ascribed to emetine and four to aconitine by various authorities; where the differences in molecular weight are very considerable, some one formula should be selected and so indicated. Again, there are other instances where two alkaloids represent the activity of the plant, as in the case of nux vomica, which contains strychnine and brucine; these are present in about equal proportions, hence an average is taken of their combined molecular weights, which is 361.3 ([391.08 + 331.52] ÷ 2 = 361.3). The leaves and roots of the belladonna and the leaves and seed of the stramonium contain the alkaloids atropine and hyoscyamine, which are present in variable proportions; but being isomeric ($C_{17}H_{23}NO_3$), the alkaloid factor is the same. Hyoscyamus contains, in addition to hyoscyamine, a very small amount of hyoscine ($C_{17}H_{21}NO_4$) and atroscine (Hesse), which for general purposes may be calculated in under the head of hyoscyamine.

Volumetric methods have been applied by some authors to the estimation of the total alkaloidal residue from such drugs as cinchona, veratrum album and viride, and cevadilla seed (veratrine), in

Drug.	Alkaloid upon which Valuation is Based.	1 Cc. $\frac{N}{10}$ Acid V.S. Equivalence in Grammes.	1 Cc. $\frac{N}{20}$ Acid V.S. Equivalence in Grammes.	1 Cc. $\frac{N}{25}$ Acid V.S. Equivalence in Grammes.	1 Cc. $\frac{N}{50}$ Acid V.S. Equivalence in Grammes.	1 Cc. $\frac{N}{100}$ Acid V.S. Equivalence in Grammes.	Percentage of Alkaloid in Drug.
Belladonna, ...	Atropine, hyoscyamine. $C_{17}H_{23}NO_3 = 286.87$	0.028687	0.014344	0.011475	0.005738	0.0028687	Leaves: 0.35 — 0.45 Root: 0.35 — 0.5
Coca, ...	Cocaine. $C_{17}H_{21}NO_4 = 300.75$	0.030075	0.015038	0.01203	0.006015	0.0030075	0.5 — 0.75
Conium, ...	Coniine. $C_8H_{17}N = 126.13$	0.012613	0.006307	0.05045	0.0025226	0.0012613	0.5 — 0.6
Gelsemium, ...	Gelsemine. $C_{22}H_{26}N_2O_3 = 363.30$	0.03633	0.018165	0.014532	0.007266	0.003633	0.3 — 0.5
Hyoscyamus, ...	Hyoscyamine, scopolamine. $C_{17}H_{23}NO_3 = 286.87$	Same as under Belladonna.					0.1 — 0.5
Ipecac, ...	Emetin (isolated). $C_{30}H_{40}N_2O_5 = 504.26$	0.025213	0.012607	0.010086	0.005043	0.0025215	1.5 — 3.0
Jaborandi, ...	Pilocarpine. $C_{11}H_{16}N_2O_2 = 206.52$	0.020652	0.010326	0.00826	0.00413	0.0020652	0.3 — 0.5
Opium, ...	Morphine. $C_{17}H_{19}NO_3 + H_2O = 300.75$	0.030075	0.01504	0.01203	0.006015	0.003008	+ 9
Cinchona, ...	Quinine. $C_{20}H_{24}N_2O_2 = 321.62$	0.032162	0.016081	0.012865	0.0064324	0.0032162	+ 2.5
Nux Vomica, Ignatia, ...	Strychnine = 331.52 Brucine = 391.08 Average = 361.3	0.03613	0.018065	0.014452	0.007226	0.003613	2.0 — 3.25
Stramonium, ...	Atropin, hyoscyamine, scopolamine. $C_{17}H_{23}NO_3 = 286.87$	Same as under Belladonna.					Leaves: 0.3 — 0.35 Seed: 0.3 — 0.5
Physostigma, ...	Physostigmine (eserine). $C_{15}H_{21}N_3O_2 = 273.05$	0.027305	0.013653	0.010922	0.005461	0.0027305	0.15 — 0.2

which they select what is generally accepted as the most active alkaloid as factor. The accuracy of such results is questionable, owing to the presence in these residues of several alkaloids in variable proportions and of different composition, each of which contributes some part to the medicinal action of the drug.

Assay of Galenical Preparations.

Lloyd's Method: For this process 5 Cc. of a fluid extract, or 1 Gm. of a solid extract which has been dissolved in about 5 to 8 Cc. of an alcoholic menstruum, or a corresponding volume of the tincture is evaporated to this bulk. In a flat-bottomed porcelain mortar with a good lip, mix 5 Cc. of the fluid extract with about 2 Cc. of a solution of perchloride of iron. To this is added sodium bicarbonate with constant trituration until a stiff magma results.* Extract this magma by repeated trituration with chloroform, using first 20 Cc., and then three portions of 10 Cc. each, decanting them severally by means of a guiding rod, carefully avoiding drawing off any of the suspended particles of the magma. To ascertain if all of the alkaloid has been removed, the mass is extracted once more with about 5 Cc. of chloroform, and this, when evaporated on a watch-glass and the residue, if any, dissolved in dilute sulphuric acid, should not precipitate upon the addition of a few drops of either Lugol's or Mayer's solution.†

The mixed chloroformic extracts are collected and estimated volumetrically according to any one of the three following methods. If the chloroformic extract is not colored, method *a* is applicable; otherwise either method *b* or *c* should be followed:

(*a*) The chloroformic solution is evaporated to dryness in a flask or beaker glass placed on a water-bath. To this residue, unless highly colored,‡ is added an accurately measured excess of from 5 to 20 Cc. of $\frac{N}{25}$ acid V. S., to which has been added, if necessary, a little water. This acid solution is rotated about and then allowed to stand a few minutes in order to permit a complete solution of the alkaloid, while the wax and resinous matter remain undissolved. The indicator is added to the solution, which should show a distinct

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* The ferric hydroxide produced serves to attract most of the tannates, gums, albumins, vegetable acids, and colors, while the excess of bicarbonate liberates the alkaloids, which are dissolved by the chloroform. Should the magma have a tendency to become friable when the chloroform is added, or if it takes up the chloroform and does not separate it again (which will happen when the fluid extract is strongly alcoholic), the addition of 2 to 5 Cc. of water containing a very little glucose or honey will cause a sharp separation.

† *Mayer's Solution:*

Mercuric Chloride, . . .	6.775 Gm.
Potassium Iodide,	25.00 "
Distilled Water to make	1000 Cc.

Lugol's Solution (Wagner's Reagent):

Iodine, ...	12.66 Gm.
Potassium Iodide, ...	32.00 "
Distilled Water to make	1000 Cc.

‡ For colored residues, especially those containing chlorophyl, I especially recommend method *b* with fluorescein as indicator.

acid reaction; if not, a further measured volume of the standard acid should be added. The excess of standard acid is now estimated by slowly adding $\frac{N}{50}$ alkali V. S. until the solution shows a neutral reaction; the number of cubic centimeters of the $\frac{N}{50}$ alkali V. S. used, divided by 2 and subtracted from the volume of $\frac{N}{25}$ acid V. S. originally added, will indicate the number of cubic centimeters of the latter required for the alkaloid, which, multiplied by the equivalent for the latter, will give the total alkaloid present in the drug or extract. In the above case, 5 Cc. of fluid extract represent 5 Gm. of the drug; hence multiplying the weight of the alkaloidal residue by 20 converts it direct into percentage.

Example: The chloroformic residue obtained from 5 Cc. of a fluid extract of belladonna root was dissolved in 10 Cc. of $\frac{N}{25}$ acid V. S.; to neutralize the excess of acid, 16.4 Cc. of $\frac{N}{50}$ alkali V. S. were required. The 16.4 Cc. of $\frac{N}{50}$ V. S. are equivalent to 8.2 Cc. of a $\frac{N}{25}$ V. S.; then,

10 Cc. $\frac{N}{25}$ acid V. S. originally added excess
8.2 Cc. equivalent of $\frac{N}{50}$ alkali V. S. in $\frac{N}{25}$ units
1.8 Cc. $\frac{N}{25}$ acid V. S. required for the alkaloid.

If 1 Cc. of $\frac{N}{25}$ acid V. S. is equivalent to 0.011475 Gm. alkaloids,
1.8 Cc. " " " " are " " $1.8 \times 0.011475 = 0.020655$ Gm. $\times 20 =$ 0.4131 per cent.

(*b*) If the indicator fluorescein is employed, the residue, even if highly colored,* is dissolved in about 10 Cc. of alcohol (free from acid); then water is added to slight turbidity, followed by a measured excess of $\frac{N}{25}$ acid V. S., when the titration is completed with $\frac{1}{50}$ alkali V. S. In order to assist the eye in noting the approach of neutrality, it is advisable to remove from time to time a portion of the fluid to a test-tube, and, after adding a drop or so of the alkali solution, to note the first appearance of fluorescence, which is best observed by holding the tube over a dark surface, viewing by reflected light. This is returned to the main solution, and, after mixing and adding more of the alkali, the experiment repeated if necessary.

(*c*) All alkaloidal indicators except fluorescein require an almost colorless solution of the alkaloid, hence it is necessary to remove as much of the color substances as possible from the chloroformic solution. For this purpose the chloroform extracts of the magma, which have been collected in a separatory flask (Fig. 20), are extracted by shaking with three successive portions (10 Cc. each) of diluted sulphuric acid (1 part in 50), after which a few drops of the chloroformic solution, when removed to a watch-glass and evaporated, then dissolved in diluted sulphuric acid, should not show the presence of any

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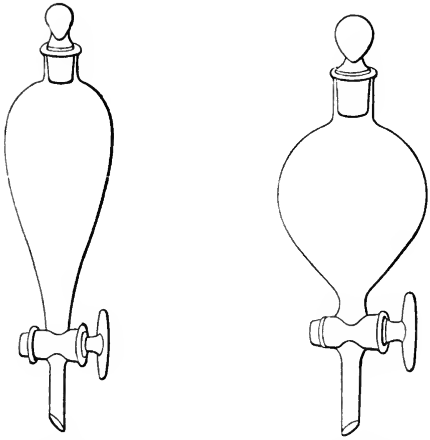
* As in fluid extracts of hyoscyamus, belladonna leaf, coca, etc.

further traces of alkaloid upon the addition of Mayer's reagent; otherwise the extraction must be continued. (The treatment with acidulated water serves to abstract the alkaloid, leaving the fat, resins, colors, etc., in the chloroform.) The acid alkaloidal solutions are collected in a second separator and 20 Cc. of ether are added, followed by sufficient aqua ammonia to render the fluid alkaline; the alkaloids are then extracted by rotating (avoid shaking), and, after removing the ether, the operation is repeated with three successive portions of 10 Cc. each of ether.* The mixed etherial solutions should be



Squibb's. Spherical.

FIG. 20.—SEPARATING FLASKS OR SEPARATORS.

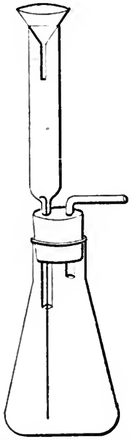


FIG. 21.—FILTERING APPARATUS FOR EMULSIONS.

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* In order to avoid the inconvenience and possible loss attending the removal of the alkaline alkaloidal solution from the ether (which floats) after each separate extraction, some operators prefer to mix ether and chloroform in the proportions of 2 volumes of the former with 3 volumes of the latter, which mixture, owing to its greater density, will sink to the bottom of the separator and can be drawn off after each extraction.

The extraction of alkaloids from alkaline fluids by mixtures of ether and chloroform, more especially the latter, frequently results in the formation of emulsions, particularly so if the mixture has been violently shaken. This may be avoided to a large extent by giving the separator a rotary motion; however, the extraction proceeds slowly, and must be repeated oftener than if shaking were resorted to, for the complete extraction of the alkaloids.

Various devices have been suggested for breaking up these annoying emulsions, such as cooling the fluid by placing the separator in ice or by heating. Moerk recommends the use of stearic acid (Am. Jour. Phar., 1899, p. 112). Perhaps the only effectual method is that of Chas. Platt, which consists in filtering the emulsion through a layer of absorbent cotton which is packed to the height of 4 Cm. in a tube (Fig. 21) 12.5 Cm. long and 14 Mm. in diameter. In the narrowed neck of this tube is placed a platinum wire which has been bent at right angles at its tip to prevent the absorbent cotton from being drawn through; the apparatus is connected with a filter-pump and the emulsion poured through, taking care to avoid loss by washing the cotton with several small portions of ether or chloroform. The filtered separated fluids are then transferred to the separator, when either the volatile or aqueous layer may be drawn off, as the case requires.

thoroughly washed with distilled water in order to remove any traces of dissolved ammoniacal solution.

To be certain of the complete removal of the alkaloid from the alkaline aqueous solution, a few drops are removed, and, after acidifying, no precipitation should occur upon the addition of Mayer's reagent.

According to Lloyd, this method is applicable to the assay of the following drugs:

FLUID EXTRACT.	PER CENT. ALKALOID.
Ipecac,	1.5
Belladonna Root,	0.5
Nux Vomica,	1.5
Hyoscyamus,	0.2
Belladonna Leaves,	0.4
Coca,	0.5

Volumetric Alkaloidal Assay of Crude Drugs.

Only a few selected methods of general application are presented, while for details of special processes reference may be had to Lyons' "Assay of Drugs."

Keller's Method (Kebler's modification).

Place 10 Gm. of the powdered drug in a 250 Cc. flask, add 25 Gm. of chloroform and 75 Gm. of ether, cork the flask securely, agitate well for several minutes, add 10 Gm. of 10 per cent. ammonia water, and agitate frequently during one hour. (It is advisable to extend this time to four hours or more.) On adding five grammes more of water of ammonia, the suspended powder agglutinates into a lump; the liquid becomes clear after standing a few minutes and can be poured off almost completely. Fifty grammes of the clear fluid (representing 5 Gm. of the drug) are taken for assay and treated by either one of the following processes:

(*a*) Place the etherial fluid in a beaker, evaporate on a water-bath, add 10 Cc. of ether, and evaporate once more. Dissolve the residue in 15 Cc. of alcohol and proceed according to method *b*, page 85.

(*b*) The etherial fluid is transferred to a separator which contains 20 Cc. of dilute sulphuric acid (5 per cent.); after thorough agitation and complete separation, the aqueous solution is transferred to a second separator. The above operation is repeated twice more with 15 Cc. each of slightly acidulated water. To the mixed acid alkaloidal solutions aqua ammonia is added in slight excess and the liberated alkaloid extracted by rotating with three successive portions (20, 15, and 15 Cc.) of a mixture of chloroform three volumes and acid-free ether one volume. The mixed ether-chloroform extracts are shaken with about an equal volume of water in order to remove any traces of dissolved alkali, after which the volatile fluid is carefully drawn off and evaporated to dryness in a beaker or flask. The alkaloidal residue is then titrated as directed in *a*, page 84.

The operator should not fail to test each solution after extraction, in order to assure himself of the complete removal of the alkaloid.

Lyons' Process No. 1.

Put into a 4-ounce prescription vial 10 Gm. of the drug in moderately fine powder. Pour in exactly 100 Cc. of Prollius' fluid,* generally the weaker; cork securely and shake vigorously several times at intervals of a minute or two. Place in the mechanical shaker four hours, or else shake at frequent intervals during that time. Draw off by means of a pipette exactly 50 cubic centimeters of the clear fluid, representing 5 Gm. of the drug, which is transferred to a small flask and evaporated to dryness, after which the residue is taken up with acid-free ether, which is drained off, and again evaporated. Once more 10 Cc. of pure ether, together with 5 Cc. of $\frac{N}{25}$ acid, are added, the ether is evaporated off, and, after adding an indicator, the excess of acid is titrated back with $\frac{N}{25}$ alkali. The volume of alkali consumed, deducted from 5 Cc., represents the number of cubic centimeters of $\frac{N}{25}$ acid required for the alkaloid; which, multiplied by the proper alkaloidal factor and the product by 20, will give the percentage of total alkaloid in the drug.

Lyons' Process No. 2.

Put into a 4-ounce prescription vial 12 Gm.† of the drug in fine powder. Pour in exactly 100 Cc. of a mixture of ether 8 volumes and chloroform 1 volume, cork securely, and shake well. After ten minutes, shake once more, add 5 Cc. of water of ammonia (10 per cent.), cork, and immediately shake vigorously, repeating this several times at intervals of a minute or two. Allow to macerate, shaking at frequent intervals, for at least four hours. Exactly 50 cubic centimeters (representing one-half of the weight of the drug) are drawn off and treated as directed under Process 1.

Although these methods are of general application, yet, owing to differences in the solvent action of the different fluids employed, one method may be somewhat better adapted to the extraction of a drug than another; in view of this, suggestions are made in the fol-

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**Prollius' Fluid:*

Concentrated ether,	325 Cc.
Alcohol,	25 "
Aqua Ammonia (28 per cent.),	10 "

The "weaker" Prollius' mixture contains only one-half as much ammonia.

Prollius' Fluid Modified (Employed for extraction of alkaloids sparingly soluble in ether from such drugs as cinchona and nux vomica):

Concentrated Ether,	250 Cc.
Chloroform,	80 "
Alcohol,	25 "
Stronger Water of Ammonia (28 per cent.),	10 "

† This quantity is suitable in the case of drugs containing less than 0.8 per cent. of alkaloid. If there is as much as 1 per cent., 10 Gm. of the drug are sufficient; if 5 per cent., not more than 4 Gm. should be used.

lowing. Where a greater degree of accuracy is desirable, two different methods should be applied and the average selected.

Belladonna Leaves and Root,	Keller.	Lyons No. 2.
Cinchona Bark,	Modified Prollius' Fluid.	See U. S. P.
Coca Leaves,	Keller.	Lyons No. 1 (weaker Prollius).
Gelsemium,	Keller.	Lyons No. 2.
Hyoscyamus,	Keller.	Lyons No. 2.
Ipecac,	Keller.	Lyons No. 2.
Jaborandi,	Keller.	Lyons No. 1 or No. 2. (Stem.)
Nux Vomica,	Keller.	Lyons No. 2, with modified Prollius.
" Ignatia,		
Opium,	See U. S. P.	
Stramonium,	Keller.	Lyons No. 2.

Conium Assay.

This assay process requires a slight modification, owing to the presence of the volatile alkaloid coniine. As given by Lyons put into a 4-ounce vial 12 Gm. of the powdered drug. Add 100 Cc. of the weaker Prollius' fluid (page 88); shake well at frequent intervals for four hours. Let settle and draw off exactly 50 Cc.; add normal sulphuric acid drop by drop, just sufficient to render distinctly acid (use sensitive litmus paper). Dissipate ether by a gentle heat, add alcohol 15 Cc., and set aside in a cool place a few hours for the separation of the ammonia as sulphate. Filter, wash residue with a little alcohol, concentrate filtrate and washings (make sure that free acid is nearly neutralized previously) by a very gentle heat; to 3 Cc. add water 3 Cc. and a few drops of dilute sulphuric acid. Wash twice with ether, 10 Cc. each, to remove fatty matters; reject the ether. To the acid alkaloidal solution contained in a separator add sodium carbonate solution in excess and extract with three successive portions of ether (15, 10, and 10 Cc.). The etherial extracts are collected in another separator and washed with clean water, after which titration is carried out with a $\frac{N}{20}$ or $\frac{N}{50}$ acid, using iodeosin as indicator.

Physostigma (Lyons' Process).

Into a 4-ounce vial put 15 Gm. of powdered calabar bean (No. 60) with 105 Cc. of ether; shake, and let stand one hour. Add 7.5 Cc. of a saturated solution of common salt and 1 Cc. of dilute hydrochloric acid, 5 per cent., shake well, and macerate one hour, occasionally shaking. Then add solution of ammonia (10 per cent.) 5 Cc.; shake well and macerate four hours with frequent shaking. Seventy Cc. of the clear fluid (representing 10 Gm. of the drug) are drawn off and the alkaloid extracted as directed under *c* of Lloyd's method (page 85), using *larger* volumes of ether as solvent. The ether takes up only the physostigmine.

Gordin's Alkalimetric Method for Alkaloid Estimation with Phenolphthalein as Indicator.*

This method consists in dissolving the alkaloidal residue in an accurately measured *excess* of $\frac{N}{20}$ HCl V. S. Wagner's or Mayer's reagent is then added in small quantities at a time, shaking carefully after each addition, until no further precipitation results. The mixture is diluted with water until it measures exactly 100 Cc.; then it is shaken until the double salt of the alkaloid and reagent completely separate; when allowed to stand a few minutes, the supernatant liquid should be clear, and if Wagner's reagent has been employed, this will be of a dark red color. The liquid is now filtered and to 50 Cc. of the filtrate (representing just one-half of the alkaloid) a 10 per cent. solution of sodium thiosulphate is added drop by drop until the color produced by the free iodine disappears.

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* H. M. Gordin, Phar. Archives, Vol. 2, No. 10.

This decolorization procedure is not necessary if Mayer's solution has been used. A few drops of phenolphthalein solution are now added and the excess of acid estimated by titrating back with $\frac{N}{20}$ KOH V. S.; this, deducted from one-half of the volume of acid employed, indicates the number of cubic centimeters of $\frac{N}{20}$ HCl V. S. which have combined with the alkaloid contained in the 50 Cc. of the solution. The number of cubic centimeters of the latter, when multiplied by the given factor, and this product by 2, gives the total quantity of alkaloid.

Example: An alkaloidal residue consisting of strychnine was dissolved in 30 Cc. of $\frac{N}{20}$ HCl V. S.; to this was added about 50 Cc. of water, followed by Wagner's reagent,* added as above directed. The mixture was then diluted with water until it measured exactly 100 Cc., after which 50 Cc. (representing one-half of the alkaloid) were filtered off and decolorized with sodium thiosulphate; 10 Cc. of $\frac{N}{20}$ KOH V. S. were required to neutralize the excess of uncombined acid, which corresponds to 20 Cc. of $\frac{N}{20}$ KOH V. S. for the entire solution.

Then

30 Cc. = total $\frac{N}{20}$ HCl V. S. added.
20 Cc. = $\frac{N}{20}$ KOH V. S. to neutralize excess of $\frac{N}{20}$ HCl V. S.
10 Cc. = $\frac{N}{20}$ HCl V. S. required to neutralize the alkaloid.

Therefore if 1 Cc. of $\frac{N}{20}$ HCl V. S. = 0.0160 Gm. of strychnine, 10 Cc. = 10 × 0.0160 = 0.160 Gm.; hence there are 0.160 Gm. of alkaloid in the residue.

The following factors given by Gordin are somewhat lower than the theoretical equivalents, and were obtained by comparing the molecular weights of other alkaloids with that of morphine, which factor was ascertained by experiment with a sample of the anhydrous alkaloid.

1 Cc. of $\frac{N}{20}$ HCl V. S. is equivalent to 0.0137 Gm. Morphine.
" " " " " " " " 0.0184 " Hydrastine.
" " " " " " " " 0.0160 " Strychnine.
" " " " " " " " 0.0102 " Caffeine Cryst.
" " " " " " " " 0.0146 " Cocaine.
" " " " " " " " 0.0139 " Atropine.

Iodometric Estimation of Alkaloids as Higher Periodides.†

The chief advantages claimed for this iodometric method are sharp end-reactions and accurate results. The operation being carried on in acid solution, the presence of alkalies or ammonia would necessarily not interfere, as in the alkalimetric methods.

The general mode of procedure in the estimation of the strength of an aqueous solution of an alkaloidal salt is as follows: To about 10 Cc. of decinormal iodine solution diluted with a little water 1 Cc. of the acidulated alkaloidal solution is added, and the mixture

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* Iodine, 12.66 Gm.; potassium iodide, 32 Gm.; water to make 1000 Cc. (Lugol's solution).

† Proceed. Amer. Phar. Ass'n, 1898, p. 370.

well shaken for a few minutes. Should the precipitate separate out very quickly and the clear supernatant liquid have only a light yellow or greenish color or be altogether colorless, the alkaloidal valuation is too strong and must be diluted, till after a few trials the clear supernatant liquid retains a very dark red color after the separation of the precipitate. The acidulated alkaloidal solution is then made up to a given volume, and 10 or 15 Cc. of it are run from a burette into a graduated vessel, into which has been previously put 25 or 30 Cc. decinormal iodine solution diluted with a little water. The mixture is then made up to a given volume and shaken till the supernatant liquid is perfectly transparent, and is of a very dark red iodine color. This point is very important, and should the clear liquid not have this dark red color, the experiment with most alkaloids (except morphine and possibly some others) should be repeated, putting more decinormal iodine into the graduated vessel, or decreasing the number of Cc. of the alkaloidal solution. It would not do to add more decinormal iodine to the same mixture, as the iodine must be in large excess during the whole operation, in order to prevent the formation of lower periodides, which, once formed, might not take up fresh iodine, and form higher periodides. Only with morphine, which in such solutions forms but one periodide, these precautions are unnecessary. When the liquid has become perfectly clear, an aliquot portion of it is filtered off, and the excess of iodine determined by standard sodium thiosulphate. From these data is obtained the quantity of iodine consumed. This quantity of iodine, multiplied by the "ratio of alkaloid to one of iodine," gives the quantity of alkaloid sought. If preferred, but generally with less convenience to the chemist, the number of Cc. of decinormal solution of iodine consumed may be multiplied by the "alkaloidal factor of 1 Cc. $\frac{N}{10}$ Iodine V. S."

IODINE FACTORS OF THE ALKALOIDS SO FAR DETERMINED.

	Higher Periodide Formed.	Ratio of Alkaloid to 1 of Iodine.	Alkaloid Factor of 1 Cc. $\frac{N}{10}$ I Sol.
Aconitine,	$C_{33}H_{45}NO_{12}.HI.I_6$,	. . .	
Atropine,	$C_{17}H_{23}NO_3.HI.I_8$,	0.2849	0.0036048
Brucine,	$C_{23}H_{26}N_2O_4.HI.I_6$,	0.5179	0.00655299
Caffeine,	$C_8H_{10}N_4O_2.HI.I_4$,	0.3834	0.00485
Morphine,	$C_{17}H_{19}NO_3.HI.I_3$,	0.74918	0.00947937
Strychnine,	$C_{21}H_{22}N_2O_2.HI.I_6$,	0.4390	0.00555467

CHAPTER III.

ANALYSIS BY OXIDATION AND REDUCTION.

These methods, which are based on the oxidizing and reducing power of various reagents, admit of great accuracy and simplicity in application, hence are preferred to the slower gravimetric operations.

The oxidizing agents employed are the standard solutions of potassium permanganate, potassium dichromate, and iodine ; these, when brought into contact with solutions of substances which readily take up oxygen, cause the oxidation of the latter, while the former are deoxidized.

The end-reaction in these operations is readily ascertained ; as, for example, when a standard potassium permanganate solution is dropped into an acid solution of a ferr*ous* salt, an immediate decolorization of the reagent takes place, but the instant the last trace of the ferrous salt has been oxidized to the ferr*ic* condition, the rose color which the permanganate produces ceases to disappear and the solution takes on a permanent rose tint. If standard dichromate is employed as the oxidizing agent, the completion of oxidation is ascertained by testing the oxidized mixture for the presence of *ous* compounds. The end-reaction with standard iodine solution is readily ascertained by means of the blue color produced by the action of the excess of iodine on starch paste.

Since the employment of the above standard solutions depends solely upon their oxidizing action, it is necessary in estimating *ic* compounds to first effect a complete reduction to the *ous* condition. This is usually accomplished by such reducing agents as sulphurous acid, zinc or magnesium in acid solution, stannous chloride, sodium thiosulphate, arsenous oxide, etc. Except in special cases, zinc or magnesium is generally preferred ; if the former is used, it should be free from iron, or the quantity of this present in a definite weight of the metal is estimated in a separate experiment and deducted from the final result. Magnesium ribbon is always preferable to zinc, but has the disadvantage of comparatively high cost.

VOLUMETRIC ESTIMATIONS WITH POTASSIUM PERMANGANATE.

When a standard solution of potassium permanganate is added to a solution of any readily oxidizable substance acidified with sulphuric acid, this reagent undergoes de-oxidation in accordance with the general equation :

$$K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + O_5.$$

If brought into contact with a solution of ferrous sulphate, the ferr*ous* salt is oxidized to a ferr*ic*; thus:

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Sulphuric acid is employed in all reactions with permanganate, in order to dissolve the precipitate of brown manganic hydroxide, forming thereby a colorless manganic sulphate. The presence of this brown precipitate would render it next to impossible to recognize the pink color of the end-reaction.

The titrations with permanganate are carried on at ordinary temperature, excepting in the case of oxalic acid, where the solution is warmed between 60° and 80° C.

The presence of hydrochloric acid or chlorides should be avoided in warm solutions owing to the liberation of chlorine. Thus:

$$K_2Mn_2O_8 + 16HCl = 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2.$$

This difficulty may be avoided through a conversion of the chloride into a sulphate by adding a slight excess of sulphuric acid and heating the solution until no more hydrochloric acid vapors are given off. This also applies to all nitrates. It is to be understood that all substances of an oxidizing or reducing action are excluded from the solutions being examined. Among substances of this class are hydriodic acid, sulphuretted hydrogen, nitrous acid, hypophosphorus, phosphorus, thiosulphuric and sulphurous acids and their salts, also *ous* salts and peroxides of all metals.

Decinormal Potassium Permanganate Volumetric Solution.

$K_2Mn_2O_8 = 313.88$

1000 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. contain 3.1388 Gm. $KMnO_4$.

Potassium permanganate ($KMnO_4$) enters into its various reactions (in the presence of an acid) as a double molecule ($2KMnO_4$ or $K_2Mn_2O_8$), *five* atoms of oxygen being liberated:

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + O_5.$$

Since the standard solutions of the volumetric system are based on a valency corresponding to one atom of hydrogen or its equivalent, then a normal solution of permanganate would be one in which a quantity of the salt is taken equivalent to one-half of an atom of oxygen (O^{II}).

If 5 atoms of oxygen are yielded by 2 molecules of $KMnO_4$ (313.88 p.), then ½ of an atom of oxygen would correspond to $\frac{1}{10}$ of 313.88 p., or 31.388 p. of $KMnO_4$.

If 31.388 Gm. of potassium permanganate are necessary for 1000 Cc. of a normal V. S., then 3.1388 Gm. should be contained in one liter of a *deci*normal V. S.

The solution cannot be prepared directly by weighing 3.1388 Gm. of the salt, because it is rarely absolutely pure; also the water employed contains oxidizable substances which consume some of the permanganate. The adjustment must, therefore, be made indirectly by means of oxalic acid, iron or iodometrically.

3.5 Gm. of pure, crystallized potassium permanganate are placed in a flask, 1000 Cc. of boiling distilled water added, and the solution boiled until complete solution has taken place. The flask is then closed with a tight-fitting plug of absorbent cotton and set aside for several days in order to allow the complete subsidence of suspended matter consisting of reduced oxides of manganese. When wanted for immediate use, the solution may be boiled in a flask for about half an hour and then filtered through a compact plug of glass-wool, when it is standardized either by method A, B, or C.

Owing to the readiness with which these solutions deteriorate on standing, many operators prefer to fix the titer of the solution and employ it at once in this condition without diluting it to that of a decinormal solution. Examples of such are given on pages 98, 100, 101, 102, and 107.

Solutions of permanganate should be kept in glass-stoppered bottles, away from the light, and burettes with rubber fittings should be avoided.

A. Standardization with Oxalic Acid ($H_2C_2O_4 + 2H_2O$).

For this purpose an *accurately standardized* decinormal solution of oxalic acid is selected. Into a flask introduce 10 Cc. of the $\frac{N}{10}$ $H_2C_2O_4$ V. S., and after diluting with about 100 Cc. of distilled water, add 1 Cc. of pure concentrated sulphuric acid, and while still warm (*retaining the temperature between 60° and 80° C.*) add gradually from a burette the permanganate solution, shaking after each addition. When a drop of the latter added is no longer decolorized, but imparts a faint pink tint to the solution, the titration is at an end, and the number of cubic centimeters consumed should be noted. The permanganate solution is then diluted so that 10 Cc. of it will correspond exactly to 10 Cc. of the oxalic acid. The reaction proceeds as follows:

$$\underset{313.88}{K_2Mn_2O_8} + \underset{625.4}{5(H_2C_2O_4 + 2H_2O)} + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

If 625 4 parts of oxalic acid are equivalent to 313.88 parts of permanganate,

6.254 Gm. oxalic acid (1000 Cc. $\frac{N}{10}$ V. S.) = 3.1388 Gm. permanganate (1000 Cc. $\frac{N}{10}$ V. S.).

1 Cc. $\frac{N}{10}$ oxalic acid V. S. (0.006254 Gm.) = 1 Cc. $\frac{N}{10}$ permanganate (0.0031388 Gm.).

Example: Assuming that 8.5 Cc. of the trial solution of permanganate were consumed for 10 Cc. of the $\frac{N}{10}$ oxalic acid V. S., then each 8.5 Cc. of the former must be diluted with distilled water to 10 Cc., or 850 Cc. to 1000 Cc. This will bring the titer of both solutions exactly alike. After making the dilution another estimation should be carried out.

B. Iodometric Standardization.

This is by far the most accurate and rapid method of standardization. In 150 Cc. of water contained in a flask about 0.5 Gm. of potassium iodide is dissolved, and about 5 Cc. of pure sulphuric acid added, followed by an accurately measured volume of 10 Cc. of the permanganate solution to be standardized. This latter is added slowly, with constant shaking The permanganate liberates an equivalent amount of iodine, which is, in turn, estimated by a $\frac{N}{10}$ sodium thiosulphate V. S. Each 10 Cc. of the permanganate solution is then diluted to equal the volume of the decinormal thiosulphate consumed. The reactions are as follows:

$$(a)\ \underset{313.88}{K_2Mn_2O_8} + 8H_2SO_4 + 10KI = 6K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{1258.9}{5I_2}.$$

$$(b)\ \underset{2\times 125.89}{I_2} + \underset{\substack{\text{Sodium Thiosulphate.}\\ 2\times 246.46}}{2(Na_2S_2O_3 . 5H_2O)} = \underset{\substack{\text{Sodium}\\ \text{Iodide.}}}{2NaI} + \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6} + 10H_2O.$$

Since 313.88 parts of $KMnO_4$ liberate 1258.9 parts of iodine (equation *a*), 31.388 parts liberate one atom, or 125.89 parts, of iodine. 1000 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. (containing 3.1388 Gm.) will liberate 12.589 Gm. of iodine (contained in 1000 Cc. $\frac{N}{10}$ iodine V. S.), which are equivalent to 1000 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. (containing 24.646 Gm.). Hence 1 Cc. $\frac{N}{10}$ $KMnO_4$ (0.0031388 Gm.) = 0.012589 Gm. Iodine = 1 Cc. $\frac{N}{10}$ $Na_2S_4O_6$ V. S.

Example: To about 150 Cc. of water, approximately 0.5 Gm. of potassium iodide and 5 Cc. of pure sulphuric acid were added; then an accurately measured volume of 10 Cc. of the permanganate solution which was to be standardized, the latter being added very slowly under constant agitation. To the mixture, which was brown from liberated iodine, a $\frac{N}{10}$ sodium thiosulphate V. S. was slowly run in, stirring constantly, until the color became quite faint, when a few drops of starch paste were added, followed by further portions of the thiosulphate solution until the blue or greenish-blue color of the mixture was discharged, 14.5 Cc. having been required for this purpose. Then if each 1 Cc. of $\frac{N}{10}$ thiosulphate V. S. is equivalent to 0.0031388 Gm. of $KMnO_4$ or 1 Cc. of its $\frac{N}{10}$ V. S, 14.5 Cc. of the former would indicate the presence of 14.5 × 0.0031388 Gm. of permanganate, which is equivalent to 14.5 Cc. of a $\frac{N}{10}$ V. S. Therefore each 10 Cc. of the total permanganate solution is diluted sufficiently to measure 14.5 Cc., or 689.7 Cc. of the former are made up to 1000 Cc.

$$(10 : 14.5 :: x : 1000;\ x = 689.7.)$$

C. Standardization with Metallic Iron.

The permanganate solution is standardized to such a strength that 18.02 Cc. will completely oxidize one decigramme of pure metallic iron. For this purpose "piano" or "flower" wire, which consists of 99.6 per cent. of pure iron, is selected, and, after thorough cleansing, any definite quantity (between 0.1 and 0.2 Gm.) is accurately weighed off. A flask of from 200 to 250 Cc. capacity is selected and provided with a close-fitting rubber stopper, through which passes a short glass tube (*a*, Fig. 22), which is fitted into a rubber tube (*b*) closed at its other extremity by a glass plug (*d*);

in the side of the rubber tube an incision (*c*) is made, which will permit steam and gases to pass out, and prevent air being admitted.* Into the flask pour about 50 Cc. of diluted (1 to 5) pure sulphuric acid, followed by a small crystal (about 1 Gm.) of sodium carbonate, when the valved stopper is replaced while the liberated carbolic acid gas displaces the air contained in the flask. The weighed quantity of the iron wire is now quickly introduced, the flask securely stoppered, and *gently* heated (not boiled) until the iron has completely dissolved.† As soon as cold, the stopper is removed and its lower extremity as well as the neck of the flask are rinsed back into the fluid with recently boiled distilled water; then the trial permanganate solution is slowly added from a burette, shaking well after each addition, until the mixture acquires a faint rose color.‡

Carb

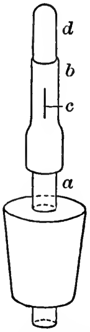

FIG. 22.—BUNSEN'S VALVE STOPPER.

Knowing that each 0.1 Gm. of iron consumes 18.02 Cc. of a true $\frac{N}{10}$ $KMnO_4$ V. S., then from the number of cubic centimeters of the trial solution used for a known weight of iron we may readily calculate the dilution necessary.

The first stage of the reaction is the solution of the metallic iron as ferrous sulphate:

$$\underset{555\ Fe}{5Fe_2} + 10H_2SO_4 = \underset{1508.5\ (555\ Fe)}{10FeSO_4} + 5H_2.$$

The second stage embraces the oxidation of the ferr*ous* to ferr*ic* sulphate by the permanganate solution:

$$\underset{313.88}{K_2Mn_2O_8} + \underset{555}{10FeSO_4} + 8H_2SO_4 = 5(Fe_2(SO_4)_3) + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

If 313.88 p. of $KMnO_4$ oxidize 555 p. of metallic iron, then 0.1 Gm. Fe will require 0.056555 Gm. of $KMnO_4$.

$$(555 : 313.88 :: 0.1 : x; \qquad x = 0.056555.)$$

If 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. contains 0.0031388 Gm. of the salt, then 0.056555 Gm. of permanganate would be contained in 18.02 Cc. of the $\frac{N}{10}$ V. S.

$$(0.0031388 \text{ Gm.} : 1 \text{ Cc.} :: 0.056555 \text{ Gm.} : x; \qquad x = 18.02 \text{ Cc.})$$

Example: 0.1265 Gm. of iron piano wire, representing 0.12599 Gm. of *pure* iron $\left(\frac{99.6 \times 0.1265}{100}\right)$, was dissolved in dilute sulphuric acid under the proper precautions and

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[*] This is to prevent any possible oxidation of the ferr*ous* iron to ferr*ic*, through contact with the air during solution.

[†] Minute quantities of carbon which float about in the fluid after solution of the iron has taken place should not be mistaken for undissolved iron.

[‡] If allowed to stand for some time, the pink solution will decolorize; this is due to the decomposition of the permanganate by the manganous salts present.

15.55 Cc. of the trial permanganate were consumed in its oxidation. Since 0.00555 Gm. Fe $= 1$ Cc. $\frac{N}{10}$ $KMnO_4$ V. S., then 0.12599 Gm. Fe would require 22.70 Cc. $(\frac{0.12599}{0.00555} = 22.70)$. Our trial solution, being too strong, requires a dilution of each 15.55 Cc. to 22.70 Cc., or 685.02+ Cc. are diluted with boiled and cooled distilled water to 1000 Cc.

One Cubic Centimeter of Decinormal Potassium Permanganate V. S. is the equivalent of:

	GRAMME.
Potassium Permanganate, $KMnO_4$,	0.0031388
Barium Dioxide, BaO_2,	0.008408
Calcium Hypophosphite, $Ca(PH_2O_2)_2$,	0.0021103
Ferric Hypophosphite, $Fe_2(PH_2O_2)_6$,	0.0020753
Iron, in ferrous compounds, Fe,	0.00555
Ferrous Carbonate, $FeCO_3$,	0.011504
Ferrous Chloride, $FeCl_2$,	0.012586
Ferrous Oxide, FeO,	0.007138
Ferrous Sulphate, anhydrous, $FeSO_4$,	0.015085
Ferrous Sulphate, crystals, $FeSO_4 + 7H_2O$,	0.027601
Ferrous Sulphate, dried, $2FeSO_4 + 3H_2O$,	0.017767
Hydrogen Dioxide, H_2O_2,	0.001688
Hypophosphorous Acid, HPH_2O_2,	0.00163775
Oxalic Acid, crystallized, $H_2C_2O_4 + 2H_2O$,	0.006254
Oxygen, O,	0.000794
Potassium Hypophosphite, KPH_2O_2,	0.00258325
Sodium Hypophosphite, $NaPH_2O_2 + H_2O$,	0.00263175
Sodium Nitrite, $NaNO_2$,	0.0034285

The permanganate methods are applicable to the analysis of oxidizable (reducing) as well as oxidizing substances. In the first-named group, which is classed under the *direct* methods, the permanganate is added to the solution of the substance in the presence of an excess of acid, until complete oxidation has taken place, which is known by the production of a permanent pink tint due to the presence of a slight excess of the added reagent. The second group, classed under the *indirect* methods, embraces oxidizing substances which are first treated with a known excess of a reducing agent, and then the unoxidized portion of the latter is estimated by means of permanganate solution.

I. DIRECT METHODS.

These embrace the direct estimation of ferrous compounds, oxalic acid, oxalates, nitrites, hypophosphorous acid and its salts, and hydrogen dioxide.

Estimation of Pure Iron in Metallic Iron.

From 0.1 to 0.2 Gm. of the sample are accurately weighed off and dissolved in dilute sulphuric acid, employing the same quantities and observing the same precautions as directed under C on page 95. The resulting solution contains the iron as ferr*ous* sulphate:

$$\underset{555}{5Fe_2} + 10H_2SO_4 = \underset{1508.5\ (555\ Fe)}{10FeSO_4} + 10H_2.$$

The $\frac{N}{10}$ $KMnO_4$ V. S. is now added until the solution, after constant agitation, retains a faint pink color. The number of cubic centimeters of the standard solution consumed, multiplied by 0.00555, gives the quantity of pure iron, expressed in grammes, contained in the sample. The oxidation proceeds as follows:

$$\underset{313.88}{K_2Mn_2O_8} + \underset{1508.5\ (555\ Fe)}{10FeSO_4} + 8H_2SO_4 = 5(Fe_2(SO_4)_3) + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

313.88 p. $KMnO_4$ oxidize 1508.5 p. of $FeSO_4$ containing 555 p. of Fe. One Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. (containing 0.0031388 Gm.) is therefore necessary for the oxidation of 0.00555 Gm. of metallic iron.

Example: A sample of iron filings weighing 0.225 Gm. required 40 Cc. of $\frac{N}{10}$ KMnO V. S. for oxidation. If 1 Cc. = 0.00555 Gm. of Fe, 40 Cc. = 40 × 0.00555, or 0.2220 Gm. of pure iron, corresponding to 98.66 per cent.

$$0.2220 : 0.225 :: x : 100; \qquad x = 98.66.$$

Titration with an Empirical Permanganate Solution.—

Example: 0.311 Gm. of finely powdered spathic iron was dissolved as directed on page 95, and, after cooling, was titrated with a solution of permanganate, 1 Cc. of which was equivalent to 0.0057 Gm. of iron; 26 Cc. were consumed in the operation.

If 1 Cc. of the permanganate is equivalent to 0.0057 Gm. Fe, 26 Cc. are equivalent to 26 × 0.0057, or 0.1482 Gm. Fe, which, in turn, is equivalent to 0.1906+ Gm. of FeO; for:

$$\overset{Fe}{55.5} : \overset{FeO}{71.38} :: 0.1482 : x; \qquad x = 0.1906+.$$

In the 0.311 Gm. of the sample, 0.1906 Gm., or 61.28+ per cent., consists of ferrous oxide:

$$\overset{FeO}{0.1906\text{ Gm.}} : 0.311\text{ Gm.} :: x : 100; \qquad x = 61.28.$$

Estimation of Metallic Iron in Ferrum Reductum.

This is best estimated according to the method of the U. S. Pharmacopœia, as follows: "Introduce 0.555 Gm. of reduced iron into a glass-stoppered bottle, add 50 Cc. of mercuric chloride solution (5 Gm. in 100 Cc.), and heat the bottle, well stoppered, during one hour on a water-bath, frequently agitating." The mercuric chloride reacts only with the metallic iron present, and not the oxides, which occur as impurities.

$$Fe + HgCl_2 = FeCl_2 + Hg.$$

"Allow to cool, dilute the contents with water to a volume of 100 Cc., and filter. To 10 Cc. of the filtrate (containing 0.0555 Gm. Fe), contained in a glass-stoppered bottle (of 100 Cc. capacity), add 10 Cc. of diluted sulphuric acid and subsequently $\frac{N}{10}$ $K_2Mn_2O_8$ V. S. until a permanent red color is produced. The number of cubic centimeters of the volumetric solution required, when multiplied by 10, will indicate the percentage of metallic iron."

$$\underset{313.88}{K_2Mn_2O_8} + \underset{555\ Fe}{10FeSO_4} + 8H_2SO_4 = 5[Fe_2(SO_4)_3] + 2MnSO_4 + K_2SO_4 + 8H_2O$$

If 313.88 parts of $KMnO_4$ are equivalent to 555 parts of metallic iron,

3.1388 Gm. $KMnO_4$ (contained in 1000 Cc. $\frac{N}{10}$ V. S.) = 5.55 Gm. Fe.

1 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. (containing 0.0031388 Gm.) = 0.00555 Gm. Fe.

If 10 Cc. of the iron solution, representing 0.0555 Gm., are taken for assay, then each 1 Cc. of the $\frac{N}{10}$ $KMnO_4$ V. S. (equivalent to 0.00555 Gm. Fe) consumed will correspond to $\frac{1}{10}$ part, and represents 10 per cent. of pure iron. Thus, for example, if 8.5 Cc. of the permanganate solution had been required, then the percentage of pure iron present would be 8.5 × 10, or 85 per cent.

Estimation of Ferrous Sulphate ($FeSO_4 + 7H_2O$).

The reaction proceeds as follows:

$$\underset{313.88}{K_2Mn_2O_8} + \underset{2760.1\ (555\ Fe)}{(10FeSO_4 + 7H_2O)} + 8H_2SO_4 = 5[Fe_2(SO_4)_3] + 2MnSO_4 + K_2SO_4 + 15H_2O.$$

313.88 parts of $KMnO_4$ = 555 parts of Fe = 2760.1 parts of $FeSO_4 + 7H_2O$. 1000 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. (containing 3.1388 Gm.) are equivalent to 5.55 Gm. of metallic iron, which represents 27.601 Gm. of crystallized ferrous sulphate, therefore each 1 Cc. of $\frac{N}{10}$ $KMnO_4$ is equivalent to 0.027601 Gm. of $FeSO_4 + 7H_2O$.

Example: 0.5 Gm. of a sample of commercial crystalline ferrous sulphate was dissolved in a mixture of about 20 Cc. of diluted sulphuric acid and 150 Cc. of water. For the production of a permanent rose tint 18 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. were required. Since 1 Cc. of the standard solution is equivalent to 0.027601 Gm. of pure crystallized sulphate, 18 Cc. would represent 18 × 0.027601, or 0.496818 Gm. The sample would therefore be 99.36 per cent. pure.

$$(5 : 0.496818 :: 100 : x; \qquad x = 99.36.)$$

If a molecular equivalent quantity of the salt is taken, —as, for example, 2.7601 Gm.,—then each 1 Cc. of the permanganate solution consumed will correspond to 1 per cent. of pure sulphate; or if 0.27601 Gm. are taken, then each 1 Cc. of the standard solution will represent 10 per cent. of the salt.

Estimation of Ferrous Carbonate ($FeCO_3$).

The reaction is as follows:

$$(a)\ \underset{1150.4\ (555\ Fe)}{10FeCO_3} + 10H_2SO_4 = \underset{1508.5\ (555\ Fe)}{10FeSO_4} + 10CO_2 + 10H_2O.$$

$$(b)\ \underset{313.88}{K_2MnO_8} + \underset{1508.5\ (555\ Fe)}{10FeSO_4} + 8H_2SO_4 = 5[Fe_2(SO_4)_3] + 2MnSO_4 + K_2SO_4 + 8H_2O$$

313.88 parts $KMnO_4$ = 1508.5 parts $FeSO_4$ (555 Fe) = 1150.4 parts $FeCO_3$. 3.1388 Gm. or 1000 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. are equivalent to 15.085 Gm. of ferrous sulphate (5.55 Gm. Fe), which represent 11.504 Gm. of ferrous carbonate; or 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. is equivalent to 0.011504 Gm. of $FeCO_3$.

Example: 2 Gm. of saccharated ferrous carbonate were dissolved in about 20 Cc. of diluted sulphuric acid (1 to 5), diluted with 100 Cc. of water; decinormal permanganate solution was then slowly added until the fluid assumed a permanent rose tint, 20 Cc. having been added for this purpose. Since 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. is equivalent to 0.011504 Gm. of $FeCO_3$, 20 Cc. will correspond to 20 × 0.011504 or 0.23008 Gm. of true ferrous carbonate, which represents 11.504 per cent. of the sample.

$$2 : 0.23008 :: 100 : x; \qquad x = 11.504.$$

Titration with an Empirical Permanganate Solution.—

One Cc. of the permanganate solution was found, on standardizing, to be equivalent to 0.0049 Gm. of metallic iron.

If, according to the equation *a*, 555 parts of metallic iron are equivalent to 1150.4 parts of ferrous carbonate, then 0.0049 Gm. of iron would correspond to 0.010156 Gm. of carbonate; for:

$$555 : 1150.4 :: 0.0049 : x; \qquad x = 0.010156.$$

Then each 1 Cc. of the empirical permanganate solution would be equivalent to 0.010156 Gm. of pure ferrous carbonate.

Estimation of Hydrogen Dioxide (H_2O_2).

Ten Cc. of the sample are accurately measured into a graduated cylinder and diluted with water until the volume measures exactly 100 Cc. Of this diluted solution, 10 Cc. (containing 1 Cc. of H_2O_2 solution) are transferred to a flask, 5 Cc. of diluted sulphuric acid (1 to 5) added, and then $\frac{N}{10}$ $KMnO_4$ V. S., shaking after each addition until the fluid retains a faint pink color. In a trial experiment 20 Cc. of the permanganate solution were consumed.

The reaction proceeds as follows:

$$\underset{313.88}{K_2Mn_2O_8} + \underset{168.8}{5H_2O_2} + 3H_2SO_4 = 5O_2 + 8H_2O + K_2SO_4 + 2MnSO$$

If 313.88 parts of $KMnO_4$ are equivalent to 168.8 parts of H_2O_2,

1000 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. (containing 3.1388 Gm.) = 1.688 Gm. H_2O_2.

1 Cc. " " " (" 0.0031388 Gm.) = 0.001688 Gm. H_2O_2.

Then 20 Cc. of the permanganate solution would be equivalent to 20 × 0.001688 or 0.03376 Gm. of absolute hydrogen dioxide contained in the 1 Cc. (1 Gm.) of the solution, which corresponds to 3.376 per cent.

Titration with an Empirical Permanganate Solution.—

One Cc. of a permanganate solution on comparison with iron (page 95) was found to be equivalent to 0.0057 Gm. of the latter. Since 2 molecules of $KMnO_4$ (312.88 p.), equivalent to 10 atoms (555 p.) of pure iron, represent 5 molecules (168.8 p.) of hydrogen dioxide, then:

$$55.5 \text{ p. of Fe} = 31.288 \text{ p. } KMnO_4 = 16.88 \text{ p. } H_2O_2.$$

Example: 2 Cc. (2 Gm.) of a solution of hydrogen dioxide were diluted with about 100 Cc. of water, made strongly acid with sulphuric acid, and a permanganate solution (1 Cc. = 0.0057 Gm. Fe) added until the mixture retained a permanent pink tint. Of the latter, 32.9 Cc. were required. The weight of absolute H_2O_2 contained in the 2 Gm. of solution taken would be $\frac{0.0057 \times 32.9 \times 16.88}{55.5} = 0.05703$ Gm., or 100 Cc. (100 Gm.) of this solution would contain:

$$\frac{0.0057 \times 32.9 \times 16.88 \times 100}{55.5 \times 2} = 2.85+ \text{ Gm.} = 2.85 \text{ per cent.}$$

Valuation of Barium Dioxide (BaO_2).

The commercial value of barium dioxide depends upon the percentage of real dioxide present, which, owing to the presence of available oxygen, is capable of producing an equivalent amount of hydrogen dioxide. The first step in this valuation consists in preparing from a weighed amount of the sample a solution of hydrogen dioxide; the second is to ascertain the quantity of the latter produced. For this purpose 4.204 Gm. of the sample of barium dioxide are thoroughly mixed with about 25 Cc. of ice-cold water in a graduated 100 Cc. cylinder; then 15 Cc. of phosphoric acid (85 per cent.) are added, followed by sufficient ice-water to make the volume measure exactly 100 Cc. Mix by inverting the cylinder several times. The reaction which takes place is as follows:

$$\underset{504.48}{3BaO_2} + 2H_3PO_4 = Ba_3(PO_4)_2 + \underset{101.28}{3H_2O_2}.$$

From the clear supernatant fluid 20 Cc. (representing 0.8408 Gm. of BaO_2) are drawn off by means of a pipette, and, after adding 10 Cc. of diluted sulphuric acid (1 to 5), $\frac{N}{10}$ $KMnO_4$ V. S. is slowly run in, with constant agitation, until the mixture retains a permanent pink tint. Each 1 Cc. of the permanganate added corresponds to one per cent. of true barium dioxide present in the sample.

$$504.48\text{ p. }BaO_2 = 101.28\text{ p. }H_2O_2 = 188.328\text{ p. }KMnO_4$$

$$\left(\overset{H_2O_2}{168.8\text{ Gm.}} : \overset{KMnO_4}{313.88\text{ Gm.}} :: 101.28\text{ Gm.} : x; \qquad x = 188.328\text{ Gm.}\right)$$

$$188.328\text{ Gm. or 60 liters of }\frac{N}{10}\ KMnO_4\text{ V. S.} = 101.28\text{ Gm. }H_2O_2 = 504.48\text{ Gm. }BaO_2.$$

$$3.1388\text{ Gm. (1 L. }\frac{N}{10}\ KMnO_4\text{ V. S.)} = 1.688\text{ Gm. }H_2O_2 = 8.408\text{ Gm. }BaO_2.$$

100 Cc. $\frac{N}{10}$ $KMnO_4$ containing 0.31388 Gm. = 0.8408 Gm. BaO_2.
1 Cc. " " " 0.0031388 Gm. = 0.008408 Gm. BaO_2.

If 0.8408 Gm. of BaO_2 are taken for analysis, then each 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. consumed, which corresponds to $\frac{1}{100}$ part (0.008408 Gm.), will represent one per cent. of pure barium dioxide.

Titration with an Empirical Permanganate Solution.—

A permanganate solution which had lost its titer was found, on comparison with a $\frac{N}{10}$ oxalic acid solution (A, page 94), that 12.5 Cc. of the former were required for 10 Cc. of the latter. An analysis of a sample of barium dioxide prepared as directed in the preceding required 80 Cc. of this empirical permanganate solution. The 80 Cc. of this weaker solution corresponded to 64 Cc. of a true $\frac{N}{10}$ $KMnO_4$ V. S.; according to this, the purity of the barium dioxide was 64 per cent.

$$\overset{\text{Empirical Sol.}}{12.5\text{ Cc.}} : \overset{\text{Real }KMnO_4.}{10\text{ Cc.}} :: 80\text{ Cc.} : x; \qquad x = 64\text{ Cc}$$

Oxalic Acid and Oxalates.

The estimation of oxalic acid is carried out with a permanganate solution which has been standardized by means of metallic iron. 0.6254 Gm. of the sample of crystals is weighed off, dissolved in about 100 Cc. water which has been strongly acidified with sulphuric acid, and, while being kept between the temperatures of 40°

and 50° C., the solution of permanganate is added, with constant agitation, until the fluid retains a faint rose tint; each 1 Cc. added indicates 1 per cent. of absolute crystalline oxalic acid present. (Compare with page 71.)

Titrating with an Empirical Permanganate Solution.

In titrating with a permanganate solution set with iron, we must take into consideration that 2 mol. of $KMnO_4$ oxidize, on the one hand, 5 mol. of oxalic acid (625.4 parts), and 10 atoms of Fe (555 parts) on the other. For the estimation of a weighed sample of oxalic acid 43 Cc. of a permanganate solution were consumed; the titer of this was found on experiment to be 1 Cc. = 0.0057 Gm. Fe. The quantity of iron represented by 43 × 0.0057 Gm., multiplied by $\frac{62.54}{55.5}$, or $\frac{43 \times 0.0057 \times 62.54}{55.5} = 0.27619+$ Gm. of crystalline oxalic acid.

Oxalates.—To a mixture of the weighed sample and a comparatively large volume of water, a sufficiently excessive volume of sulphuric acid must be added which not only serves to dissolve the manganese hydroxide as fast as formed, but also to liberate the oxalic acid from its alkali combination. The presence of precipitates—as barium, calcium, and lead sulphates—does not interfere with the distinguishing of the end-reaction; however, it should not be forgotten that the mixture should be kept at a temperature between 40° and 50° C. and be constantly agitated while titrating. This method may be applied to the estimation of calcium oxide or carbonate in dolomite or limestone.

Example: A sample of dolomite weighing 0.395 Gm. was dissolved by aid of hydrochloric acid in about 250 Cc. of water; to this about five drops of nitric acid were added and the solution boiled a few minutes; then an excess of ammonia water was added and the precipitate of aluminium and ferric hydroxides removed by filtration, washing the precipitate thoroughly with hot water. To the filtrate, containing calcium and magnesium salts and an excess of ammonia, a solution of oxalic acid is added until no more calcium oxalate precipitates. The precipitate is collected, washed, and redissolved in water by aid of hydrochloric acid, and, after adding an excess of ammonia, the calcium is again precipitated by aid of oxalic acid. After thoroughly washing the precipitate, it is mixed with about 100 Cc. of water and sufficient diluted sulphuric acid; then a solution of permanganate is added under constant agitation until the mixture retains a faint rose tint. For this purpose 45.2 Cc. of a permanganate solution, 1 Cc. of which required 0.0057 Gm. Fe, were consumed. The calculation is based on the fact that one molecule or 89.32 p. of oxalic acid (anhydrous) precipitates 55.68 p. of CaO. The quantity of oxalic acid found is then multiplied by the quotient $\frac{55.68}{89.32}$. Since 1 Cc. of the permanganate solution is equivalent to 0.0057 Gm. Fe, and 45.2 Cc. were consumed, then:

$$\frac{0.0057 \times 45.2 \times 46.66 \times 55.68}{55.5 \times 89.32} = \frac{0.0057 \times 45.2 \times 55.68}{2 \times 55.5} = 0.129238 \text{ Gm., or } 32.72$$
per cent. of CaO.

(55.5 parts Fe = 44.66 parts oxalic acid (anhydrous)).

Another method is based on precipitating the calcium from a measured excess of decinormal oxalic acid V. S. and titrating back the uncombined excess by means of a standard permanganate V. S. To the solution of the calcium salt in diluted hydrochloric acid, contained in a graduated vessel, an accurately measured excess of

$\frac{N}{10}$ oxalic acid V. S. is added; then the liquid is made alkaline with ammonia water and the mixture boiled; after cooling, the fluid is made up to any definite volume. An aliquot portion is filtered through dry paper, and, after diluting with water and acidifying strongly with sulphuric acid, the excess of $\frac{N}{10}$ oxalic acid is determined as usual with $\frac{N}{10}$ $KMnO_4$ V. S. Since 1 Cc. of $\frac{N}{10}$ $H_2C_2O_4$ V. S. is equivalent to 1 Cc. $\frac{N}{10}$ $KMnO_4$ V. S., then the volume of the latter consumed in producing a pink tint, deducted from the total added volume of the former, will represent the number of Cc. of standard oxalic acid solution which have combined with the calcium present in the solution. Each 1 Cc. $\frac{N}{10}$ oxalic acid V. S. multiplied by 0.002784 = CaO, or by 0.004967 = $CaCO_3$ present. Thus:

$$\underset{125.08}{H_2C_2O_4} + 2H_2O + \underset{55.68}{CaO} = CaC_2O_2 + H_2O$$

$$\underset{125.08}{H_2C_2O_4} + 2H_2O + \underset{99.34}{CaCO_3} = CaC_2O_4 + C_2O + H_2O$$

Since 125.08 parts of oxalic acid = 55.68 parts of calcium oxide or 99.34 parts of calcium carbonate,

then 62.54 $\left(\frac{125.08}{2}\right)$ " " " = 27.84 $\left(\frac{55.68}{2}\right)$ parts of calcium oxide or 49.67 $\left(\frac{99.34}{2}\right)$ parts of calcium carbonate.

6.254 Gm. oxalic acid (1000 Cc. $\frac{N}{10}$ V.S.) = 2.784 Gm. of calcium oxide or 4.967 Gm. of calcium carbonate.

1 Cc. $\frac{N}{10}$ oxalic acid V. S. (0.006254 Gm.) = 0.002784 Gm. of calcium oxide or 0.004967 Gm. of calcium carbonate.

Example: To a solution of a calcium salt in diluted hydrochloric acid, 50 Cc. of $\frac{N}{10}$ oxalic acid V. S. were added, and, after making alkaline with ammonia, boiling, and cooling, the volume was made up to 500 Cc. Of this, 100 Cc. were filtered off, about 2 Cc. of sulphuric acid added, and then $\frac{N}{10}$ $KMnO_4$ V. S. until the fluid retained a faint pink tint; for this purpose 20 Cc. were consumed. Then, since:

50 Cc. = excess volume of $\frac{N}{10}$ oxalic acid V. S. added.
20 Cc. = volume of $\frac{N}{10}$ permanganate V. S. required for the uncombined $\frac{N}{10}$ oxalic acid [V. S.
30 Cc. = volume of $\frac{N}{10}$ oxalic acid V. S. combined with the calcium.

If 1 Cc. of $\frac{N}{10}$ oxalic acid V. S. is equivalent to 0.002784 Gm. of CaO or 0.004967 Gm. of $CaCO_3$, then 30 Cc. would represent 0.08352 Gm. of calcium oxide or 0.14901 Gm. of calcium carbonate present in one-fifth part (100 Cc.) of the solution, or 0.4176 Gm. of the former and 0.74505 Gm. of the latter present in original or entire sample.

Estimation of Nitrites.

For this purpose 100 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. are accurately measured into a flask and 5 Cc. of diluted (1 to 5) sulphuric acid added. To this solution, warmed to about 40° C., a solution of a weighed quantity of the nitrite is added from a burette, shaking constantly until the permanganate has become completely decolorized. The 100 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. represent 0.42255 Gm. of KNO_2, or 0.34285 Gm. of $NaNO_2$, or 0.23345 Gm. of HNO_2; knowing the quantity of the specimen added, the percentage of absolute purity is readily calculated.

$$\underset{313.88}{K_2Mn_2O_8} + \underset{233.45}{5HNO_2} + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

$$\underset{313.88}{K_2Mn_2O_8} + \underset{422.55}{5KNO_2} + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

313.88 Gm. $KMnO_2$ = 233.45 Gm. HNO_2, or 422.55 Gm. KNO_2, or 342.85 Gm. $NaNO_2$
100 Cc. $\frac{N}{10}$ $KMnO_4$ (0.31388 Gm.) = 0.23345 Gm. HNO_2, or 0.42255 Gm. KNO_2, or 0.342.85 Gm. $NaNO_2$.

Example: 1 Gm. of a sample of potassium nitrite was dissolved in water sufficient to make exactly 100 Cc. This was then slowly added from a burette, shaking constantly, to 100 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. acidified with 5 Cc. of diluted sulphuric acid (1 to 5) until decolorization was complete, 60 Cc. being required. Since the 100 Cc. of permanganate solution represent 0.42255 Gm. of pure nitrite, and the 60 Cc. of solution added 0.6 Gm. of the salt being examined, then the sample must be 70.425 per cent. pure; for:

Sample Used. Real Salt.
0.6 Gm. : 0.42255 Gm. :: 100 : x; $x = 70.425$.

Estimation with an empirical permanganate solution the titer of which has been set with $\frac{N}{10}$ oxalic acid V. S. may be carried out as directed under Barium Dioxide.

Ferric Iron Determinations.

Ferric compounds are best estimated by iodometric methods (page 132); however, it is frequently necessary to estimate ferrous in the presence of or with ferric salts, and in such cases titration with permanganate is to be preferred. The estimation of ferric iron in compounds by potassium permanganate is based on its oxidation from the ferrous to the ferric condition, the ferric salts having been previously reduced to the ferrous state by means of metallic zinc or magnesium in the presence of diluted sulphuric acid. To the solution of a weighed quantity of the ferric salt (which should not contain more than 0.15 Gm. of metallic iron), dissolved in about 250 Cc. of water, 10 Gm. of metallic zinc and 25 Cc. of sulphuric acid are added. The flask is kept at a temperature between 60° and 80° C. until the zinc has all dissolved, when the solution is brought to a boil, and, after inserting a Bunsen valve-stopper, it is allowed to cool, then the titration is carried out with a $\frac{N}{10}$ $KMnO_4$ V. S. All kinds of granulated zinc, even the chemically pure, contain traces (more or less) of carbon and iron, which reduce the permanganate solution; hence in these operations a blind experiment should be made in which 10 Gm. of the same lot of zinc are dissolved in 250 Cc. of water by aid of 25 Cc. of sulphuric acid, and, after solution is complete (disregarding the presence of floating particles of carbon), the potassium permanganate solution is added until a permanent rose tint results; the number of cubic centimeters consumed is then deducted from that employed in the above operation, the difference representing the volume of permanganate consumed by the ferrous iron. Metallic magnesium, owing to its purity, is to be preferred to zinc when obtainable.

Example: Estimation of Real Ferric Salt in Ferric Chloride.—A sample of dry ferric chloride weighing 0.320 Gm. was dissolved in 250 Cc. of water containing 25 Cc. of sulphuric acid to which exactly 10 Gm. of metallic zinc had been added. The flask, with contents, was placed upon a water-bath and gently warmed until the zinc had entirely dissolved and a drop of the fluid, when removed with a glass rod, failed to give a coloration with a solution of potassium sulphocyanide. To the cooled solution $\frac{N}{10}$ $KMnO_4$ V. S. was added, shaking after each addition, until a faint permanent pink resulted; 27.5 Cc. were required for this purpose. In a previous experiment carried out with 10 Gm. of the same sample of zinc with acid the metal required 9.5 Cc. of the permanganate solution.

27.5 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. consumed by the Fe of the compound and the impurities of the zinc.
9.5 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. consumed by the impure zinc.
18.0 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. required to oxidize the $FeCl_2$ to Fe_2Cl_6.

If 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. is equivalent to 0.00555 Gm. of metallic iron, which, in turn, represents 0.016104 Gm. of ferric chloride $\left(\frac{K_2Mn_2O_8}{313.88} = \frac{Fe}{555} = \frac{Fe_2Cl_6}{1610.4}\left(\frac{3220.8}{2}\right)\right)$, then 18 Cc. would be equivalent to 18 × 0.016104, or 0.289872 Gm. of ferric chloride. The sample weighing 0.320 Gm. contains, therefore, 0.289872 Gm., or 90.58+ per cent., of real ferric chloride.

If the permanganate solution has lost its titer, and upon trial it is found that 1 Cc. = 0.0057 Gm. Fe, then we may have recourse to the following calculation:

$$\frac{0.0057 \times 18 \times 161.04}{55.5} = \text{Gm. } Fe_2Cl_6.$$

Estimation of Ferric Oxide in Presence of Ferrous Oxide.

The mixed oxides are dissolved in diluted sulphuric acid contained in a flask provided with a Bunsen valved stopper, and the ferr*ous* salt present is estimated in the usual manner, as directed on page 99. The number of cubic centimeters of the permanganate solution consumed, multiplied by 0.007138 (the factor for FeO), gives the total quantity of ferrous oxide present.

$$\underset{313.88 \text{ p.}}{K_2Mn_2O_8} = \underset{555 \text{ p.}}{Fe} = \underset{713.8 \text{ p.}}{FeO}$$

The ferric oxide, which is estimated by difference, is determined by weighing off a fresh portion of the substance, and, after dissolving and reducing as directed on page 104, the total iron is estimated as a ferrous salt. The difference between the number of cubic centimeters of permanganate first employed for the ferrous compound and that required for the total ferrous iron, when multiplied by 0.007932 (the factor for Fe_2O_3), gives the quantity of ferric compound present:

$$\underset{313.88}{K_2Mn_2O_8} = \underset{555}{Fe} = \underset{793.2}{Fe_2O_3}\left(\frac{1586.4}{2}\right)$$

Example: 0.3022 Gm. of ferric oxide containing some ferrous oxide was dissolved in a mixture of 150 Cc. of water and 25 Cc. of sulphuric acid, which was afterward made up to 200 Cc. Of this solution, 100 Cc. were titrated direct with potassium permanganate V. S., whereby 9 Cc. were consumed. The remaining 100 Cc., after reducing with magnesium ribbon, required 39 Cc. of permanganate.

39 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. required for total ferrous iron.
9 Cc. " " " $\times$ 0.007138 = 0.06424+ Gm. FeO.
30 Cc. " " " $\times$ 0.007932 = 0.23796 Gm. Fe_2O_3.
0.30220 Gm. total.

The sample contains, therefore, 0.06424+ Gm. of ferrous and 0.23796 Gm. of ferric oxides.

II. INDIRECT METHODS.

Under this head are embraced those methods in which an oxidizing agent is brought into reaction with a known excess of a reducing agent, and, after completion of the reaction, the unoxidized portion is estimated by means of permanganate solution. As a deoxidizing agent either a ferrous salt or oxalic acid is usually employed; the former in the analysis of nitrates and chromates, while the latter is used for metallic peroxides, as manganese dioxide.

Chromic Acid and Chromates.

An accurately weighed quantity of ferrous ammonium sulphate ($FeSO_4 + (NH_4)_2SO_4 + 6H_2O$), the permanganate titer of which is known, is dissolved in moderately diluted sulphuric acid contained in a flask;* to this is added a weighed amount of the chromic acid or chromate in concentrated aqueous solution; through this flask, while warming on a water-bath, carbonic acid gas is passed until the fluid has taken on a pure green color, showing a complete deoxidation of the chromate. After reduction is complete, which takes but a few minutes, the flask is allowed to cool while the gas is still passing through. The cold solution is now transferred to a large beaker (300 Cc.), and, after strongly acidifying with sulphuric acid and diluting to 600 or 800 Cc., the unoxidized ferrous salt is estimated with potassium permanganate solution. High dilution is necessary in order to distinguish a color change due to the presence of the permanganate in the green-colored fluid. This method is applicable to the estimation of insoluble chromates, as those of lead, bismuth, and barium, in which the precipitate is added and shaken directly with the ferrous salt and water. The dilution in these cases is greater and the temperature of heating higher. The reaction is as follows:

$$\underset{\substack{\text{Ferrous}\\ \text{Sulphate.}\\ 6\times55.5\text{ Fe}}}{6FeSO_4\dagger} + 6H_2SO_4 + \underset{\substack{\text{Chromic}\\ \text{Oxide.}\\ 2\times99.34}}{2CrO_3} = \underset{\substack{\text{Chromium}\\ \text{Sulphate.}}}{Cr_2(SO_4)_3} + \underset{\substack{\text{Ferric}\\ \text{Sulphate.}}}{3Fe_2(SO_4)_3} + 6H_2O$$

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* This flask is provided with a doubly perforated stopper; through one perforation passes a glass tube, which reaches close to the surface of the fluid, while the other short one serves as an outlet; through the longer tube the carbonic acid gas enters the flask.

† Only the $FeSO_4$ of the ferrous ammonium sulphate enters into the reaction, each molecule of which represents 55.5 parts of metallic iron.

According to the equation, one molecule (99.34 p.) of chromic oxide is equivalent to three molecules (166.5 p.) of metallic iron. The quantity of iron which has undergone oxidation, multiplied by $\frac{99.34}{166.5}$, gives the weight of chromic oxide present, and, from this, its equivalent in potassium, lead, bismuth, or barium chromate may be calculated.

Example: To 1.50 Gm. of ferrous ammonium sulphate (containing 0.2138+ Gm. Fe) 0.12863 Gm. of $K_2Cr_2O_7$ (mol. wt. 292.2) was added, and, after oxidation was complete, the unoxidized ferrous salt remaining required 12 Cc. of a permanganate solution, 1 Cc. of which was found to be equivalent to 0.0056 Gm. Fe.

In this reaction 12 × 0.0056 or 0.0672 Gm. of iron was *not* oxidized by the dichromate; then 0.2138 — 0.0672 = 0.1466 Gm. of iron oxidized. Then,

$$\frac{0.1466 \times 99.34}{166.5} = 0.08746+ \text{ Gm. } CrO_3\text{; or,}$$

$$\frac{0.1466 \times 99.34 \times 292.2}{166.5 \times 2 \times 99.34} = 0.1286+ \text{ Gm. } K_2Cr_2O_7.$$

Example: To 1.25 Gm. of ferrous ammonium sulphate (containing 0.1782 Gm. Fe) are added a barium chromate precipitate resulting from 0.2015 Gm. of $BaCl_2 + 2H_2O$ (mol. wt. 242.52), and, after completion of the oxidation, 7 Cc. of a permanganate solution (1 Cc. = 0.0057 Gm. Fe) were consumed in titrating the unoxidized iron. In this reaction 7 × 0.0057 or 0.0399 Gm. of Fe remained unoxidized; then 0.1782 — 0.0399 = 0.1383 Gm. of Fe oxidized by the barium chromate; then:

$$\frac{0.1383 \times 242.52}{166.5} = 0.20144+ \text{ Gm. } BaCl_2.$$

Manganese Dioxide or Pyrolusite.

Through the action of oxalic acid upon manganese dioxide (or pyrolusite) in the presence of sulphuric acid, and heating, the manganese is converted into a sulphate, while an equivalent amount of the oxalic acid is oxidized to carbonic acid gas. Thus:

$$\underset{86.36}{MnO_2} + \underset{125.08}{(COOH + 2H_2O)_2} + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O.$$

If a measured volume of a *normal* oxalic acid is employed, then after the reaction is complete the unoxidized excess may be estimated by means of $\frac{N}{10}$ $KMnO_4$ V. S.; each 1 Cc. of the $\frac{N}{1}$ $H_2C_2O_4$ V. S. corresponds to 0.04318 Gm. of MnO_2.

125.08 parts of $H_2C_2O_4$ correspond to 86.36 parts of MnO_2 (absolute).
62.54 Gm. $H_2C_2O_4$ (1000 Cc. $\frac{N}{1}$ V. S.) = 43.18 Gm. MnO_2.
1 Cc. $\frac{N}{1}$ $H_2C_2O_4$ (containing 0.06254 Gm.) = 0.04318 Gm. MnO_2.

Weigh off 0.4318 Gm. of the finely powdered sample of manganese dioxide or pyrolusite and transfer to a flask containing 25 Cc. of diluted sulphuric acid (1 to 5) and 10 Cc. of the $\frac{N}{1}$ $H_2C_2O_4$ V. S.; the mixture is shaken and boiled until the entire quantity, excepting traces of silica, has dissolved. As soon as the entire amount of the manganese has been decomposed, which is known by absence of brown or black sediment, the fluid is made up to 200 Cc. in volume, and, after well mixing, filtering if necessary, one-half, or 100 Cc., is taken for titration. To this solution, after making strongly acid with sulphuric acid, $\frac{N}{10}$ $KMnO_4$ V. S. is added, with constant agitation, until the solution retains a faint rose tint. From the number of cubic centimeters of $\frac{N}{1}$ $H_2C_2O_4$ V. S. present (10 Cc.) deduct the number of cubic centimeters of the $\frac{N}{10}$ $KMnO_4$ V. S. which have been added, multiplied by 2, and divided by 10; the difference represents the volume of the normal oxalic acid V. S. consumed by the MnO_2, which, multiplied by the factor 0.04318, yields the number of grammes of real MnO_2 present in the sample. This calculation is, however, unnecessary, for we have taken a molecular equivalent amount, and each 1 Cc. of the normal acid consumed multiplied by 2 will correspond to 10 per cent. purity.

Example: A sample of pyrolusite weighing 0.4318 Gm. was dissolved as directed and heated with 10 Cc. of a $\frac{N}{1}$ $H_2C_2O_4$ V. S., and, after diluting to 200 Cc., one-half, or 100 Cc., was taken for titration; for titrating back the unoxidized excess of normal acid, 20 Cc. of a $\frac{N}{10}$ $KMnO_4$ V. S. were consumed. Since 20 Cc. of permanganate represent one-half of the pyrolusite, 40 Cc. (20 × 2) represent the entire 0.4318 Gm. taken. Then, since 40 Cc. of a $\frac{N}{10}$ V. S. correspond to 4 Cc. $\left(\frac{40}{10}\right)$ of a $\frac{N}{1}$ V. S., we have 10 Cc. (oxalic acid) — 4 Cc. (permanganate) = 6 Cc. of $\frac{N}{1}$ $H_2C_2O_4$ V. S. consumed, which corresponds to 60 per cent. of real MnO_2 present.

Estimation of Hypophosphorous Acid and its Salts.*

To an accurately weighed quantity of the acid or its salt dissolved in water, sulphuric acid with a measured excess of $\frac{N}{10}$ $KMnO_4$ V. S. is added. This mixture is boiled for about fifteen minutes to facilitate the oxidation; then the unreduced excess of permanganate is estimated by titrating back with $\frac{N}{10}$ $H_2C_2O_4$ V. S. The reaction is as follows:

$$\underset{2 \times 313.88}{2K_2Mn_2O_8} + \underset{5 \times 65.51}{5HPH_2O_2} + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5H_3PO_4.$$

If 2 × 313.88 parts of $KMnO_4$ = 327.55 parts of HPH_2O_2
313.88 parts " = 163.775 parts "

One Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. (0.0031388 Gm.) is equivalent to 0.00163775 Gm. of hypophosphorous acid or an equivalent amount of any hypophosphite (see page 97).

Hypophosphorous Acid.—HPH_2O_2.—

One gramme of the diluted acid was mixed with 100 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. and 10 Cc. of sulphuric acid; after boiling the mixture for about fifteen minutes, 25 Cc. of $\frac{N}{10}$ oxalic acid V. S. were required for decolorization. Since each 1 Cc. of $\frac{N}{10}$ $H_2C_2O_4$ V. S. is equivalent to 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S., the difference would corre-

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* Owing to the possible presence of phosphites, sulphites, and hyposulphites in the commercial hypophosphites, which likewise reduce the permanganate solution, this method is open to error. See The Chemist and Druggist, 1897, p. 286.

spond to the number of cubic centimeters of the latter solution oxidized. Then:

100 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. originally added.
25 Cc. $\frac{N}{10}$ $H_2C_2O_4$ V. S. required for the unoxidized excess of $KMnO_4$.

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75 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. consumed for the oxidation of the hypophosphorous acid.

Since 1 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. = 0.00163775 Gm. HPH_2O_2, then 75 Cc. = 75 × 0.00163775, or 0.1228+ Gm. of absolute acid, or 12.28+ per cent. present in the sample.

Potassium Hypophosphite (KPH_2O_2).

Of the dry sample, 0.1 Gm. was dissolved in 10 to 15 Cc. of water, followed by about 10 Cc. of sulphuric acid; then exactly 40 Cc. of $\frac{N}{10}$ $KMnO_4$ V. S. were added and the mixture boiled for fifteen minutes. The excess of permanganate was determined by adding decinormal oxalic acid solution until decolorization took place; to accomplish this 2 Cc. were required.

40 Cc. = $\frac{N}{10}$ $KMnO_4$ V. S. added.
2 Cc. = $\frac{N}{10}$ $H_2C_2O_4$ V. S.

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38 Cc. = $\frac{N}{10}$ $KMnO_4$ V. S. consumed for oxidation of the KPH_2O_2.

Since 1 Cc. of permanganate is equivalent to 0.00258325 Gm. KPH_2O_2, 38 Cc. = 38 × 0.00258325, or 0.0982 Gm. absolute potassium hypophosphite present, being equivalent to 98.2 per cent. pure.

The reaction is as follows:

$$\underset{4 \times 313.88}{4K_2Mn_2O_8} + \underset{10 \times 103.33}{10KH_2PO_2} + 17H_2SO_4 = 9K_2SO_4 + 8MnSO_4 + 10H_3PO_4 + 12H_2O.$$

If 4 × 313.88 Gm. $K_2Mn_2O_8$ = 10 × 103.33 Gm. KH_2PO_2,
then 313.88 " " = 258.325 Gm. $\left(\frac{1033.3}{4}\right)$ KH_2PO_2.
1 Cc. $\frac{N}{10}$ $KMnO_4$ V. S. (0.0031388 Gm.) = 0.00258325 Gm. KH_2PO_2.

VOLUMETRIC ESTIMATIONS WITH POTASSIUM DICHROMATE.

Potassium dichromate, like the permanganate, is employed as an oxidizing agent in the estimation of iron and its compounds; it is likewise of value in adjusting the titer of sodium thiosulphate V. S. Solutions of potassium dichromate possess decided advantages over those of the permanganate in being absolutely permanent, the readiness with which they may be prepared, and that they may be used in presence of hydrochloric acid.

The end-reaction in iron estimations is ascertained by removing a drop of the mixture being titrated to a white slab or plate and adding a drop of *freshly made* solution of potassium ferr*i*cyanide.[*] As long as any ferr*ous* salt is present, a blue to greenish-blue color is produced; but as soon as the oxidation to the ferr*ic* state is complete, a clear brown color results.

Decinormal Potassium Dichromate Volumetric Solution.

$K_2Cr_2O_7 = 292.2$. 4.87 Gm. in 1 Liter.

This *decinormal* solution is prepared by dissolving 4.87 Gm. of pure potassium dichromate[†] (crystals) in sufficient distilled water, at any selected standard temperature, to make exactly 1000 Cc. If greater accuracy is desirable, the solution may be standardized by means of pure iron, as described on page 95. That one-sixth of the molecular weight of the salt expressed in grammes is taken for the preparation of a decinormal solution is explained as follows:

Upon heating one molecule of the dichromate with an acid (H_2SO_4), *three atoms* of nascent oxygen are liberated. Thus:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3.$$

These *three atoms* of oxygen possess the power to convert *six atoms* of iron from the *ferrous* to the *ferric* state, according to the equation—

$$6FeO + O_3 = 3Fe_2O_3.$$

Therefore each molecule of the dichromate, yielding *three* atoms of oxygen, is equivalent to *six atoms* of hydrogen. Hence, according to the principle expressed on page 17, we take one-sixth of the molecular weight of a decinormal solution of the dichromate (one-sixth of 29.22 = 4.87), thereby reducing it to the valency corresponding to one atom of replaceable hydrogen.

As a decinormal solution, it is the equivalent of an equal volume of decinormal potassium permanganate V. S., or, in the case of iodine liberated from potassium iodide, it is the equivalent of an equal volume of decinormal sodium thiosulphate V. S. Decinormal potassium dichromate V. S. may also be used, in conjunction with potassium iodide (from which it liberates iodine) and sulphuric acid, for adjusting the titer of sodium thiosulphate (hyposulphite) V. S. and, indirectly, that of the decinormal iodine V. S.

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[*] It is absolutely necessary that the ferricyanide solution employed should be free from ferrocyanide, and as solutions of the former soon show the presence of the latter, it is best to dissolve a few grains of the salt in distilled water just previous to testing.

[†] The dichromate should respond to the U.S.P. tests for purity, showing absence of sulphates, chlorides, and calcium. If the commercial salt only is available, it should be recrystallized three times, then powdered, and dried at 130° C. until of constant weight.

One Cubic Centimeter of Decinormal Potassium dichromate V. S. is the equivalent of:

Potassium Dichromate, $K_2Cr_2O_7$,	0.00487
Iron, in ferrous compounds,	0.00555
Ferrous Carbonate, $FeCO_3$,	0.011504
Ferrous Sulphate, anhydrous, $FeSO_4$,	0.015085
Ferrous Sulphate, crystallized, $FeSO_4 + 7H_2O$,	0.027601
Ferrous Chloride, anhydrous, $FeCl_2$,	0.012586
Ferric Chloride, anhydrous, Fe_2Cl_6,	0.016104
Sodium Thiosulphate (Hyposulphite), $Na_2S_2O_3 + 5H_2O$,	0.024646

(A) Ferrous-Iron Estimations.

Metallic Iron.—Any definite quantity of the sample (0.2 to 0.5 Gm.) is accurately weighed off (if it is intended for standardizing, piano wire should be selected), then dissolved by the aid of heat in diluted sulphuric acid (1 to 5) contained in a flask provided with a Bunsen slit (page 96). As soon as complete solution has taken place, the dichromate is slowly added, with constant agitation, until when a drop of the fluid removed by means of a glass rod to a white porcelain surface fails to produce a blue color with a drop of freshly prepared solution of potassium ferricyanide, indicating the completion of the oxidation of the ferr*ous* iron to ferr*ic*.

The first operation embraces the solution of the metallic iron, yielding ferrous sulphate, the operation being performed under conditions which obviate any possible formation of ferric salts resulting from contact with air:

$$\underset{6 \times 55.5}{6Fe} + 6H_2SO_4 = \underset{6 \times 150.85}{6FeSO_4} + 3H_2$$

The second operation embraces the oxidation of the ferr*ous* to the ferr*ic* iron, as follows:

$$\underset{\substack{\text{Ferrous Sulphate.} \\ 905.1 \\ (6 \times 150.85)}}{6FeSO_4} + \underset{\substack{\text{Potassium} \\ \text{Dichromate.} \\ 292.2}}{K_2Cr_2O_7} + 7H_2SO_4 = \underset{\substack{\text{Ferric} \\ \text{Sulphate.}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{Chromium} \\ \text{Sulphate.}}}{Cr_2(SO_4)_3} + K_2SO_4 + 7H_2O$$

If one molecule of $\underset{292.2 \text{ parts}}{K_2Cr_2O_7}$ will oxidize $\underset{6 \times 150.85 \text{ parts.}}{6FeSO_4}$, which correspond to $\underset{6 \times 55.5 \text{ parts.}}{6Fe}$,
then 48.7 parts $\left(\frac{292.2}{6}\right)$ = 150.85 parts = 55.5 parts.

1000 Cc. $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. containing 4.87 Gm. = 15.085 Gm. $FeSO_4$ = 5.55 Gm. Fe.
Each 1 Cc. " " " " 0.00487 Gm. of dichromate is then equivalent to 0.00555 Gm. of metallic iron.

Ferrous Carbonate (*Saccharated*).—One gramme of saccharated carbonate of iron was dissolved in about 10 Cc. of diluted sulphuric acid (1 to 5) and about 100 Cc. of water. Standard $\frac{N}{10}$ dichromate V. S. was slowly added, shaking constantly, until a drop of the mixture, when removed by means of a glass rod, failed to produce a blue color with a freshly prepared solution of potassium ferricyanide. In this experiment 12 Cc. of dichromate were consumed.

Since 1 Cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. = 0.011504 Gm. $FeCO_3$, 12 Cc. will represent 12 × 0.011504, or 0.138048 Gm. $FeCO_3$, which is equivalent to 13.8+ per cent. of real ferrous carbonate present.

The equation is as follows:

$$\underset{292.2}{K_2Cr_2O_7} + \underset{6 \times 115.04}{6FeCO_3} + 13H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 13H_2O + 6CO_2$$

292.2 parts of $K_2Cr_2O_7$ are necessary for the oxidation of 6 × 115.04 parts of ferrous carbonate.
48.7 " " " " " " " 115.04 " " " "

If 1000 Cc. $\frac{N}{10}$ V. S. containing 4.87 Gm. of $K_2Cr_2O_7$ are necessary for the oxidation of 11.504 Gm. of $FeCO_3$, then 1 Cc. of the dichromate solution (or 0.00487 Gm. of the salt) is equivalent to 0.011504 Gm. of ferrous carbonate.

Ferrous Sulphate.—($FeSO_4 + 7H_2O$).—An accurately weighed amount of the salt is dissolved in from 50 to 100 Cc. of water, from 2 to 3 Cc. of H_2SO_4 are added, and the titration carried out as directed above.

$$\underset{292.2}{K_2Cr_2O_7} + \underset{6 \times 276.01}{6FeSO_4.7H_2O} + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 14H_2O$$

292.2 parts of $K_2Cr_2O_7$ are necessary for the oxidation of 6 × 276.01 parts of ferrous sulphate.
48.7 " " " " " " " 276.01 " " " "

If 1000 Cc. $\frac{N}{10}$ V. S. containing 4.87 Gm. of $K_2Cr_2O_7$ are necessary for the oxidation of 27.601 Gm. of $FeSO_4 + 7H_2O$, then 1 Cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. would be equivalent to 0.027601 Gm. of crystallized ferrous sulphate.

(B) Ferric Iron Estimations.

In these estimations it is first necessary to reduce the ferr*ic* to ferr*ous* iron which is accomplished in acid solution either by means of magnesium ribbon, sulphurous acid, or stannous chloride, the latter being usually preferred. To the hot solution of a weighed quantity of the iron salt dissolved in diluted hydrochloric acid (1 acid, 2 water) a solution of stannous chloride * is added drop by drop, shaking and waiting a short interval after each addition. The completion of the reduction ($Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$) is ascertained by adding a drop of potassium sulphocyanide solution to a drop of the mixture, when no color should appear. An excess of tin salt must be avoided, for this would reduce the dichromate as well as the ferrous salt; also a complete reduction of the iron must have taken place. In order to avoid any possibility of incomplete reduction some prefer to add a slight excess of the stannous solution to the boiling iron mixture; then after rinsing down the sides of the beaker or flask with water which has been previously boiled and allowed to cool, the vessel is covered and set aside until cold. An excess of mercuric chloride is then added and the titration completed in the usual manner with dichro-

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* This should be freshly prepared when wanted for use by placing about 1 Gm. of pure tin in small pieces with a strip of platinum foil in a capsule containing about 20 Cc. of pure concentrated hydrochloric acid; through galvanic action the tin dissolves readily, after which the fluid is diluted with distilled water to 100 Cc. The platinum foil may be dispensed with by heating the acid and tin; however, solution proceeds less rapidly.

mate solution. The mercuric chloride serves to convert all traces of stannous chloride into the stannic, while mercurous chloride precipitates; neither of these interferes with the final titration ($SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$).

Example: A sample of dry ferric chloride weighing 0.279 Gm. was dissolved in about 20 Cc. of diluted hydrochloric acid (1 : 2), and while hot a solution of stannous chloride was added as directed above until potassium sulphocyanide solution failed to produce a red color with a drop of the mixture. After diluting with water, 14 Cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. were required for the complete oxidation; that is, until a drop of the mixture failed to produce a blue color with a freshly prepared solution of potassium ferricyanide.

The reaction proceeds as follows:

$$\underset{292.2}{K_2Cr_2O_7} + \underset{755.16}{6FeCl_2} + 14HCl = \underset{966.24}{3Fe_2Cl_6} + 2KCl + Cr_2Cl_6.$$

Since 292.2 parts of dichromate are necessary for the oxidation of 755.16 parts of ferrous chloride to 966.24 parts of ferric chloride, 48.7 Gm. of $K_2Cr_2O_7$ $\left(\frac{292.2}{6}\right)$ $= 125.86$ Gm. $FeCl_2 = 161.04$ Fe_2Cl_6; or, 1 Cc. $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. (0.00487 Gm.) corresponds to 0.016104 Gm. Fe_2Cl_6.

Since 1 Cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. $= 0.016104$ Gm. Fe_2Cl_6, 14Cc. will represent 14 $\times$ 0.016104, or 0.22545 Gm. of real ferric chloride in 0.279 Gm. of the sample, which corresponds to 80.8+ per cent.

DETERMINATIONS INVOLVING THE APPLICATION OF IODINE AND SODIUM THIOSULPHATE* V. S.

Iodine in the form of a decinormal solution is employed as an indirect oxidizing agent in the estimation of such oxidizable substances as arsenous oxide, arsenites, sulphurous acid, sulphites, sulphuretted hydrogen, thiosulphates, etc. This reagent reacts upon the elements of water, in the presence of these oxidizable bodies, liberating the oxygen necessary for their oxidation, while the hydrogen combines with the iodine to form hydriodic acid, causing thereby a complete decolorization of the standard solution. Thus,

$$2I_2 + 2H_2O = 4HI + O_2$$
$$As_2O_3 + O_2 = As_2O_5$$

or,

$$2I_2 + \underset{\substack{\text{Arsenous}\\\text{Oxide.}}}{As_2O_3} + 2H_2O = \underset{\substack{\text{Arsenic}\\\text{Oxide.}}}{As_2O_5} + \underset{\substack{\text{Hydriodic}\\\text{Acid.}}}{4HI}$$

$$I_2 + \underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3} + H_2O = \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} + 2HI$$

Since the added iodine solution is decolorized in this process of oxidation, it is necessary that a sharp terminal reaction should mark its completion; this is accomplished by the addition of starch

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* Commercially (but incorrectly) termed sodium hyposulphite.

paste, which strikes a blue color in the presence of the slightest trace of free iodine.

Iodine also plays a very important but indirect part in the estimation of ferr*ic* iron salts, chlorine, or such substances which evolve chlorine when heated with hydrochloric acid, as the chromates, manganates, and metallic peroxides; these substances, when brought in contact with a solution of potassium iodide under proper conditions, liberate a molecular equivalent of iodine, which, in turn, may be readily estimated by means of a decinormal solution of sodium thiosulphate, which causes a decolorization of the mixture, the reaction being as follows:

$$\underset{\substack{\text{Sodium}\\\text{Thiosulphate.}}}{2Na_2S_2O_3} + I_2 = \underset{\substack{\text{Sodium}\\\text{Tetrathionate.}}}{Na_2S_4O_6} + 2NaI$$

The following solutions are necessary in carrying out the estimations included under this class:

1. Decinormal Iodine Volumetric Solution.

Iodine = 125.89.

$\frac{N}{10}$ Iodine V. S. = 12.589 Gm. Iodine in 1 Liter (1000 Cc.).

This solution is stable and retains its titer for a long time. It is prepared by dissolving 12.589 Gm. of chemically pure iodine* in a solution of 18 Gm. of potassium iodide (free from iodate) in about 300 Cc. of distilled water; this is then further diluted until the volume measures exactly 1000 Cc. at the selected standard temperature, usually 15° C.

This standard solution may be prepared far more conveniently and rapidly by means of a standard decinormal sodium thiosulphate V. S. An approximate solution of iodine is first prepared by dissolving about 14 Gm. of commercial resublimed iodine, by aid of 18 Gm. of potassium iodide (free from iodate), in sufficient water to make 1000 Cc. Into a beaker or flask 10 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. are accurately measured from a burette; this is then diluted with from 25 to 50 Cc. of water; about 1 Cc. of starch solution is added, and then the above prepared iodine solution is slowly run in from a burette, under constant stirring or shaking, until the mixture retains a faint but permanent blue tint. This operation should be repeated with fresh portions until the results correspond. The number of cubic centimeters of the iodine solution consumed are noted and the remainder of the fluid so diluted that exactly 10 Cc. will be required for each 10 Cc. of the decinormal sodium thiosulphate V. S.

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* Commercial resublimed iodine is best purified by triturating with about one-fifth of its weight of potassium iodide and gently heating the mixture between two large watch-glasses or porcelain dishes; the lower vessel being placed upon a heated iron plate, the iodine sublimes upon the cooler inner surface of the inverted vessel. The sublimed crystals are pulverized and placed overnight in a desiccator.

Example: To 10 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S., diluted with 25 Cc. of water, about 1 Cc. of starch solution was added, and for the production of a faint blue color 9.3 Cc. of the trial iodine solution were required. In order to make these solutions equivalent to one another, each 9.3 Cc. of the iodine solution must be diluted with distilled water to exactly 10 Cc., or 930 Cc. are made up to 1000 Cc., observing the usual precautions as to temperature.

Standard solutions of iodine should be preserved in glass-stoppered containers away from the direct sunlight.

2. Decinormal Sodium Thiosulphate Volumetric Solution.

$Na_2S_2O_3 + 5H_2O = 246.46$.

$\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 24.646 Gm. Sodium Thiosulphate in 1 Liter (1000 Cc.).

An approximate decinormal solution is first prepared by dissolving about 30 Gm. of the pure crystalline salt in one liter of distilled water which has been previously boiled and cooled. The exact titer of this is then ascertained either by means of potassium dichromate or a decinormal solution of iodine.

Solutions of sodium thiosulphate are not very stable; they undergo decomposition through the influence of sunlight and carbonic acid gas, hence the water employed in their preparation should be thoroughly boiled and the solutions preserved in well-stoppered vessels kept away from the light. The products of decomposition are sulphites, and ultimately sulphates; the presence of the former may be established by the addition of solutions of barium chloride and iodine, whereby a precipitate of barium sulphate forms. The titer of the thiosulphate solution should be ascertained from time to time.

Standardization with Potassium Dichromate.

For this purpose either an accurately weighed quantity of the dry crystalline salt is taken, or, if a decinormal solution of potassium dichromate is at hand, an accurately measured volume (10 Cc.) is added to a solution of potassium iodide (free from iodate)* and strongly acidified. Each molecule of the dichromate (292.2 parts) liberates 755.34 parts of iodine, or each cubic centimeter of the decinormal dichromate V. S. (0.00487 Gm.) will liberate 0.012589 Gm. of iodine, which, in turn, is equivalent to 0.024646 Gm. or 1 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. Then, since each 1 Cc. of $\frac{N}{10}$ thiosulphate V. S. corresponds to 1 Cc. of the $\frac{N}{10}$ dichromate V. S., the number of cubic centimeters of the sodium thiosulphate trial solution required for the decolorization of the mixture are diluted until

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* A sufficient quantity of potassium iodide must be present not only to react with the dichromate, but also to dissolve the liberated iodine. For this purpose a slight excess over double the theoretical quantity is employed. If iodate be present, iodine will be liberated upon acidulating the solution, in consequence of the following reaction: $HIO_3 + 5HI = 3H_2O + 3I_2$.

its volume will be equal to that of the decinormal dichromate. The reactions are as follows:

$$\underset{292.2}{K_2Cr_2O_7} + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + \underset{755.34}{3I_2}.$$

292.2 parts of $K_2Cr_2O_7$ will liberate 755.34 parts of iodine.

4.87 Gm. $K_2Cr_2O_7$ $\left(\frac{292.2}{6}\right)$ or 1000 Cc. $\frac{N}{10}$ V. S. = 1.2589 Gm. iodine $\left(\frac{755.34}{6}\right)$.

1 Cc. $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. (0.00487 Gm.) = 0.012589 Gm. I = 0.024646 Gm., or 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S.

$$\underset{2 \times 125.89}{2I} + \underset{2 \times 246.46}{2Na_2S_2O_3.5H_2O} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

If 125.89 parts of iodine require 246.46 parts of sodium thiosulphate,
0.012589 Gm. " " 0.024646 Gm. or 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S.

Example 1: To a solution of about 0.5 Gm. of potassium iodide in 20 Cc. of water contained in a flask, 10 Cc. of a $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. are added from a burette, followed by 10 Cc. of diluted sulphuric acid (1 : 5); the mixture is then rotated about in the flask for a few minutes in order to facilitate the reaction and solution of the liberated iodine, when about 100 Cc. of water are added. To this brown-colored mixture the trial thiosulphate solution is slowly added from a burette, shaking constantly, until the color changes to a pale yellowish-brown, when 1 Cc. of starch solution is added and the addition of the thiosulphate continued until the blue color just disappears. Care should be taken not to overstep the end-point of the reaction by the too rapid addition of the thiosulphate. In the above example, 8.8 Cc. of the trial sodium thiosulphate solution were required for decolorization; then in order to bring this up to a dilution equivalent to that of the 10 Cc. of the decinormal dichromate, 880 Cc. of the former should be diluted with distilled water (previously boiled and cooled) sufficient to make 1000 Cc., observing the usual precautions as to temperature.

Example 2: A sample of pure potassium dichromate which had been recrystallized, powdered, and dried at 130° C., weighing 0.185 Gm., was dissolved in about 10 Cc. of water and poured into about 100 Cc. of a solution of 2 Gm. of potassium iodide (free from iodate), carefully rinsing the vessel which contained the dichromate solution. After acidifying this mixture with from 5 to 10 Cc. of concentrated hydrochloric acid, the flask was rotated for awhile and then a trial sodium thiosulphate solution added drop by drop from a burette, with constant shaking, until the brown color of the mixture changed to a yellow; then, after adding the starch paste, the addition of the thiosulphate was continued until the blue color produced just disappeared. For this purpose 36.2 Cc. of the latter were required. The 0.185 Gm. of dichromate employed liberated 0.47823 Gm. of iodine,* which corresponds to 37.98 Cc. of a decinormal iodine V. S., and this is, in turn, equivalent to 37.98 Cc. of a decinormal sodium thiosulphate V. S.† Hence each 36.2 Cc. of our trial thiosulphate solution must be diluted to measure 37.98 Cc. or 362 Cc. to 379.8 Cc.

3. Starch Solution.

About 1 Gm. of finely powdered potato starch is mixed with 10 Cc. of cold water, and then sufficient boiling water added, under constant stirring, to make about 200 Cc. of a uniform thin, transparent jelly.

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* $K_2Cr_2O_7$. Iodine.
292.2 Gm. : 755.34 Gm. : : 0.185 : x; $x = 0.47823$ Gm. iodine.

† Gm. I. Cc. $\frac{N}{10}$ V. S.
12.589 : 1000 : : 0.47823 : x; $x = 37.98$ Cc. $\frac{N}{10}$ iodine V. S.
Since 1 Cc. of $\frac{N}{10}$ iodine V. S. is equivalent to 1 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S.,
37.98 Cc. of " " " are " " 37.98 Cc. " "

This solution serves the purpose of assisting the operator in accurately noting the terminating point of iodometric estimations; it is sufficiently sensitive to detect one part of iodine in 3,000,000. A good starch paste, of which about 1 Cc. is usually sufficient, should give a distinct and intense blue color in the presence of iodine. Partially decomposed solutions give a red to brown color.

Owing to the readiness with which starch solutions deteriorate, it is advisable to prepare them fresh when wanted.

Direct Iodometric Estimations.

Determinations of this class are carried out by adding the decinormal iodine V. S. in small portions at a time to the (usually) alkali solution of the substance, shaking after each addition, and regulating the flow to drops toward the end of the operation. As soon as the color produced by the influx of the iodine solution no longer disappears on shaking, but is not deeper than very pale blue, the number of cubic centimeters of the iodine V. S. consumed is noted.

In these estimations the iodine acts as an indirect oxidizing agent, in that in the presence of an oxidizable body the elements of water are broken up, the hydrogen uniting with the iodine to hydriodic acid, while active oxygen is liberated.

$$H_2O + I_2 = 2HI + O.$$

The presence of an alkali serves the purpose of converting the liberated hydriodic acid into a stable alkali iodide; otherwise a secondary reverse reaction will take place, owing to the active reducing properties of this acid.

Arsenous Acid, As_2O_3.—(Arsenous Oxide, Arsenous Anhydride.)—An accurately weighed portion of from 0.1 to 0.2 Gm. of the sample is dissolved in a small volume of boiling water by aid of potassium hydroxide * (free from sulphur); the solution is then made acid with hydrochloric acid and finally alkaline with either sodium or potassium *bicarbonate*. The U. S. Pharmacopœia directs that the arsenous oxide be dissolved by boiling with ten times its weight of sodium bicarbonate and sufficient water. To the cold alkali solution of the arsenic prepared after either one of these methods, about 1 Cc. of starch paste is added, followed by a $\frac{N}{10}$ iodine V. S. in small portions at a time, shaking after each addition and regulating the flow to drops toward the end of the operation, the completion of which is known by the production of a pale blue tint which remains permanent after shaking.

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* Arsenous oxide dissolves more readily in caustic than carbonated alkalies, hence the preference. The *final alkalinity* of the solution must be brought about through the addition of a *bicarbonate*, owing to the action of normal carbonates upon the blue iodide of starch, the end-reaction being less sharp. In addition, bicarbonates are less liable to contain sulphur compounds, sulphites, and thiosulphites, which likewise react with the standard iodine V. S. For this reason sodium bicarbonate is to be preferred to the potassium salt.

The addition of the iodine to the arsen*ous* acid solution causes its oxidation to arsen*ic* acid according to the following equations:

$$2H_2O + 2I_2 = 4HI + O_2 ; \quad As_2O_3 + O_2 = As_2O_5.$$

In the presence of the carbonated alkali, which serves to combine with the liberated hydriodic acid, we have the following:

$$\begin{array}{ccccccccccccc} As_2O_3 & + & 4I & + & 4NaHCO_3 & = & As_2O_5 & + & 4NaI & + & 4CO_2 & + & 2H_2O. \\ \text{Arsenous Acid.} & & \text{Iodine.} & & \text{Sodium} & & \text{Arsenic} & & \text{Sodium} & & & & \\ 196.54 & & 4 \times 125.89 & & \text{Bicarbonate.} & & \text{Acid.} & & \text{Iodide.} & & & & \end{array}$$

Since 4 × 125.89 parts of iodine are necessary for the oxidation of 196.54 parts of arsenous oxide, 125.89 parts of the former will oxidize 49.135 parts $\left(\frac{196.54}{4}\right)$ of the latter.

1000 Cc. $\frac{N}{10}$ iodine V. S. containing 12.589 Gm. iodine = 4.9135 Gm. As_2O_3.
1 Cc. " " " " 0.012589 Gm. " = 0.0049135 Gm. "

Therefore each 1 Cc. of the $\frac{N}{10}$ iodine V. S. is equivalent to 0.0049135 Gm. of arsenous oxide.

Example a: 0.1 Gm. of white arsenic was dissolved by aid of 1 Gm. of potassium bicarbonate in 20 Cc. of boiling water; after cooling and diluting with a little water 1 Cc. of starch paste was added, followed by decinormal iodine V. S. until a faint blue color was produced, 18 Cc. being consumed for this purpose.

Since 1 Cc. $\frac{N}{10}$ iodine V. S. = 0.0049135 Gm. As_3O_3,
18 Cc. " " = 18 × 0.0049135 or 88 443 Gm., or
88.443 per cent. of real arsenous oxide present in the sample.

Example b: 0.49135 Gm. or $\frac{1}{100}$ part of the molecular equivalent quantity of the same sample was taken and 88.44 Cc. of the decinormal iodine solution were required for oxidation. Since 0.49135 Gm. of *absolute* As_2O_3 require 100 Cc. of $\frac{N}{10}$ iodine V. S., then each 1 Cc. of the latter consumed would correspond to $\frac{1}{100}$ part, or 1 per cent. purity; 88.44 Cc. would represent 88.44 per cent. of absolute arsenous oxide present.

Example c: 0.100 Gm. of a sample of arsenic required 20 Cc. of an empirical iodine solution (1 Cc. = 0.0120 Gm. iodine). The sample would therefore contain

$$\frac{20 \times 0.0120 \times 49.135}{125.89} = 0.936 + \text{Gm.},$$

or 93.6+ per cent. of true arsenous oxide.

Györy's Method.—Arsenous acid may be estimated in *acid* solution titrimetrically according to the method of Györy,* which is based on the oxidation of arsenous to arsenic oxide by means of a standard decinormal potassium bromate solution in the presence of hydrochloric acid; an equal volume of 10 per cent. hydrochloric acid being used for a 1 per cent. solution of arsenous acid. The reaction is as follows:

$$2KBrO_3 + 2HCl + 3As_2O_3 = 2KCl + 2HBr + 3As_2O_5.$$

As indicator, one drop of methyl-orange solution (0.1 Gm. in 100 Cc. water) is added to the acid solution, whereby a rose color is produced; the slightest excess of bromate causes a complete decolorization of the solution. A large excess of the standard solution causes a yellowish coloration of the fluid due to liberated bromine. The standard decinormal bromate V. S. is prepared by dissolving 2.7634 Gm. of the pure recrystallized potassium bromate, dried at 110° C., in sufficient distilled water to make 1000 Cc. Each 1 Cc. of $KBrO_3$ V. S. = 0.0049135 Gm. As_2O_3.

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* Zeitschr. f. analyt. Chem. 32, 415 (1893).

Fowler's Solution.—(Liquor Potassii Arsenitis.)—30 Cc. of a sample solution were boiled a few minutes with about 2 Gm. of sodium bicarbonate, and diluted with water to 100 Cc.; when cold, 1 Cc. of starch solution was added; 50 Cc. of a $\frac{N}{10}$ iodine V. S. were required to produce a permanent blue tint. Since 1 Cc. of $\frac{N}{10}$ iodine V. S. corresponds to 0.0049135 Gm. of arsenous anhydride (As_2O_3), 50 Cc. would represent 50 × 0.0049135, or 0.245675 Gm., which, in turn, corresponds to 8.1892 Gm. in 1000 Cc. of the solution.

$$30 \text{ Cc.} : 0.245675 \text{ Gm.} :: 1000 \text{ Cc.} : x; \qquad x = 8.1892 \text{ Gm.}$$

Antimony Compounds.—The estimation of antimonious oxide (Sb_2O_3) or any of its compounds is carried out under practically the same conditions as those of arsenous oxide (As_2O_3), in that the antimon*ous* oxide is oxidized to antimon*ic* oxide through the action of the added iodine solution, in the presence of a bicarbonate.

$$\underset{\substack{\text{Antimonous}\\ \text{Oxide.}\\ 286.64}}{(Sb_2O_3)} + \underset{4 \times 125.89}{2I_2} + 4NaHCO_3 = \underset{\substack{\text{Antimonic}\\ \text{Oxide.}}}{Sb_2O_5} + 4NaI + 4CO_2 + 2H_2O.$$

Solution of the oxide is brought about by aid of tartaric acid, which also serves to prevent the precipitation of the antimony upon the addition of the sodium bicarbonate previous to titrating. To the boiling mixture of the weighed oxide and water, tartaric acid is added in small portions until solution is complete; the excess of acid is then carefully neutralized by means of sodium carbonate, when a saturated solution of sodium bicarbonate is added, employing 10 Cc. for each 0.1 Gm. of the Sb_2O_3 present. To the resulting clear solution 1 Cc. of starch paste is added, followed by a $\frac{N}{10}$ iodine V. S. until a permanent pale blue color is produced. The titration should begin immediately after adding the bicarbonate. If, according to the preceding equation, 4 × 125.89 parts of iodine are equivalent to 286.64 parts of antimonous oxide, then—

$$125.89 \text{ Gm. of iodine} = 71.66 \text{ Gm.} \left(\frac{286.64}{4}\right) \text{ of } Sb_2O_3, \text{ or}$$

$$1 \text{ Cc. } \frac{N}{10} \text{ iodine V. S. } (0.012589 \text{ Gm.}) = 0.007166 \text{ Gm. of } Sb_2O_3.$$

Otherwise the oxide may be dissolved in hydrochloric acid, tartaric acid added, then the solution is diluted with water and an excess of sodium bicarbonate added, after which the titration is carried out as usual.

Antimony and Potassium Tartrate.—(Tartar Emetic.)—0.330 Gm. of a sample of the crystallized salt ($2K(SbO)C_4H_4O_6 + H_2O$) was dissolved in about 10 Cc. of water and 20 Cc. of a saturated solution of sodium bicarbonate; 1 Cc. of starch solution was added, followed by a $\frac{N}{10}$ iodine V. S. until a permanent faint blue resulted; 20 Cc. were required for this purpose. If, in accordance with the preceding equation, 4 × 125.89 parts of iodine correspond to

286.64 parts of antimonous oxide, which, in turn, represent 660.04 parts of crystallized tartar emetic,* then—

125.89 Gm. iodine = 71.66 Gm. Sb_2O_3 = 165.01 Gm. tartar emetic;
1 Cc. of $\frac{N}{10}$ iodine V. S. (0.012589 Gm.) = 0.016501 Gm. " "
20 Cc. " " = 20 × 0.016501, or 0.330 Gm. of absolute salt in the 0.330 Gm. taken.

The sample is therefore 100 per cent. pure.

Györy's Method.—Györy found that the end-reaction in the preceding estimation was not sharp under varied conditions, and therefore recommended his potassium bromate method to be carried out in *acid* solution. The operation is the same as that described under arsenous acid (oxide); however, sufficient hydrochloric acid must be added to prevent precipitation of the antimony during titration in consequence of the increasing dilution of the solution. For 0.330 Gm. of tartar emetic Györy recommends the addition of 25 Cc. of 10 per cent. hydrochloric acid; more than this will not influence the reaction. The equation is as follows:

$$2KBrO_3 + 2HCl + 3Sb_2O_3 = 2KCl + 2HBr + 3Sb_2O_5.$$

1 Cc. of $\frac{N}{10}$ $KBrO_3$ V. S. (containing 0.0027634 Gm.) = 0.007166 Gm. Sb_2O_3, which, in turn, represents 0.016501 Gm. of tartar emetic.

Metallic Antimony.—Where the metal is in solution and free from arsenic and tin, it is precipitated as a sulphide (Sb_2S_3) and thoroughly washed in the usual manner; then, dissolving in hydrochloric acid, the solution is boiled until all traces of sulphuretted hydrogen have been removed, and after diluting with water and adding tartaric acid, the solution is made alkaline with sodium bicarbonate, starch solution added, and titration completed with $\frac{N}{10}$ iodine V. S. in the usual manner. Each 1 Cc. $\frac{N}{10}$ iodine V. S. = 0.005975 Gm. of metallic antimony.

Type metal containing lead and antimony may be examined as follows: 0.412 Gm. of the metal was dissolved in the smallest possible quantity of aqua regia, and after adding an excess of aqua ammonia and yellow ammonium sulphide, the mixture was allowed to digest for several hours, when the precipitated lead sulphide was filtered off and thoroughly washed. (Where great accuracy is desirable, the precipitate is dissolved in hydrochloric acid and again treated with ammonia and ammonium sulphide as before.) The filtrate and washings were made quite acid with diluted sulphuric acid and boiled until all traces of sulphuretted hydrogen had been eliminated; the resulting precipitate of antimony sulphide was dissolved in hydrochloric acid, boiled, tartaric acid added (about 1 Gm.), then made alkaline with sodium bicarbonate. Twenty Cc. of $\frac{N}{10}$ iodine V. S. were required to produce a permanent blue tint, starch solution being present as indicator. The alloy therefore con-

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$$* \underset{\substack{\text{Antimonous}\\ \text{Oxide.}\\ 286.64}}{Sb_2O_3} + \underset{\substack{\text{Acid Potassium}\\ \text{Tartrate.}}}{2(KHC_4H_4O_6} + H_2O = \underset{\substack{\text{Antimony and Potassium}\\ \text{Tartrate.}\\ 660.04}}{2(KSbO)C_4H_4O_6 + H_2O)} + H_2O.$$

tained 20 × 0.005975 or 0.1195 Gm. of metallic antimony, which correspond to 29+ per cent.

Antimony in Type and Britannia Metal.—According to Clark, a weighed quantity of the alloy is treated with hydrochloric acid so long as there is any reaction; then powdered iodine is added in small portions, heating until complete solution results. The excess of iodine is removed by boiling, and the solution cooled, diluted, and starch solution added. Should the addition of the latter produce a blue color, due to a trace of free iodine, a very weak solution of sodium sulphite is added drop by drop till the blue color disappears. The solution should then be heated to boiling in order to remove any remaining traces of sulphurous acid; and when cold, tartaric acid is added, followed by sodium bicarbonate until alkaline; then, after adding the starch paste, $\frac{N}{10}$ iodine V. S. is run in till a faint permanent blue color is produced. The iodine assists the solution of the antimony which remains in the *ous* condition, while the tin is oxidized to the stannic condition. The lead present exerts no influence upon the result.

Sulphurous Acid ($SO_2 = 63.59$) and Sulphites.—The methods for the estimation of this acid and its salts are based upon their oxidation to sulphuric acid or sulphates by a standard solution of iodine, according to the following equation:

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI.$$

One Cubic Centimeter of $\frac{N}{10}$ Iodine V. S. is the equivalent of:

Calcium bisulphite, $Ca(HSO_3)_2$,	0.010037 Gm.
Potassium sulphite, cryst., $K_2SO_3 + 2H_2O$,	0.0096435 "
" " dry, K_2SO_3,	0.0078555 "
Sodium bisulphite, $NaHSO_3$,	0.0051675 "
" sulphite, cryst., $Na_2SO_3 + 7H_2O$,	0.012520 "
Sulphur dioxide, SO_2,	0.0031795 "

The analysis may be carried out either by adding the standard iodine to the alkali carbonate solution of the acid or salt, or indirectly by adding a measured excess of the standard iodine V. S. to the acid or its salt and then estimating the unconsumed iodine by means of a standard thiosulphate V. S.

Method a: A measured volume of the diluted acid solution which represents a weighed quantity of the sample of acid (from 1 to 3 Gm.) is poured into a solution of sodium bicarbonate.* The latter being in decided excess, starch solution is added, and then $\frac{N}{10}$ iodine V. S. in small portions, shaking thoroughly after each addition until a permanent pale blue is produced. Of a neutral sulphite an accu-

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* For making the solution alkaline, only bicarbonate of soda should be employed, because caustic alkalies react with the added iodine, causing decolorization; neutral carbonates are rarely free from caustic alkali and sulphides, also they do not permit as sharp an end-reaction as the bicarbonates.

rately weighed quantity, representing about 0.5 Gm., and an acid sulphite from 0.2 to 0.3 Gm., are sufficient for an assay; the salt is dissolved in about 30 Cc. of boiled and cooled water, sodium bicarbonate added, then the starch solution and $\frac{N}{10}$ iodine V. S.

Example: * 10 Cc. of a sample of sulphurous acid (sp. gr. 1.035) were diluted to 100 Cc., and of this solution 20 Cc., representing 2.07 Gm. (2 × 1.035) of the original acid, were taken for analysis, and 35 Cc. of $\frac{N}{10}$ iodine V. S. were required for oxidation. According to the equation:

$$\begin{array}{ccccccccc} I_2 & + & H_2O & + & SO_2 . H_2O & = & H_2SO_4 & + & 2HI. \\ \text{Iodine.} & & & & \text{Sulphurous Acid.} & & \text{Sulphuric Acid.} & & \\ 2 \times 125.89 & & & & 63.59 & & & & \end{array}$$

If 2 × 125.89 parts of iodine are equivalent to 63.59 parts of sulphurous oxide,
125.89 " " " " " " 31.795 " " " "
1000 Cc. $\frac{N}{10}$ iodine V. S. (12.589 Gm.) are equivalent to 3.1795 Gm. of sulphurous oxide,
1 Cc. " " (0.012589 Gm.) is " " 0.0031795 Gm. " "

If 1 Cc. of $\frac{N}{10}$ iodine V. S. is equivalent to 0.0031795 Gm. of sulphurous oxide, then the 35 Cc. consumed in the above operation would represent 35 × 0.0031795, or 0.1112825 Gm., or 5.37+ per cent. of the acid gas in the solution. For:

$$0.1112825 \text{ Gm. } SO_2 : 2.07 \text{ Gm. solution} :: x : 100; \; x = 5.37+, \text{ or } 5.37+ \text{ per cent.}$$

Example: † 0.25 Gm. of a sample of sodium bisulphite ($NaHSO_3$) was dissolved in about 25 Cc. of a solution of approximately 0.5 Gm. of sodium bicarbonate, and, after adding the starch solution, 40 Cc. of $\frac{N}{10}$ iodine V. S. were required to produce a permanent pale blue tint. Since 1 Cc. of the standard iodine V. S. is equivalent to 0.0051675 Gm. of real sodium bisulphite, then 40 Cc. would be equivalent to 40 × 0.0051675, or 0.2067 Gm., which corresponds to 82.7 per cent. of pure salt in the sample. The reaction is as follows:

$$\begin{array}{ccccccccc} I_2 & + & NaHSO_3 & + & H_2O & = & NaHSO_4 & + & 2HI. \\ 2 \times 125.89 & & \text{Sodium Bisulphite.} & & & & \text{Sodium Bisulphate.} & & \\ & & 103.35 & & & & & & \end{array}$$

2 × 125.89 parts of iodine are equivalent to 103.35 parts of sodium bisulphite.
125.89 " " " " " " 51.675 " " " "
1 Cc. $\frac{N}{10}$ iodine V. S. (0.012589 Gm.) is equivalent to 0.0051675 Gm. of sodium bisulphite.

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* If 3.1795 Gm. or $\frac{1}{10}$ of the molecular equivalent quantity is taken, then each 1 Cc. of $\frac{N}{10}$ iodine V. S. added would represent 0.1 per cent. of sulphurous acid present. Thus:

1 Cc. $\frac{N}{10}$ iodine V. S. = 0.0031795 Gm. SO_2;
1000 Cc. " " " = 3.1795 Gm. "

Each 1 Cc. of $\frac{N}{10}$ iodine V. S. (0.0031795 Gm. SO_2) would then represent the $\frac{1}{1000}$ part, or 0.1 per cent., of sulphurous anhydride.

† If 0.51675 Gm. or $\frac{1}{100}$ of the molecular equivalent quantity is taken, then each 1 Cc. of $\frac{N}{10}$ iodine V. S. added will represent 1 per cent. of real $NaHSO_3$. For:

100 Cc. $\frac{N}{10}$ iodine V. S. = 0.51675 Gm. $NaHSO_3$;
1 Cc. " " " = 0.0051675 Gm. "

Then each 1 Cc. of $\frac{N}{10}$ iodine V. S. represents $\frac{1}{100}$ part, or 1 per cent., of the molecular quantity taken.

Method b: This method, devised by Giles and Shearer (Jour. Soc. Chem. Ind., III, 197; IV, 303), is a modification of the previous one, and consists in adding the weighed amount of the acid or salt (in powder) to an accurately measured excess of $\frac{N}{10}$ iodine V. S. without diluting with water, and, after allowing the mixture to stand for a short time for the completion of the reaction, the *excess* of iodine is ascertained by titrating back with a $\frac{N}{10}$ sodium thiosulphate V. S. The number of cubic centimeters of the latter consumed, deducted from that of the former added, will represent the volume of $\frac{N}{10}$ iodine V. S. required for the oxidation; this, when multiplied by the proper equivalent, will indicate the actual quantity of the pure substance present.

Example: To 50 Cc. of $\frac{N}{10}$ iodine V. S. measured from a burette into a glass-stoppered vial 0.5 Gm. of finely powdered crystals of sodium sulphite is added; after securely closing the flask it is allowed to stand for about an hour, shaking at frequent intervals. Upon removing the stopper the adhering fluid is carefully rinsed back into the vial, and then a $\frac{N}{10}$ sodium thiosulphate V. S. is gradually added in small portions from a burette, shaking after each addition, and regulating the flow to drops toward the end of the operation, until the brown color of the iodine changes to a yellow. The starch paste is now added, followed by the thiosulphate solution in drops, shaking well after each addition, until the blue tint is discharged.

50 Cc. = added excess of $\frac{N}{10}$ iodine V. S.
20 Cc. = volume of thiosulphate V. S. corresponding to volume of uncombined iodine V. S.*

30 Cc. = volume of $\frac{N}{10}$ iodine V. S. consumed by the sodium sulphite.

Since 1 Cc. of $\frac{N}{10}$ iodine V. S. corresponds to 0.01252 Gm. of pure crystalline sodium sulphite ($Na_2SO_3 + 7H_2O$), then 30 Cc. would represent 30×0.01252 or 0.3756 Gm. of real sulphite present in the 0.5 Gm. of the sample, which corresponds to 75.12 per cent.

ESTIMATION OF FREE IODINE.

Free iodine is estimated by means of a decinormal solution of sodium thiosulphate. The iodine, whether dry or in the form of a tincture, is first brought into a dilute aqueous solution by means of potassium iodide, which must be free from iodate (KIO_3). To the

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* 1 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. is equivalent to 1 Cc. of $\frac{N}{10}$ iodine V. S.

$$\underset{2 \times 246.46}{2Na_2S_2O_3.5H_2O} + \underset{2 \times 125.89}{I_2} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

2 × 246.46 parts of sodium thiosulphate = 2 × 125.89 parts of iodine.
246.46 " " " " = 125.89 " " "
1000 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. or 24.646 Gm. = 1000 Cc. $\frac{N}{10}$ iodine V. S. or 12.589 Gm.
1 Cc. " " " " or 0.024646 Gm. = 1 Cc. " " " or 0.012589 Gm.

aqueous solution contained in a flask, the $\frac{N}{10}$ sodium thiosulphate V. S. is added in small portions at a time, shaking after each addition, and regulating the flow to drops toward the end of the operation—that is, till the liquid takes on a pale yellowish-brown, when sufficient starch solution is added to produce a deep blue color; then the addition of the thiosulphate is continued until the blue color of the fluid is just discharged. Care should be exercised not to overstep the decolorization point by the too rapid addition of the standard solution and failure to sufficiently agitate the solution.

Since the appearance of the blue color is more readily distinguished than its exact disappearing point, some operators prefer to add a measured excess of decinormal thiosulphate solution and then to titrate back with a decinormal iodine to the production of a faint blue. Deducting the number of cubic centimeters of $\frac{N}{10}$ iodine V. S. added from the excess of $\frac{N}{10}$ sodium thiosulphate V. S. the difference will represent the volume of the latter solution consumed by the iodine being standardized. The reaction involved is as follows:

$$\underset{\substack{\text{Sodium Thiosulphate.}\\ 2\times 246.46}}{2Na_2S_2O_3.5H_2O} + \underset{\substack{\text{Iodine.}\\ 2\times 125.89}}{I_2} = \underset{\text{Sodium Iodide.}}{2NaI} + \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6} + 10H_2O.$$

If 2 × 246.46 parts of sodium thiosulphate are equivalent to 2 × 125.89 parts of iodine,

246.46 " " " " = 125.89 parts of iodine;

then 1000 Cc. $\frac{N}{10}$ V. S. containing 24.646 Gm. sodium thiosulphate are equivalent to 12.589 Gm. of iodine or 1000 Cc. of $\frac{N}{10}$ V. S.

1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (0.024646 Gm.) = 0.012589 Gm. iodine or 1 Cc. $\frac{N}{10}$ V. S.

Conversely, 1 Cc. of $\frac{N}{10}$ iodine V. S. (0.012589 Gm.) = 0.024646 Gm. $Na_2S_2O_3$ or 1 Cc. $\frac{N}{10}$ V. S.

*Example a:** A sample of *resublimed iodine* weighing 0.260 Gm. was dissolved in about 50 Cc. of water by aid of about 1 Gm. of potassium iodide. To this, $\frac{N}{10}$ $Na_2S_2O_3$ V. S. was slowly added, with constant agitation, until the red-brown fluid changed to a pale yellowish-brown, when about 1 Cc. of starch solution was added and the addition of thiosulphate continued until the blue color was just discharged. For this purpose 20 Cc. of the $\frac{N}{10}$ $Na_2S_2O_3$ V. S. was required. Since 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 0.012589 Gm. of iodide, 20 Cc. would be equivalent to 20 × 0.012589 or 0.25178 Gm. of absolute iodine present in the sample, which corresponds to 96.84 per cent.

Example b: To the solution of the above-mentioned weight of iodine an excess consisting of 30 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. was added, and, after adding the starch solution,

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* If 0.12589 Gm. (0.1259 Gm.) is taken, then each 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 10 per cent. of iodine.

If 0.25178 Gm. (0.2518 Gm.) is taken, then each 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 5 per cent. of iodine.

10 Cc. of $\frac{N}{10}$ iodine V. S. were required for the production of a blue tint—that is, for titrating back the excess of thiosulphate. Then:

30 Cc. = total excess of thiosulphate V. S. added.
10 Cc. = iodine V. S. equivalent to uncombined thiosulphate.

20 Cc. = decinormal thiosulphate V. S. required for the sample of iodine.

Example c: A sample of iodine weighing 0.258 Gm. was dissolved in about 50 Cc. of water by aid of 1 Gm. of potassium iodide. To this an excess consisting of 45 Cc. of sodium thiosulphate solution (1 Cc. = 0.0059 Gm. iodine) was added, followed by a sufficient quantity of starch paste; then for titrating back 2.8 Cc. of an iodine solution (1 Cc. = 0.0058 Gm. iodine) were required. Both reacting solutions being empirical, it will be necessary to set the value of the iodine solution used in thiosulphate units. 1 Cc. of the iodine solution is equivalent to $\frac{58}{59}$ Cc. of the sodium thiosulphate solution. Then $\frac{2.8 \times 58}{59} = 2.75+$ Cc., the volume of iodine solution consumed in titrating back expressed in thiosulphate units.

45 Cc. = excess of added thiosulphate solution.
2.75 Cc. = uncombined thiosulphate estimated from added iodine solution.

42.25 Cc. = volume of empirical thiosulphate required for the iodine.

Since 1 Cc. of the thiosulphate solution corresponds to 0.0059 Gm. of iodine, then 42.25 Cc. would represent 42.25 × 0.0059, or 0.249275 Gm. of pure iodine contained in the sample of 0.258 Gm., which would accordingly represent 96.6 per cent. purity.

Example d: 5 Cc. of a sample of *tincture of iodine* were accurately measured into about 25 Cc. of an aqueous solution of 2 Gm. of potassium iodide. Decinormal solution of sodium thiosulphate was cautiously added, with constant agitation, until the color of the mixture changed from a red-brown to yellow; then, after adding 1 Cc. of starch paste, the addition of the thiosulphate was continued until the blue color was just discharged; 27.7 Cc. were consumed for this purpose. Since 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 0.012589 Gm. of iodine, 27.7 Cc. would represent 27.7 × 0.012589, or 0.348+ Gm. of iodine contained in 5 Cc. of the sample, or 6.96+ Gm. in 100 Cc.

Indirect Iodometric Estimations.

These methods are classed among the most accurate of volumetric analysis, and present the advantages of greater accuracy and rapidity over corresponding gravimetric processes. Iodine plays an indirect part in these estimations, in that such substances as chlorine, bromine, ferric salts, metallic peroxides, chromates, and manganates, when added to or caused to react indirectly with a solution of potassium iodide, liberate a molecular equivalent of iodine, which, in turn, is readily estimated by means of decinormal sodium thiosulphate V. S. From the volume of the latter consumed, the quantity of liberated iodine, and from this the weight of the substance in question, may be readily calculated. The quantity of potassium iodide employed should be in sufficient excess to retain the liberated iodine in solution as KI.I.

According to the method of manipulation, these estimations are carried out either by distillation or a process of digestion.

1. Distillation Methods.

The process of distillation is applicable to the estimation of manganates, chromates, metallic peroxides, bromides, and iodides. These substances (excepting the latter two), when heated with concentrated hydrochloric acid, liberate an equivalent amount of chlorine, which when passed into a solution of potassium iodide liberates, in turn, an equimolecular quantity of iodine. This latter is then estimated by means of a standard solution of sodium thiosulphate, each cubic centimeter of which will therefore represent a molecular equivalent of the original substance. For carrying out this operation the weighed substance is placed in a pear-shaped long-necked flask[*] (*d*, Fig. 23), which is filled to about two-thirds of its capacity with concentrated pure hydrochloric acid; this is then quickly connected by means of the rubber hose (*c*) with a long-bulbed tube (*a*), which passes into a small inverted retort (*b*) filled to at least one-third of its capacity with a solution (10 per cent.) of potassium iodide.[†] The retort with contents should be kept as cool as possible during the distillation. As soon as the evolution of chlorine gas begins to diminish, the flask (*d*) is gradually heated to boiling, taking care that the reaction does not become too violent; and as soon as about one-third of the acid fluid has distilled over and the reaction is presumably complete, the flask (*a*) with its delivery tube is slowly removed, while *still heating*, in order to prevent the contents of the retort from being drawn over owing to the great affinity of the evolved hydrochloric acid gas toward water. As soon as removed the delivery tube *a* is detached from the flask *d*, and is thoroughly rinsed by means of a spritz bottle into a beaker; then, after cooling the still inverted retort, the fluid inside should be agitated in order to secure complete absorption of any traces of chlorine gas which may have escaped into the space above; the solution is then transferred to the same beaker and the retort thoroughly rinsed. The beaker containing the liberated iodine in solution is now ready for titration with sodium thiosulphate V. S.[‡] In case there is any doubt of the reaction

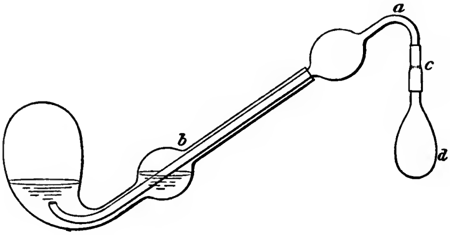

FIG. 23.—BUNSEN DISTILLATION APPARATUS.

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[*] A round-bottomed Florence flask of about 100 Cc. capacity is selected and the neck broken off evenly just below the lip. This may be accomplished either by means of a diamond or by winding a cord (from three to five turns being sufficient) around the place to be broken off, and after moistening with alcohol, it is ignited, and when it has burned for a few seconds the neck is suddenly immersed in cold water. The sharp edges may be rounded by means of a wetted file.

[†] The KI must be free from iodate, for in the presence of acids iodine is liberated by interaction as follows:

$$(a)\ 5KI + KIO_3 + 6HCl = 6KCl + 5HI + HIO_3.$$
$$(b)\ 5HI + HIO_3 = 3I_2 + 3H_2O.$$

[‡] Titration should begin immediately, owing to liberation of iodine from the very acid KI solution, through action of the air.

being complete, the apparatus may be again placed together, and, after introducing a small volume of fresh KI solution into the retort, flask *d* is again heated; the slightest discoloration of the former would indicate a further liberation of chlorine gas.

In order to avoid the difficulty of regurgitation, which frequently occurs through suction of the retort contents over into the distilling flask, a small piece of magnesite may be added, which from the action of the hydrochloric acid is slowly dissolved, liberating a constant flow of carbonic acid gas, the pressure of which is sufficient to prevent any back flow of fluid.

In view of this difficulty, a number of modifications of the previously described Bunsen apparatus have been suggested, and among these that of Fresenius is perhaps the simplest (Fig. 24). The weighed substance, with the hydrochloric acid, is placed in the distilling flask *a*; this is connected with a wide-bulbed tube *b*, which is drawn out into a long, narrow, curved tube *c*; the lower extremity of this terminates just above the potassium iodide solution (1 : 10), which is contained in two bulbed U-shaped tubes (*d* and *e*), placed in a vessel of ice-water. The mixture of manganese and hydrochloric acid (60 to 75 Cc.) contained in the flask *a* is gradually heated, regulating the temperature so that a steady current of chlorine will pass over; finally the mixture is brought to a boil and the heating continued until about one-third of the acid has distilled over.* The apparatus is allowed to stand for a few minutes in order to permit the complete absorption of any possible remaining traces of chlorine;† then the tube *b* is detached from the

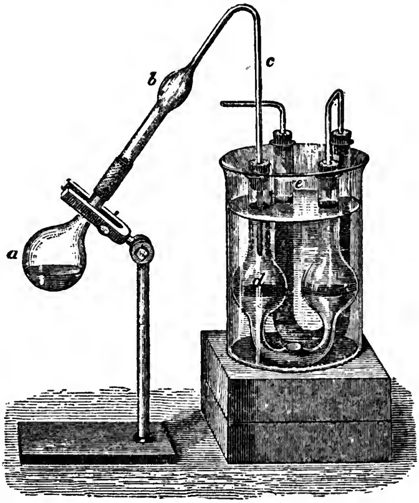

FIG. 24.—FRESENIUS' DISTILLATION APPARATUS.

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* This is done in order to secure complete decomposition of the substance and removal of all traces of chlorine from the distilling flask to the iodine solution.

† Should any chlorine (readily distinguishable by its yellow color) remain above the fluid in the front U-tube, the rear outlet tube should be connected with a suction pump or aspirator, and while in operation the distilling flask *a* is gradually loosened, admitting sufficient air to cause a slow current to pass through the apparatus.

flask *a*, and after removing it, with the stopper, from the U-tube, its lower extremity is rinsed back into the potassium iodide solution. The two U-tubes, with their stoppers, are thoroughly rinsed into a flask or beaker preparatory to beginning titration. Cork stoppers only should be used, and these, after pressing, perforating, and fitting, should be dipped into hot paraffin ; the operator is cautioned to see that all the fittings are air-tight in order to avoid any possible leakage of gas.

Estimation of Manganese Dioxide ($MnO_2 = 86.36$).

Example: 0.4318 Gm. of a dry and finely powdered sample of manganese was weighed and transferred to the distillation flask (*d*, Fig. 23 ; or *a*, Fig. 24), which was then filled to about two-thirds its volume of pure concentrated hydrochloric acid (60 to 75 Cc.) and quickly connected with the apparatus which contained the potassium iodide solution (1 : 10). The mixture of manganese and acid was then very gradually heated, regulating the temperature so that a slow but steady current of gas passed over; finally the mixture was brought to a boil, and as soon as about one-third of the acid had passed over, the delivery tube was removed, and, with the potassium iodide and its container, rinsed into a flask. The resulting red-brown solution of iodine was immediately titrated directly with decinormal sodium thiosulphate V. S.,* 62.5 Cc. being consumed.

The reaction is as follows:

$$\underset{86.36}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{2 \times 35.18}{Cl_2}.$$

Since 2 × 35.18 parts of chlorine are liberated by 86.36 parts of MnO_2, then one atom, or 35.18 parts, of Cl is liberated by 43.18 parts of MnO_2.

$$\begin{array}{ccccccc} Cl_2 & + & 2HI & = & HCl & + & I_2. \\ 2 \times 35.18 & & & = & & & 2 \times 125.89 \\ 35.18 & & & & & & 125.89 \end{array}$$

Since 35.18 parts of chlorine liberate 125.89 parts of iodine, which, in turn, are equivalent to 246.46 parts of sodium thiosulphate, then 1000 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. containing 24.646 Gm. = 12.589 Gm. iodine (1000 Cc. $\frac{N}{10}$ V. S.) = 3.518 Gm. chlorine = 4.318 Gm. MnO_2 ; or 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (containing 0.024646 Gm.) is equivalent to 0.004318 Gm. of manganese dioxide.

Having taken $\frac{1}{100}$ part of a molecular equivalent (0.4318 Gm.) of the manganese for assay, each 1 Cc. of the thiosulphate V. S. consumed will then represent 1 per cent. purity—that is, $\frac{1}{100}$ part or 0.004318 Gm. Hence the 62.5 Cc. employed represent the sample as containing 62.5 per cent. of real MnO_2.

Example: A sample of oxide weighing 0.350 Gm. liberates a quantity of iodine which requires 30.8 Cc. of an empirical thiosulphate V. S. (1 Cc. = 0.0180 Gm. iodine). The sample contains, accordingly, $\frac{30.8 \times 0.018 \times 43.18}{125.89} = 0.1901$ Gm. of MnO_2, which corresponds to 54.3 per cent. purity.

Freshly precipitated manganese dioxide may be more conveniently estimated by the digestion process, as described on page 130.

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* The titration may be carried out by adding a measured excess of the decinormal thiosulphate V. S., and titrating back with decinormal iodine V. S. as directed on page 124 ; however, unless the operation is carried out rapidly, a decomposition of the thiosulphate is brought about through the strong acid solution, in which sulphurous acid is liberated, which likewise reduces the standard solution.

(*a*) $Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S.$

(*b*) $2SO_2 + 2I_2 + 2H_2O = 2SO_3 + 4HI.$

Estimation of Chromic Acid and Chromates.—Chromic anhydride (CrO_3) and chromates, when boiled with concentrated hydrochloric acid, liberate for each one equivalent of the anhydride present three equivalents of chlorine, according to the following equations:

$$(a)\ \underset{2 \times 99.34}{2CrO_3} + 12HCl = Cr_2Cl_6 + 6H_2O + \underset{6 \times 35.18}{3Cl_2}.$$

Since 2 × 99.34 parts of CrO_3 liberate 6 × 35.18 parts of Cl, 99.34 parts liberate 3 × 35.18 parts of Cl; or one atom, or 35.18 parts, of chlorine represents 33.113+ parts of CrO_3. Or 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (containing 0.024646 Gm.), equivalent to 0.003518 Gm. of Cl, represents 0.003313 Gm. of CrO_3.

$$(b)\ \underset{292.2}{K_2Cr_2O_7} + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + \underset{6 \times 35.18}{3Cl_2}.$$

Since 292.2 parts of $K_2Cr_2O_7$ (containing 2 molecules of CrO_3) liberate 6 × 35.18 parts of chlorine, one atom of chlorine, or 35.18 parts, will represent 48.7 parts of the dichromate; then, 1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (containing 0.024646 Gm.), equivalent to 0.003518 Gm. Cl, represents 0.00487 Gm. of $K_2Cr_2O_7$.

This same line of reasoning is applicable to all chromates.

Far more convenient is the simple method of digestion, for upon adding the anhydride or a chromate or dichromate to an alkali iodide in the presence of hydrochloric acid, decomposition with liberation of an equivalent of iodine takes place at once.

Estimation of Alkali Iodides.—1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. represents 0.016471 Gm. KI, or 0.014877 Gm. NaI, or 0.014382 Gm. NH_4I.

The following method of Mohr is based on the observation that ferric salts liberate iodine quantitatively from its alkali combinations. From their iodine content the quantity of absolute alkali iodide present in commercial samples may be accurately determined. The reaction is as follows:

$$Fe_2(SO_4)_3 + 2KI = K_2SO_4 + 2FeSO_4 + I_2;$$

or—

$$\underset{\text{Ferric Ammonium Sulphate.}}{Fe_2(SO_4)_3.(NH_4)_2SO_4} + \underset{2 \times 164.71}{2KI} = K_2SO_4 + (NH_4)_2SO_4 . 2FeSO_4 + \underset{2 \times 125.89}{I_2}.$$

As reacting salt the ammonio-ferric alum is to be preferred to either ferric chloride or sulphate;* about ten parts of the salt are usually employed for each part of the iodide. Into the 100 Cc. distillation flask *a* (Fig. 25), about 5 Gm. of ammonio-ferric alum, 60 Cc. of water, 10 Cc. of diluted sulphuric acid (1 : 5), and the accurately weighed quantity (0.3 to 0.5 Gm.) of the iodide are

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* Ferric chloride is objectionable because of the tenacity with which it retains the last traces of iodine; also this salt, as well as ferric sulphate, because of their color, render the distinguishing of the end-reaction uncertain. These two salts frequently contain nitrates which if present will react with the chlorides, causing a liberation of chlorine.

placed; this is then secured by means of a short section of rubber hose to the distilling tube *c*. The Volhard wash-flask *b*, which contains the potassium iodide solution (1 : 10), presents a large absorbing surface to the iodine vapors which distil over. The stopper should be well paraffined and the flask placed in a vessel of ice-water. The distilling-flask *a* is now heated very gradually, beginning with a small flame in order to secure a slow and steady evolution of iodine; after the greater portion of the iodine has passed over, the temperature is raised to boiling, which is continued until about one-fourth of the liquid has distilled over and the remaining fluid is no longer of a brown color. As soon as the flask *b* has sufficiently cooled it is disconnected, and, after rinsing the lower extremity of the stopper and tube into the solution, the flask is cautiously shaken in order to dissolve any particles of free iodine which may have escaped solution. The solution of iodine is now thoroughly rinsed into a flask and titrated with decinormal sodium thiosulphate as already directed.

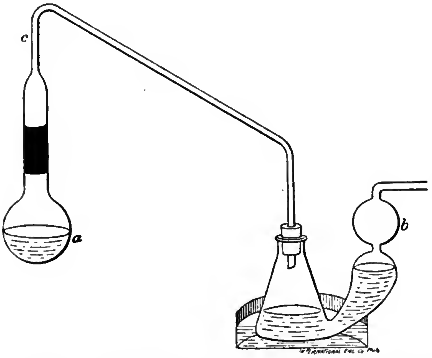

FIG. 25.—DE KONINCK'S DISTILLATION APPARATUS.

In the analysis of freshly precipitated manganese dioxide, chromic acid, lead superoxide, iodates, bromates, and ferric salts this distillation method may be replaced by the more convenient digestion process.

2. Digestion Process.

Many substances, by mere digestion with hydrochloric acid and potassium iodide (free from iodate) in a closed vessel at a slightly elevated temperature, undergo complete decomposition, as already explained under the process of distillation. For this purpose a bottle of from 50 to 150 Cc. capacity is selected which is provided with a very close-fitting ground-glass stopper. Before using, the vial should be first tested by securely tying down the stopper and entirely immersing in hot water; if any bubbles of air escape from the inside, it is useless; unless the stopper is reground with a little very fine emery and water. The substance to be examined is weighed into the vial, and, if insoluble, a small quantity of coarsely powdered glass is added in order to prevent caking; then a sufficient excess of potassium iodide solution, followed by pure concentrated hydrochloric acid. The stopper is then securely inserted and tied down and the vial placed in a cold water-bath which is afterward gradually heated to boiling, continuing this temperature until decomposition is complete; in most instances half an hour suffices. The vial is then removed and allowed to cool slowly, and, after shaking, its contents are thoroughly rinsed out into a beaker and the liberated iodine estimated in the usual manner with sodium thiosulphate V. S.

Estimation of Chlorates, Bromates, and Iodates.—

$$1 \text{ Cc. } \frac{N}{10}\ Na_2S_2O_3 \text{ V. S. is equivalent to } \left\{\begin{array}{lll} KClO_3, & \ldots\ldots & 0.0020273+ \text{ Gm.} \\ NaClO_3, & \ldots & 0.0017616+ \text{ "} \\ KIO_3, & \ldots\ldots & 0.0035391+ \text{ "} \\ KBrO_3, & \ldots & 0.0027633+ \text{ "} \end{array}\right.$$

The estimation of these oxyacid salts is based on their power of liberating a molecular equivalent quantity of chlorine when heated with concentrated hydrochloric acid; this, in turn, reacts on a solution of potassium iodide present, setting free an equivalent molecular quantity of iodine which is held in solution by the excess of iodide. By means of a decinormal sodium thiosulphate V. S., the iodine is estimated, and from this the quantity of real salt present in the sample may be readily calculated. For example:

$$(a)\ \underset{\substack{\text{Potassium Chlorate.}\\ 121.64}}{KClO_3} + 6HCl = 3H_2O + KCl + \underset{6 \times 35.18}{3Cl_2}.$$

$$(b)\ \underset{6 \times 35.18}{3Cl_2} + 6KI = 6KCl + \underset{6 \times 125.89}{3I_2}.$$

If 6 atoms (6 × 35.18 parts) of chlorine are liberated by one molecule (121.64 parts) of potassium chlorate, then one atom (35.18 parts) of chlorine will represent $\frac{1}{6}$ of 121.64, or 20.273+ parts of the chlorate.

According to equation *b*, each 35.18 parts of chlorine liberate 125.89 parts of iodine, which, in turn, are equivalent to 246.46 parts of sodium thiosulphate (see page 123). Then:

$Na_2S_2O_3$.		IODINE.		CHLORINE.		$KClO_3$.
246.46 Gm.	=	125.89 Gm.	=	35.18 Gm.	=	20.273 Gm.
24.646 "	=	12.589 "	=	3.518 "	=	2.0273 "
0.024646 "	=	0.012589 "	=	0.003518 "	=	0.0020273 "

Therefore, 1 Cc. of sodium thiosulphate V. S. containing 0.024646 Gm. of the salt is equivalent to 0.0020273 Gm. of potassium chlorate.

For these estimations a weighed quantity, usually from 0.1 to 0.2 Gm., or a molecular equivalent quantity representing $\frac{1}{1000}$ of $\frac{1}{6}$ part of the molecular weight of the substance, is employed. With chlorates a larger volume of hydrochloric acid is taken and the temperature of heating is higher than with the iodates and bromates, where digestion at about 50° C. is sufficient for complete decomposition.

Example: 0.2028 Gm. of a sample of potassium chlorate was dissolved in about 10 Cc. of water contained in a glass-stoppered vial (100 Cc.); then an excess consisting of about 4 Gm. of potassium iodide was added, followed by 10 Cc. of concentrated hydrochloric acid; the stopper was immediately inserted and secured with stout twine. The vial was then immersed (stopper downward) in a bath of cold water, which was gradually heated to boiling, the entire time of heating being half an hour. After cooling and shaking, the contents of the vial were washed out into a flask, and, after adding 1 Cc. of starch solution, 100 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. were required to discharge the blue color.

Since 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. is equivalent to 0.0020273 Gm. of pure $KClO_3$, 100 Cc. represents 0.20273 Gm., and, having taken this latter quantity for analysis, then each 1 Cc. of the standard V. S. consumed corresponds to $\frac{1}{100}$ part, or 1 per cent. purity.

Example: 0.2764 Gm. of potassium bromate was dissolved in about 15 Cc. of water contained in a 100 Cc. glass-stoppered vial; 4 Gm. of potassium iodide were added, followed by 3 Cc. of concentrated hydrochloric acid. The vial, after securely closing, was immersed in a bath of cold water and gradually heated to the temperature of 50° C. for about half an hour. After cooling and adding 1 Cc. of starch solution, 100 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. were required to discharge the blue tint. Since 1 Cc. of the decinormal V. S. is equivalent to 0.0027633+ Gm. of pure bromate, 100 Cc. represent 0.27633+ Gm., or practically 100 per cent. purity. The reaction is as follows:

$$\underset{165.8}{KBrO_3} + 6HCl = KBr + 3H_2O + \underset{6 \times 35.18}{3Cl_2}.$$

If 6 atoms (6 × 35.18 parts) of chlorine are liberated by one molecule (165.8 parts) of potassium bromate, then one atom (35.18 parts) of chlorine will represent ⅙ of 165.8, or 27.633+ parts of the bromate. In accordance with the arguments already presented the 35.18 parts of chlorine correspond to 125.89 of iodine and 246.46 of sodium thiosulphate, or each 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. represents 0.0027633+ Gm. of potassium bromate.

Should the bromate or iodate contain bromide or iodide, this method is not applicable, owing to the liberation of free bromine or iodine through the following reaction:

$$5KI + KIO_3 + 6HCl = 6KCl + 5HI + HIO_3.$$
$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

This may be readily ascertained by moistening a few grains of the salt with diluted sulphuric acid, when if a yellow to brown coloration results, either a bromate or an iodate is present in the respective sample. In titrating, it is advisable to add the thiosulphate solution until the brown iodine solution changes to a yellow; then the starch, followed again by the thiosulphate until the blue color is discharged. Or, as already noted (page 124), a measured *excess* of the thiosulphate is added and then the uncombined excess of the latter determined by means of decinormal iodine V. S., using starch as indicator.

Estimation of Iron in the Ferric State.—This method is based on the fact that ferric salts when added to a solution of potassium iodide (free from iodate) in the presence of hydrochloric acid liberate an equivalent quantity of iodine, which is dissolved by the excess of potassium iodide present and estimated as usual with decinormal sodium thiosulphate V. S. Ferrous salts may be estimated in this manner after having been previously oxidized to the ferric condition. All traces of such substances which liberate iodine, as chlorine, nitrous and nitric acids, must be removed from the solution. The reaction is as follows:

$$* \ FeCl_3 + KI = FeCl_2 + KCl + I.$$

Ferric Chloride. Ferrous Chloride. 125.89
161.04 (55.5 parts Fe).

Since 125.89 parts of iodine are liberated by 161.04 parts of ferric chloride containing 55.5 parts of metallic iron, 12.589 Gm. of iodine or 1000 Cc. of $\frac{N}{10}$ iodine V. S. correspond to 16.104 Gm. of anhydrous ferric chloride or 5.55 Gm. of metallic iron.

One Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (containing 0.024646 Gm.) is equivalent to 1 Cc. of $\frac{N}{10}$ iodine V. S. (containing 0.012589 Gm.); this, in turn, represents 0.00555 Gm. of metallic iron, or 0.016104 Gm. of anhydrous ferric chloride.

Sodium Thiosulphate.	Iodine.	Metallic Iron.	Ferric Chloride.
246.46 Gm. =	125.89 Gm. =	55.5 Gm. =	161.04 Gm.
24.646 " =	12.589 " =	5.55 " =	16.104 "
0.024646 " =	0.012589 " =	0.00555 " =	0.016104 " .

Since 1 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. represents 0.00555 Gm. of metallic iron in ferric salts, the equivalent quantity of each salt in question is readily ascertained. Thus, 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. is equivalent to:

Ferric chloride, Fe_2Cl_6,	0.016104 Gm.
" " cryst, $Fe_2Cl_6 + 12H_2O$,	0.026832 "
" citrate, $Fe(C_6H_5O_7)$,	0.024306 "
" ammonium sulphate, $Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$,	0.047869 "
" " " " dry,	0.026413 "
" nitrate, $Fe_2(NO_3)_6$,	0.024021 "
" oxide, Fe_2O_3,	0.007932 "
" sulphate, $Fe_2(SO_4)_3$,	0.019853 "

If a dry ferric salt is to be examined, from 0.2 to 0.5 Gm., or a molecular equivalent amount representing $\frac{1}{1000}$ part † of the molecular weight, is taken; as, for example, 0.161 Gm. of ferric chloride, or 0.24 Gm. of ferric nitrate, or 0.198 Gm. of ferric sulphate. If the quantity of metallic iron present is desired, then either 0.555 or 0.0555 Gm. are taken. In the former case each 1 Cc. of the standard V.S. represents 10 per cent. of the salt; while in the latter, either 1 or 10 per cent. of metallic iron.

Ferric Chloride ($FeCl_3$ or Fe_2Cl_6).—Of the *dry salt* 0.555 Gm. are taken for the metallic iron estimation, and 0.16104 Gm. for the real ferric chloride present; and of the *solution* or liquor, double the given quantities. In the latter case each 1 Cc. of the thiosulphate will represent 0.5 per cent. of metallic iron.

$$* \text{ Or } Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

322.08 (2 × 55.5 Fe) 2 × 125.89
161.04 (55.5 Fe) 125.89

$$FeC_6H_5O_7 + KI + 3HCl = FeCl_2 + KCl + H_3C_6H_5O_7 + I.$$

243.06 (55.5 Fe) 125.89

† $\frac{1}{1000}$ part of the molecular weight if the ferric salt is formulated as Fe^{III} (for example, $FeCl_3$), or $\frac{1}{2000}$ part if $Fe_2{}^{VI}$ (as Fe_2Cl_6).

Example: 0.555 Gm. of a sample of the hydrated salt was dissolved in 10 Cc. of water contained in a glass-stoppered vial (100 Cc.); then 2 Cc. of concentrated hydrochloric acid were added, followed by 1 Gm. of potassium iodide; the vial was securely stoppered in the usual manner and then kept for fully half an hour at 50° C. After cooling and shaking, the stopper was removed, rinsed off into the vial, and decinormal sodium thiosulphate V. S. added, under constant agitation, until the mixture assumed a yellow color, when about 1 Cc. of starch paste was added, and then the thiosulphate solution until the blue color was discharged. For this purpose 25 Cc. of the standard solution were required. Since 0.555 Gm. of the sample requires, if absolute, 100 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S, one Cc. (0.00555 Gm. Fe), which is the $\frac{1}{100}$ part, will represent 1 per cent. of metallic iron; 25 Cc. therefore represent 25 per cent. of metallic iron present in the sample.

Example: 2.0 Gm. of a sample of liquor ferri chloridi were mixed with 15 Cc. of water, 2 Cc. of hydrochloric acid, and 1 Gm. of potassium iodide in a 100 Cc. glass-stoppered vial and treated as above directed. Thirty Cc. of a solution of sodium thiosulphate (1 Cc. = 0.0102 Gm. iodine) were required for decolorization. Then:

$$\frac{30 \times 0.0102 \times 55.5}{125.89} = 0.01349 \text{ Gm. Fe, or } 6.74+ \text{ per cent.}$$

Ammonio-ferric Sulphate ($Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$).

Example: 0.4787 Gm. of a sample of ammonio-ferric alum was weighed into the vial and dissolved in 15 Cc. of water; then 2 Cc. of concentrated hydrochloric acid and 1 Gm. of potassium iodide were added, and after properly securing the stopper, the vial and contents were heated for fully half an hour at 50° C. When cold, the stopper was removed, rinsed off into the vial, and the free iodine estimated as usual with $\frac{N}{10}$ $Na_2S_2O_3$ V. S.; in this instance 10 Cc. of the standard solution were required, which corresponded to 100 per cent. purity, as will be seen from the following:

$$\underset{957.38\ (2 \times 55.5\ \text{Fe}).}{Fe_2(NH_4)_2(SO_4)_4 + 24H_2O} + 2KI + 8HCl = \underset{2 \times 125.89}{I_2} + 2NH_4Cl + 2FeCl_2 + 2KCl + 4H_2SO_4 + 24H_2O.$$

Since 2 × 125.89 parts of iodine are liberated by 957.38 parts of ferric alum, then one atom of iodine, or 125.89 parts, will represent 478.69 parts $\left(\frac{957.38}{2}\right)$ of ferric alum; the 125 89 parts of iodine are represented by 246.46 parts of sodium thiosulphate. Thus:

	Sodium Thiosulphate.	Iodine.	Iron Alum.	Metallic Iron.
	246.46 Gm.	= 125.89 Gm.	= 478.69 Gm.	= 55.5 Gm.
1 L. $\frac{N}{10}$ V. S.	= 24.646 "	= 12.589 "	= 47.869 "	= 5.55 "
1 Cc. $\frac{N}{10}$ V. S.	= 0.024646 "	= 0.012589 "	= 0.047869 "	= 0.00555 "

1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (0.024646 Gm.) = 0.047869 Gm. Iron Alum.
100 Cc. " " (2.4646 Gm.) = 4.7869 Gm. " "

If 4.7869 Gm., or $\frac{1}{100}$ of the molecular equivalent, of the sample were taken, then 1 Cc. of decinormal thiosulphate V. S. would correspond to $\frac{1}{100}$ part, or 1 per cent.; but owing to the large volume of the standard solution required in such a case, $\frac{1}{1000}$ part of the molecular equivalent, or 0.4787 Gm. (0.47869), is taken; hence each 1 Cc. of the standard solution added would then correspond to 10 per cent. of pure ammonio-ferric alum.

The percentage of metallic iron present is calculated as follows: If 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 0.00555 Gm. Fe, 10 Cc. would represent 10 × 0.00555 or 0.0555 Gm. Fe, which corresponds to 11.6 per cent. of metallic iron.

$$0.0555 \text{ Gm. Fe} : 0.4787 \text{ Gm. Salt} :: x : 100; \quad x = 11.6.$$

Example: 0.57 Gm. of ammonio-ferric alum, after treating as in the preceding examples, required 10 Cc. of a solution of sodium thiosulphate, 1 Cc. of which corresponded to only 0.0015 Gm. of iodine. Then $\frac{10 \times 0.0015 \times 55.5}{125.89} = 0.06612+$ Gm. of metallic iron, which is equivalent to 11.6 per cent. in the sample.

Reduced Iron.—0.555 Gm. of reduced iron is dissolved in from 15 to 25 Cc. of diluted sulphuric acid contained in a small flask; then a dilute solution (5 : 1000) of potassium permanganate is slowly added, shaking constantly, until a faint but permanent rose tint results. The ferrous sulphate is thereby oxidized to ferric sulphate; then in order to remove the excess of permanganate, a few drops of alcohol are added and the mixture shaken until colorless. The mixture is then transferred to a graduated cylinder, rinsing the flask with distilled water until the volume measures exactly 100 Cc. Of this fluid, which has been thoroughly mixed, 10 Cc., representing 0.0555 Gm. of the sample, are transferred to a 100 Cc. glass-stoppered vial. One Gm. of potassium iodide, with 1 Cc. of hydrochloric acid, are added, and, after securely closing, the mixture is allowed to digest for half an hour at 50° C.; after cooling, the quantity of liberated iodine is estimated as directed in the preceding examples, each 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. being equivalent to 0.00555 Gm., or 10 per cent., of metallic iron.

This same iodometric method may be applied as a check to the permanganate process as given on page 97. The solution remaining after the completion of the titration with $\frac{N}{10}$ $KMnO_4$ V. S. is decolorized by the addition of a few drops of alcohol; then 1 Gm. of potassium iodide is added and the mixture digested at 50° C. for half an hour. After cooling, the quantity of liberated iodine is estimated as usual, each 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. consumed indicating 10 per cent. of metallic iron.

Solutions of Ferric Salts.—The procedure in the estimation of the percentage of metallic iron in solutions of ferric salts is identical in each case as follows: 1.110 Gm. (double $\frac{1}{100}$ of the molecular equivalent, $2 \times 55.5 \div 100$) of the fluid are weighed into a glass-stoppered vial of 100 Cc. capacity, 15 Cc. of water and 2 Cc. of concentrated hydrochloric acid added, followed by 1 Gm. of potassium iodide, and, after securing the stopper, the mixture is kept for half an hour on a water-bath at a temperature of 50° C. After cooling, the vial is shaken and the stopper removed and rinsed back into the solution; decinormal sodium thiosulphate V. S. is now added under constant agitation until the fluid has assumed a deep yellow; then, after adding 1 Cc. of starch paste, the addition of the thiosulphate solution is continued until the blue color is discharged. Each cubic centimeter of the volumetric solution consumed represents 0.5 per cent. of metallic iron. For example:

$$\underset{\text{Ferric Citrate}}{FeC_6H_5O_7} + KI + 3HCl = \underset{\text{Citric Acid}}{H_2C_6H_5O_7} + \underset{\text{Ferrous Chloride}}{FeCl_2} + KCl + \underset{125.89}{I}.$$

125.89 Gm. of iodine represent 55.5 Gm. of Fe contained in the ferric citrate
0.012589 Gm. " " (1 Cc. $\frac{N}{10}$ V. S.) represents 0.00555 Gm. Fe.
1 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (1 Cc. $\frac{N}{10}$ iodine V. S.) represents 0.00555 Gm. Fe.

If 0.555 Gm. of the solution was taken, then each 1 Cc. of volumetric solution consumed would represent (0.00555 Gm.) $\frac{1}{100}$ part or 1 per cent. of metallic iron; but owing to the dilution of these solutions, *twice* this molecular equivalent quantity—that is, 1.110 Gm.—are taken; then each 1 Cc. of added volumetric solution represents $\frac{1}{200}$ part, or 0.5 per cent., of metallic iron.

SOLUTIONS (U.S.P.).	GRAMS TAKEN	Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. REQUIRED.
FERRIC ACETATE,	1.110	15 about
" CHLORIDE,	"	26
" CITRATE,	"	15
" NITRATE,	"	2.8
" SUBSULPHATE,	"	27.2
" TERSULPHATE,	"	16
TINCTURE FERRIC CHLORIDE,	"	9.4

Separation of Iron by Ether Extraction.—This method of Rothe * serves as a very convenient means for the separation of iron from copper, manganese, nickel, aluminum, cobalt, chromium, titanium, and vanadium. It is based upon the ready solubility of ferric chloride in ether in the presence of hydrochloric acid, while the chlorides of the other metals are insoluble under these conditions.

Five Gm. of the sample of iron or steel or material containing iron are accurately weighed and dissolved in about 40 Cc. of concentrated hydrochloric acid contained in a platinum dish (porcelain will answer); the resulting solution is evaporated to dryness and heated for about two hours in an air-bath at 120° C.; to the residue is then added 20 Cc. of hydrochloric acid, the mixture heated to boiling, and, after diluting with 60 Cc. of hot water, the separated silica or graphite, if present, is filtered off. The precipitate and filter are thoroughly washed with boiling water in order to remove all adhering traces of ferric chloride; the filtrate and washings are evaporated in a porcelain dish until the vapors of hydrochloric acid gas begin to appear; then 10 Cc. of hydrochloric acid are added and approximately from 2 to 2.5 Cc. of nitric acid (sp. gr. 1.40), drop by drop, keeping the capsule covered with a clock-glass until the completion of the oxidation, which is readily noted by the change in color of the solution from a black to red. After rinsing off the clock-glass into the solution, the latter is evaporated to syrupy consistence in order to remove all traces of chlorine and nitric acid, which react upon the ether. The resulting solution of the metallic chlorides, which measures about 10 Cc., is then transferred to a separatory flask (page 86), rinsing the capsule with a little hydrochloric acid; this is extracted by thoroughly agitating with at least three separate portions of 50 Cc. each of ether. The mixed ether extracts are placed in a flask, the ether recovered by distillation, and the residue, which consists of ferric chloride, is estimated as already described.

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* Mittheilungen aus den Königh. tech. Versuchsanstalten 10, 132.

Estimation of Free Chlorine or Bromine.—The previously described iodometric methods are adapted to the estimation of all substances containing free chlorine or bromine. The substance is weighed off and added to the solution containing a slight excess of potassium iodide, whereupon the free chlorine or bromine present liberates an equivalent quantity of iodine from the potassium iodide, which, in turn, is estimated by means of decinormal thiosulphate V. S. Thus:

$$\underset{2 \times 35.18}{2Cl} + 2KI = 2KCl + \underset{2 \times 125.89}{2I}.$$

35.18 parts of chlorine are equivalent to 125.89 parts of iodine.
0.003518 " " " " 0.012589 " "

Since 1 Cc. of $\frac{N}{10}$ sodium thiosulphate V. S. (0.024646 Gm.) is equivalent to 0.012589 Gm. of iodine, and as this is equivalent to 0.003518 Gm. of chlorine, then 1 Cc. of the decinormal thiosulphate V. S. is equivalent to 0.003518 Gm. of chlorine. From the previous argument it follows that 1 Cc. of decinormal sodium thiosulphate is likewise equivalent to 0.007934 Gm. of bromine:

$$\underset{2 \times 79.34}{2Br} + 2KI = 2KBr + \underset{2 \times 125.89}{2I}.$$

79.34 parts of bromine are equivalent to 125.89 parts of iodine.
0.007934 " " " " 0.012589 " "

Chlorine Water.—

Example: 17.59 Gm. of a sample of chlorine water were added to a solution of 1 Gm. of potassium iodide in about 20 Cc of water; to the resulting deep red liquid, which should be thoroughly shaken to facilitate the completion of the reaction and solution of the liberated iodine, $\frac{N}{10}$ $Na_2S_2O_3$ V. S was slowly added under constant agitation until the mixture was completely decolorized. For the inexperienced it is advisable to add 1 Cc. of starch paste to the iodide solution and continue titration until the blue color disappears. For this titration 20 Cc of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. were required.

As already noted in previous examples, a quantity representing $\frac{1}{100}$ or $\frac{1}{1000}$ part of the molecular weight of the substance is taken in order to avoid unnecessary calculation, for each 1 Cc. of the standard solution added would then represent 1 or 10 per cent. of the active substance. Owing to the high dilution of chlorine water, one-half of the full molecular equivalent quantity which enters into reaction is taken; that is, one-half of 35.18, or 17.59 Gm. If 35.18 Gm. were taken, an unnecessarily large volume of standard thiosulphate would be required.

Had we taken 35.18 Gm. of the solution, then 100 Cc. of the decinormal thiosulphate (equivalent to 0.3518 Gm. Cl) would represent $\frac{1}{100}$ part, or 1 per cent., and 1 Cc. of the standard solution (equivalent to 0.003518 Gm. Cl) would represent $\frac{1}{10000}$ part, or 0.01 per cent.

Since 17.59 Gm. of the solution were taken, then 100 Cc. of $\frac{N}{10}$ thiosulphate V. S. (equivalent to 0.3518 Gm. Cl) $= \frac{1}{50}$ part, or 2 per cent. of chlorine.

1 Cc. of $\frac{N}{10}$ thiosulphate V. S. (equivalent to 0.003518 Gm. Cl) $= \frac{1}{5000}$ part, or 0.02 per cent. of chlorine.

Having added, in the above example, 20 Cc. of $\frac{N}{10}$ thiosulphate V. S., the percentage of chlorine present would be equivalent to 20 × 0.02, or 0.4 per cent.

The solution contains, therefore, 0.4 per cent. by weight of chlorine gas.

Chlorinated Lime ($CaOCl_2$).—The value of this product depends solely upon the percentage of available chlorine present; that is, chlorine which is liberated upon the addition of an acid. Thus:

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2.$$

A solution of the weighed amount of substance is added to an excess of potassium iodide, followed by hydrochloric acid; the chlorine which is liberated reacts upon the iodide, setting free an equivalent quantity of iodine, which is estimated by means of sodium thiosulphate solution in the usual manner.

$$(a)\ Cl_2 + 2KI = 2KCl + I_2.$$
$$(b)\ I_2 + 2Na_2S_2O_3 . 5H_2O = 2NaI + Na_2S_4O_6 + 5H_2O.$$

Example: 0.3518 Gm. of a sample of chlorinated lime was thoroughly triturated with 50 Cc. of water and carefully transferred, together with the washings, into a flask, and then about 1 Gm. of potassium iodide; after solution had taken place, 5 Cc. of diluted hydrochloric acid were added. After shaking the mixture thoroughly for a few minutes, decinormal sodium thiosulphate V. S. was slowly added until the red-brown colored solution changed to a yellow; then, after adding 1 Cc. of starch paste, the addition of the standard solution was continued until the blue color was discharged. For this purpose 30 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. were required.

Since 246.46 Gm. $Na_2S_2O_3$ = 125.89 Gm. I = 35.18 Gm. Cl.
2.4646 Gm. " = 1.2589 Gm. I = 0.3518 Gm. Cl.
Then 100 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (0.24646 Gm.) = 0.3518 Gm. Cl.
1 Cc. " " " (0.024646 Gm.) = 0.003518 Gm. Cl.

Having taken $\frac{1}{100}$ part of the molecular equivalent quantity of the sample expressed in chlorine value,—that is, 0.3518 Gm.,—then each 1 Cc. of decinormal thiosulphate V. S. added would represent 0.003518 Gm., or $\frac{1}{100}$ part, or 1 per cent., of chlorine present. Having consumed 30 Cc. of the standard solution, the sample must therefore contain 30 per cent. of available chlorine.

Solution of Chlorinated Soda.—

Example: Of a solution of chlorinated soda (Labarraque's Solution) or chlorinated potassa (Javelle water) 7.036 Gm.,* or one-twentieth of the molecular equivalent quantity of the sample (expressed in chlorine units), was taken for assay. This was added to a solution of 2 Gm. of potassium iodide in 50 Cc. of water; then 10 Cc. of hydrochloric acid, and. after thoroughly mixing, decinormal sodium thiosulphate was slowly run in under constant agitation until the red brown color of the mixture changed to yellow; after adding 1 Cc. of starch paste, the addition of the standard decinormal thiosulphate was continued until the blue color of the mixture was discharged. Fifty Cc. of the volumetric solution were consumed in this operation.

If $\frac{1}{100}$ part of the molecular equivalent quantity (0.3518 Gm.) had been taken, then each 1 Cc. of the thiosulphate (0.003578 Gm.) consumed would represent $\frac{1}{100}$ part, or 1 per cent; but since the solution should contain only 2.6 per cent. of available chlorine, this quantity would be too small for an estimation. Most convenient is a quantity representing twenty times the usual $\frac{1}{100}$ molecular equivalent, or 7.036 Gm. Then each 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. consumed would represent 0.05 per cent. of available chlorine.

1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. = 0.003518 Gm. Cl.
100 Cc. " " " = 0.3518 Gm. "
1000 Cc. " " " = 3.518 Gm. "
2000 Cc. " " " = 7.036 Gm. "

If 7.036 Gm. of substance has been taken from assay, then 1 Cc. of thiosulphate V. S. (0.003518 Gm. Cl) would represent $\frac{1}{2000}$ part, or 0.05 per cent. of available chlorine.

Having added 50 Cc. of the standard solution, then 50 × 0.05, or 2.5 per cent., represents the chlorine strength of the solution.

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* About 6.7 Cc., for 1 Cc. : 1.052 Gm. : : x : 7.036; $x = 6.7$ Cc.

CHAPTER IV.

ANALYSIS BY PRECIPITATION.

The following methods of analysis are based upon the precipitation of the substance to be estimated, through the addition of a standard solution of a precipitant, the termination of the reaction being ascertained by either of the following methods:

(*a*) *Completion of Precipitation.*—The standard solution is added, under constant agitation, until precipitation ceases. This method is of limited application, owing to the slowness with which precipitates in general subside; the necessary conditions are fulfilled in the estimation of silver and chlorine, where the precipitate of silver chloride, from its curdy nature, has a tendency to ball up and quickly subside, leaving a clear supernatant fluid, in which any further reaction may be readily observed.

(*b*) *Formation of Precipitate.*—The estimation of cyanides by standard silver nitrate, and chlorine by mercuric nitrate, is carried out by adding the standard solution to the clear solution of the substance until the first appearance of a precipitate.

(*c*) *Indicator.*—The majority of these precipitation methods are carried out in the presence of an inorganic indicator which reacts with the added reagent, producing a colored precipitate upon the termination of the reaction. For example, yellow potassium chromate unites with the added standard silver solution with the production of red silver chromate which remains permanent when the last trace of substance has been precipitated.

ESTIMATION OF COMBINED HALOGENS, THEIR ACIDS AND SILVER.

These estimations may be carried out either with standard solutions of silver nitrate and sodium chloride without an indicator in acid solution, or with an indicator in neutral solution, or by the method of Volhard, in which standard solutions of silver nitrate and ammonium thiocyanide are employed in conjunction with ammonio-ferric alum as indicator.

1. Gay Lussac's Method.

Estimations of this class are carried out in hot solutions slightly acidulated with nitric acid; this is necessary because of the failure of the precipitates of silver halides to completely settle from neutral solution, thereby masking the end-reaction—that is, the completion of precipitation. In the estimation of silver, the standard solution of sodium chloride is added to the solution of the former slightly acidulated with nitric acid (free from nitrous) and contained in a glass-stoppered vial which is heated from time to time on a water-bath ; after each addition of the standard solution, the mixture is thoroughly shaken until the precipitate settles leaving a clear supernatant fluid. The addition of the sodium chloride is continued until no further precipitate is produced. The estimation of the halogen acids and their salts is carried out in exactly the same manner, employing standard decinormal silver nitrate V. S. ; the acids are neutralized with an alkali, and again made acid with a few drops of nitric acid. The calculations are exactly the same as given in the following method of Mohr, which is given the preference:

2. Mohr's Method.

This is only applicable in *neutral* solution, and the presence of such bases as barium, lead, bismuth, etc., which unite with the indicator (potassium chromate), forming insoluble compounds, must be avoided. The completion of precipitation is accurately fixed through the production of a permanent bright red precipitate of silver chromate, which is readily seen either by natural or artificial light.

In these estimations the following solutions are necessary :

DECINORMAL SILVER NITRATE VOLUMETRIC SOLUTION.

$AgNO_3 = 168.68$.

1000 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. contains 16.868 Gm. $AgNO_3$.

This solution is prepared by weighing 16.868 Gm. of pure cryst. silver nitrate taken from a sample which has been previously pulverized and heated at 120° C. for fifteen minutes, and dissolving in sufficient distilled water to make 1000 Cc., observing the proper precautions as to temperature (p. 11). As a precaution it is advisable to standardize this solution with a $\frac{N}{10}$ sodium chloride V. S., proceeding as directed in the general directions for the estimation of haloid salts on page 142. Each 1 Cc. of the silver solution should be equivalent to 1 Cc. of the sodium chloride solution.

Silver solutions should be preserved away from the access of light.

One Cubic Centimeter of Decinormal Silver Nitrate V. S. is the equivalent of:

	GRAMME.
Silver Nitrate, $AgNO_3$,	0.016868
Ammonium Bromide, NH_4Br,	0.009727
Ammonium Chloride, NH_4Cl,	0.005311
Calcium Bromide, $CaBr_2$,	0.009924
Ferrous Bromide, $FeBr_2$,	0.010709

	Gramme.
Ferrous Iodide, FeI_2,	0.015364
Hydrocyanic Acid, absolute, HCN, with indicator,	0.002683
Hydrocyanic Acid, absolute, HCN, to first formation of precipitate,	0.005366
Hydriodic Acid, HI,	0.012689
Hydrobromic Acid, HBr,	0.008034
Lithium Bromide, LiBr,	0.008631
Potassium Bromide, KBr,	0.011816
Potassium Chloride, KCl,	0.007400
Potassium Cyanide, KCN with indicator,	0.006465
Potassium Cyanide, KCN, to first formation of precipitate,	0.012930
Potassium Iodide, KI,	0.016471
Potassium Sulphocyanate, KSCN,	0.009648
Sodium Bromide, NaBr,	0.010222
Sodium Chloride, NaCl,	0.005806
Sodium Iodide, NaI,	0.014877
Strontium Bromide, $SrBr_2 + 6H_2O$,	0.01764555
Strontium Bromide, $SrBr_2$ (anhydrous),	0.01228815
Strontium Iodide, SrI (anhydrous),	0.01693365
Strontium Iodide, $SrI_2 + 6H_2O$,	0.0223
Zinc Bromide, $ZnBr_2$,	0.011179
Zinc Chloride, $ZnCl_2$,	0.006763
Zinc Iodide, ZnI_2,	0.015834

DECINORMAL SODIUM CHLORIDE VOLUMETRIC SOLUTION.

NaCl = 58.06.

1000 Cc. $\frac{N}{10}$ NaCl V. S. contains 5.806 Gm. NaCl.

This solution is prepared by dissolving 5.806 Gm. of *pure* sodium chloride in sufficient distilled water to make one liter, observing the usual precautions as to the selected standard temperature. *Pure sodium chloride* may be prepared by passing a current of dry hydrochloric acid gas into a saturated (filtered) aqueous solution of the purest commercial sodium chloride ; the separated crystalline precipitate is collected, washed several times with pure hydrochloric acid, and, after draining, is dried on a water-bath, after which it is finely pulverized and heated to low redness.

One cubic centimeter of Decinormal Sodium Chloride V. S. is the equivalent of :

	Gramme.
Sodium Chloride, NaCl,	0.005806
Silver, Ag,	0.010711
Silver Nitrate, $AgNO_3$,	0.016868
Silver Oxide, Ag_2O,	0.011505
Silver Sulphate, Ag_2SO_4,	0.015479

Potassium Chromate Test Solution (U.S.P.).

Dissolve 1 Gm. of potassium chromate (K_2CrO_4) in sufficient distilled water to make 10 Cc. Should chlorides be present, as is frequently the case, a few drops of silver nitrate solution should be added, and, after shaking, the solution is filtered.

Chlorides are tested for by adding silver nitrate solution to a little of the chromate T. S., and the red precipitate produced should be completely dissolved by nitric acid (absence of chlorides).

Procedure: In carrying out the analysis of soluble chlorides, bromides, and iodides, from 3 to 5 Gm.* of the well-dried salt are accurately weighed off, dissolved in sufficient distilled water to make exactly 100 Cc., and 10 Cc. of this, representing $\frac{1}{10}$ part (0.3 to 0.5 Gm.), are taken for analysis. This measured volume (10 Cc.) is transferred to a porcelain dish, or if a flask or beaker is selected, it should be placed upon a white surface; to this sufficient of the chromate solution is added to impart a pale yellow tint; then $\frac{N}{10}$ $AgNO_3$ V. S. is slowly added from a burette, stirring constantly until the mixture takes on a permanent red tint. Each addition of the standard silver solution produces a red precipitate of silver chromate ($K_2CrO_4 + 2\,AgNO_3 = Ag_2CrO_4 + 2KNO_3$); this, upon stirring, immediately disappears, owing to the interaction that takes place between the silver chromate and the halogen salt ($Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$). As soon as the last trace of halogen has been precipitated the next drop of the silver solution, reacting with the chromate indicator, produces a permanent red (precipitate) coloration. The reaction and calculation may be illustrated by the following equation:

$$\underset{168.68}{AgNO_3} + \underset{58.06}{NaCl} = AgCl + NaNO_3$$

If 168.68 parts of $AgNO_3$ are required for 58.06 parts of NaCl,
then 16.868 Gm. or 1000 Cc. $\frac{N}{10}$ $AgNO_3$ V.S. = 5.806 Gm. of NaCl;
0.016868 Gm. or 1 Cc. " " " = 0.005806 Gm. NaCl.

Therefore each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.005806 Gm. of sodium chloride or $\frac{1}{10000}$ molecular part of any alkali halogen salt.

The solutions to be titrated must be as near neutral as possible; acids should be absent because of their solvent action upon silver chromate, preventing thereby the end-reaction from being seen. Should acids be present, they must be carefully neutralized with sodium or calcium carbonate; excess of alkali should be avoided owing to precipitation of the added silver salt. Excessive alkalinity may be overcome by careful neutralization of the solution with acetic acid, using sensitive litmus paper as indicator.

Free halogen acids (HCl, HBr, HI) may be estimated by this method, which, however, presents no advantages over the methods of acidimetry except when non-halogen acids or acid salts are

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* Since the alkali chlorides are usually free from other halogen salts, $\frac{1}{1000}$ of the molecular equivalent quantity may be taken for analysis; each 1 Cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. consumed will correspond to 10 per cent. purity. The equivalent quantities would be: for NH_4Cl, 0.05311 Gm.; KCl, 0.074 Gm.; NaCl, 0.05806 Gm.; $ZnCl_2$, 0.06763 Gm.

present; in such cases this method is to be preferred. Before beginning titration the acid is weighed off, diluted with water, and carefully neutralized with sodium carbonate.

Estimation of Chlorides.—The alkali or alkali-earth or metallic chlorides rarely, if ever, contain other interfering haloid salts as impurities; hence their estimation is readily carried out. The operator should not fail to add sufficient acetic acid to neutralize any traces of either oxide or hydroxide which might possibly be present in the chlorides of the alkali earths.

Example.—0.6763 Gm. of a sample of zinc chloride was dissolved in sufficient distilled water to measure 100 Cc.; of this, 10 Cc., representing 0.06763 Gm., was accurately measured into a porcelain dish, and, after adding 2 drops of potassium chromate, 9.9 Cc. of $\frac{N}{10}$ Ag_2NO_3 V. S. were required to produce a permanent pale red color. The reaction and calculation are as follows:

$$\underset{2 \times 168.68}{2AgNO_3} + \underset{135.26}{ZnCl_2} = Zn(NO_3)_2 + 2AgCl.$$

Since 2 × 168.68 parts of $AgNO_3$ are equivalent to 135.26 parts of ZnCl,
then 168.68 " " " " " " 67.63 " " "
Or 1000 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (containing 16.868 Gm.) = 6.763 Gm. of $ZnCl_2$.
1 Cc. " " " (containing 0.016868 Gm.) = 0.006763 Gm. of $ZnCl_2$.

Having taken 0.06763 Gm., or $\frac{1}{1000}$ part, of the molecular equivalent quantity (of zinc chloride) for analysis, each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. added would correspond to 10 per cent. of absolute $ZnCl_2$ present; 9.9 Cc. would then represent 10 × 9.9 or 99 per cent. purity.

Indirect Estimation of the Alkalies as Chlorides.—Mohr has applied this method to the indirect estimation of the alkalies and alkali-earths in which the compound is converted into a chloride which is then estimated volumetrically. The compounds included under this head are the oxides, hydroxides, carbonates, and nitrates. The procedure is as follows: An accurately weighed quantity (0.5 to 1 Gm.) of the substance is dissolved in a small volume of water, and, after adding an excess (10 Cc.) of hydrochloric acid, the solution is evaporated to dryness on a water-bath; the residue is then subjected to a temperature of 120° C. in a drying oven for from one to two hours. In order to be certain of the thorough decomposition of the salt, the dry residue is again moistened with water and hydrochloric acid added, and the drying operation repeated. The dry residue consisting of the alkali (or alkali-earth) chloride is dissolved in sufficient distilled water to measure exactly 100 Cc., and of this an aliquot portion consisting of 10 Cc. (representing 0.05 to 0.1 Gm.) is accurately measured off for a chlorine estimation, which is carried out as already directed.

Chlorates may also be estimated in this manner after subjecting to strong ignition.

Organic salts such as acetates, tartrates, citrates, etc., are first ignited, whereby they undergo conversion into carbonates, which are then converted into chlorides as already explained. *Each 1 Cc. of*

$\frac{N}{10}$ $AgNO_3$ V. S. is equivalent to $\frac{1}{10000}$ of the hydrogen equivalent of each salt. For example: KCl = 0.0074 Gm. $KClO_3$ = 0.012164 Gm. K_2CO_3 = 0.006859 Gm. KOH = 0.00557 Gm. KNO_3 = 0.01004 Gm. $KHC_4H_4O_6$ = 0.01867 Gm. $K_3C_6H_5O_7$ = 0.010134 Gm.

Estimation of Chlorides (as $NaCl$) in Urine.—10 Cc. of the urine are measured into a Berlin porcelain capsule and about 1 Gm. of ammonium nitrate added; the solution is cautiously evaporated to dryness and slowly ignited until the residue has become charred, when, after cooling, the soluble chlorides are removed by washing with hot water. The mixed filtered filtrates, after neutralizing with acetic acid, are then titrated in the usual manner.

Estimation of Bromides and Iodides.—In the titrimetric estimation of alkali bromides and iodides we must take into consideration the presence of interfering chlorides which occur as impurities introduced through the bromine or iodine and the alkali carbonates or hydroxides from which these salts are prepared. If from the volume of the standard silver solution consumed we deduct that required were the sample absolutely pure, the difference in cubic centimeters would represent the corresponding amount of chloride present; this is then calculated into volume of silver solution representing bromide or iodide replaced by chloride.* The following examples will serve as illustrations:

Example: 0.5 Gm. of a sample of well-dried *potassium iodide* was dissolved in about 10 Cc. of distilled water, and, after adding 2 drops of potassium chromate solution, 30.54 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. were required for the production of a permanent red tint. Were the sample absolutely pure KI, then 30.36 Cc. of the standard silver solution would have been required, for:

$$\overset{KI}{164.71} : \overset{AgNO_3}{168.68} :: 0.5 : x;$$

x = 0.512051 Gm. $AgNO_3$, equivalent to 30.36 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S.

In this instance 30.54 Cc. of silver solution were consumed by an impure salt, and were it absolutely pure, only 30.36 Cc. would have been required; hence the difference, 0.18 Cc. (30.54 — 30.36), would represent the potassium chloride present, which is now calculated into volume of silver solution representing the quantity of potassium iodide replaced by the potassium chloride.

The molecular weight of KI is 164.71
" " " " KCl " 74.00
Difference, 90.71

Then as 164.71 : 90.71 : : x : 0.18 Cc., x = 0.326+ Cc.

A quantity of the iodide corresponding to 0.326+ Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. has been consumed by the chloride; hence the equivalent quantity of each of these present would be in

KI 0.016471 × 30.214 (30.54 Cc. — 0.326 Cc.) = 0.49765 Gm.
KCl 0.0074 × 0.326 = 0.00241 "
Total = 0.50007 Gm.

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* The salts included under this class are the bromides and iodides of potassium, sodium, ammonium, calcium, and strontium.

The sample contains, therefore, 0.49765 Gm., or 99.53 per cent., of pure iodide, and 0.00241 Gm., or 0.482 per cent., of chloride.

The standard limits of purity, after being set, are calculated as follows: If it has been decided to permit the presence of 0.5 per cent. of chlorides, then

99.5 parts of KI correspond to 101.90 parts of $AgNO_3$
0.5 part " KCl corresponds " 1.14 " " "
100.0 parts mixture correspond " 103.04 " " "

0.5 Gm. of the mixture would require 0.5152 Gm. $AgNO_3$, which is represented by 30.54 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. Therefore, 0.5 Gm. of a sample of 99.5 per cent. purity should require 30.54 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S.

Example: 3 Gm. of *ammonium bromide*, dried at 100° C., were dissolved in sufficient distilled water to measure exactly 100 Cc.; 10 Cc. of this, representing 0.3 Gm. of the salt, were drawn off into a porcelain capsule, and, after adding 2 drops of potassium chromate solution, 30.9 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. were required to produce a permanent red tint. Were the sample absolutely pure, 30.84 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. would have been required, for:

$$\overset{NH_4Br}{97.27} : \overset{AgNO_3}{168.68} :: 0.3 : x;$$

$x = 5.20242$ Gm. $AgNO_3$, equivalent to 30.84 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S.

Then 30.9 Cc. — 30.84 Cc. = 0.06 Cc.

The molecular weight of NH_4Br is 97.27
" " " " NH_4Cl " 53.11
Difference, 44.16

$$97.27 : 44.16 :: x : 06; \qquad x = 0.132 \text{ Cc.}$$

An amount of the bromide corresponding to 0.132+ Cc. of the silver solution has been consumed by the ammonium chloride; hence the proportion of each of these present would be:

$NH_4Br = 0.009727 \times 30.768$ (30.9 Cc. — 0.132 Cc.) = 0.29928 Gm.
$NH_4Cl = 0.005311 \times 0.132$ = 0.00070 "
Total, 0.29998 Gm.

The sample contains, therefore, 0.29928 Gm., or 99.76 per cent., of ammonium bromide.

Example: Zinc Iodide. Since this salt is usually free from more than traces of the other halogen salts, the estimation is made direct, according to the following equation:

$$\underset{2 \times 168.68}{2AgNO_3} + \underset{316.68}{ZnI_2} = 2AgI + Zn(NO_3)_2.$$

If 2 × 168.68 parts of $AgNO_3$ represent 316.68 parts of ZnI_2
168.68 " " " " 158.34 " " "
1000 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (16.868 Gm.) = 15.834 Gm. " "
1 Cc. " " " (0.016868 Gm.) = 0.015834 Gm. "

Then each 1 Cc. of standard silver solution consumed represents 0.015834 Gm. of zinc iodide.

Estimation of Hydrobromic and Hydriodic Acids.—While the estimation of hydrobromic and hydriodic acids may be carried out with standard solutions of the alkalies, this method is not applicable to the solutions of these acids which have been prepared by interaction between the alkali haloid and tartaric acid (Fothergill's method), owing to the presence of an unavoidable excess of the latter. Mohr's method is therefore to be preferred, and is carried out as follows: From 2 to 3 Gm. of a 10 per cent. solution of hydrobromic or hydriodic acid, or ten times this quantity of a 1 per cent. solution,—as, for example, a syrup,—are accurately weighed into a flask, and, after diluting slightly with distilled water if necessary, the solution is accurately neutralized with ammonia water. After adding 2 drops of potassium chromate solution and placing the flask on a white surface, $\frac{N}{10}$ $AgNO_3$ V. S. is added in portions, shaking after each addition until a permanent pink tint is produced. Some operators prefer to use magnesia milk ($MgO + H_2O$) in place of the aqua ammonia.

Each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. corresponds to 0.008034 Gm. of HBr and 0.012689 Gm. of HI.

Example: 30 Gm. of syrup of hydriodic acid were accurately neutralized with aqua ammonia, employing litmus paper to determine the neutral point; then, after adding two drops of potassium chromate solution, 25 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. were required to produce a permanent red tint. The equation is as follows:

$$\underset{168.68}{AgNO_3} + \underset{126.89}{NH_4I(HI)} = AgI + NH_4NO_3.$$

If 168.68 parts of $AgNO_3$ are equivalent to 126.89 of HI, then 16.868 Gm. or 1000 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. are equivalent to 12.689 Gm. HI. Or 1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (0.016868 Gm.) = 0.012689 Gm. HI; 25 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. = 25 × 0.012689 or 0.3172+ Gm. of HI, which corresponds to 1.06 per cent.

Estimation of Silver Salts by Means of Decinormal Sodium Chlorid V. S.—

One Cubic Centimeter of Decinormal Sodium Chloride V. S. is the equivalent of:

	GRAMME.
Sodium Chloride, NaCl,	0.005806
Silver, Ag,	0.010711
Silver Nitrate, $AgNO_3$,	0.016868
Silver Oxide, Ag_2O,	0.011505
Silver Sulphate, Ag_2SO_4,	0.015479

In the estimation of silver the preceding methods are reversed. An accurately weighed quantity (0.3 to 0.5 Gm.) of the silver salt or combination is dissolved in about 10 Cc. of distilled water, and, after adding 2 drops of the chromate indicator, decinormal sodium chloride V. S. is added, stirring constantly, until the red color of the mixture changes to a yellow. The end-point here is generally overreached, owing to the tardy decomposition of the silver chromate by the added sodium chloride; hence a measured excess volume of standard sodium chloride is added, followed by decinormal silver nitrate V. S., with constant stirring, until the mixture takes on a red color, when the volume of the latter, deducted from that of the former, gives the number of cubic centimeters of $\frac{N}{10}$ NaCl V. S. required for the complete precipitation of the silver.

Example: A sample of *Lunar Caustic* weighing 0.25 Gm. was dissolved in about 10 Cc. of distilled water and 2 drops of chromate indicator added, or sufficient to impart a distinct red color to the solution. Decinormal sodium chloride V. S. was then added slowly, under constant stirring, until the color of the mixture changed to a distinct yellow; 20 Cc. were required for this purpose. The excess of standard sodium chloride was then ascertained by titrating back with decinormal silver nitrate until the mixture changed to a red; for this purpose 6 Cc. were required.

Generally when the quantity of silver present is approximately known, a measured excess of the standard sodium chloride is added at once; then the chromate indicator, followed by the standard silver nitrate, until a red color is produced.

Volume of $\frac{N}{10}$ NaCl V. S. added . . . . 20 Cc. (being an excess).
" " $\frac{N}{10}$ $AgNO_3$ V. S. " . . . . 6 Cc.
Volume of $\frac{N}{10}$ NaCl V. S. required for complete precipitation of the silver in the sample. 14 Cc.

If 1 Cc. $\frac{N}{10}$ NaCl V. S. is equivalent to 0.016868 Gm. of silver nitrate, 14 Cc. would be equivalent to 0.236+ Gm; the sample, which weighs 0.25 Gm., would therefore contain 9.44+ per cent. of absolute silver nitrate.

3. Volhard's or Thiocyanide (Sulphocyanide) Method.

The objectionable features of the preceding method of Mohr, which necessitates working in neutral solution, also the exclusion of all substances which react with the potassium chromate indicator, are avoided in the following process of Volhard, which admits of great accuracy in the estimation of halogens either free or combined with alkalies or metals; further, the determination of silver and copper in the presence of various other metals. The silver and halogen titrations are carried out in the presence of nitric acid; hence the estimation of the latter in the presence of phosphoric or other acids which precipitate silver in neutral solution is made possible. In outline, the method is as follows: An accurately measured excess of $\frac{N}{10}$ $AgNO_3$ V. S. is added to the solution of the halogen or its salt acidified with nitric acid; the uncombined excess of silver solution is then estimated by titrating back with a standard decinormal potassium (or ammonium) thiocyanide V. S., employing 5 Cc. of a solution of ferric ammonium sulphate as indicator; the instant that the thiocyanide solution has precipitated the last trace of silver excess it strikes a reddish-brown color with the ferric indicator, due to the formation of ferric thiocyanide, $Fe_2(SCN)_6$.

The volume of standard silver solution originally added, less that of the thiocyanate consumed, will give the number of cubic centimeters of the former which were required for the precipitation of the halogen. For the beginner the terminal color reaction is at first somewhat difficult to fix; hence the liability to overstep the end-point with an excess of standard thiocyanide. But owing to the like equivalence of the standard silver and thiocyanide solutions (1 Cc. = 1 Cc.) this is readily controlled by adding $\frac{N}{10}$ $AgNO_3$ V. S. until the color disappears, then $\frac{N}{10}$ KSCN V. S. until the reddish-brown tint again reappears. From the sum total of the number of cubic centimeters of the silver solution added, the number of cubic centimeters of the cyanide solution required for titrating back are subtracted; the difference represents the volume of the former required for the precipitation of the halogen. The reactions are as follows:

$$(a)\ \underset{\substack{\text{Silver Nitrate.}\\ 168.68}}{AgNO_3} + \underset{\substack{\text{Potassium}\\ \text{Thiocyanide.}\\ 96.48}}{KSCN} = \underset{\substack{\text{Silver}\\ \text{Thiocyanide.}}}{AgSCN} + KNO_3.$$

$$(b)\ \underset{\substack{\text{Ferric Ammonium}\\ \text{Sulphate.}}}{Fe_2(SO_4)_3\,(NH_4)_2\,SO_4} + \underset{\substack{\text{Potassium}\\ \text{Thiocyanide.}}}{6KSCN} = \underset{\substack{\text{Ferric}\\ \text{Thiocyanide.}}}{Fe_2(SCN)_6{}^{*}} + (NH_4)_2SO_4 + 3K_2SO_4.$$

It will be seen in equation *a* that 168.68 parts of silver nitrate are equivalent to 96.48 parts of potassium thiocyanide; then 16.868 Gm. or 1000 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. = 9.648 Gm. or 1000 Cc. $\frac{N}{10}$ CNSK V. S.; or each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. is equivalent to 1 Cc. of $\frac{N}{10}$ CNSK V. S.

The following standard solutions are employed:

(*a*) **Decinormal Silver Nitrate Volumetric Solution** (page 140).

(*b*) Decinormal Potassium Thiocyanide Volumetric Solution.†

(Volhard's Solution.)

KSCN = 96.48.

1000 Cc. $\frac{N}{10}$ KSCN V. S. contains 9.648 Gm. of KSCN.

"Dissolve 10 Gm. of crystals of pure potassium sulphocyanide in 1000 Cc. of water.

"This solution is yet too concentrated, and has to be adjusted so as to correspond in strength exactly with decinormal silver nitrate V. S. For this purpose, introduce into a flask 10 Cc. of decinormal silver nitrate V. S. together with 0.5 Cc. of ferric ammonium sulphate solution and 5 Cc. of diluted nitric acid. To this mixture

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* Ferric thiocyanide may be written either as $Fe(SCN)_3$ or $Fe_2(SCN)_6$, upon the same grounds that we express ferric chloride either as $FeCl_3$ or Fe_2Cl_6.

† Ammonium thiocyanide (sulphocyanide) may be employed in place of the potassium salt. NH_4SCN = 75.59.

add, from a burette, in small portions at a time, the sulphocyanide solution. At first a white precipitate of silver sulphocyanide appears; then every drop falling from the burette is surrounded by a deep brownish-red color of ferric sulphocyanide, which disappears on vigorous shaking of the flask as long as any of the silver nitrate remains unchanged. When all the silver has been converted into sulphocyanide, a single additional drop of the potassium sulphocyanide solution produces a brownish-red color which no longer disappears on shaking, but communicates a perceptible pale brownish or reddish tint to the contents of the flask. Note the number of Cc. of the potassium sulphocyanide solution used, and dilute the whole of the remaining solution so that equal volumes of this and of the decinormal silver nitrate V. S. will be required to produce the permanent brownish or reddish tint. (The same depth of pale brownish or reddish tint to which the volumetric solution is adjusted must be attained when the solution is used for volumetric assays.)

"After the dilution, a new trial should be made, in which 50 Cc. of decinormal silver nitrate V. S., 2.5 Cc. of ferric ammonium sulphate T. S., and 25 Cc. of diluted nitric acid are used, and there should be required exactly 50 Cc. of the sulphocyanide solution to produce the same depth of a permanent pale brownish or reddish tint.

"If necessary, a new adjustment should be made, to render the correspondence perfect."—(U.S.P.)

This standard solution is very stable.

One Cubic Centimeter of Decinormal Potassium Thiocyanide V. S. is the equivalent of:

	GRAMME.
Potassium Thiocyanide, KSCN,	0.009648
Copper, Cu,	0.006310
Copper Sulphate, $CuSO_4 + 5H_2O$,	0.024785
Silver, Ag,	0.010711
Silver Nitrate, $AgNO_3$,	0.016868
Silver Sulphate, Ag_2SO_4,	0.015479

Indirectly the equivalents of $\frac{N}{10}$ $AgNO_3$ V. S. given in table on page 140

(*c*) **Indicator.**

This consists of a cold saturated aqueous solution of ferric ammonium sulphate $[Fe_2(SO_4)_3.(NH_4)_2SO_4 + 24H_2O]$. Owing to the presence of free nitric acid in the solutions to be titrated, and since it tends to prevent the formation of the red ferric thiocyanide, it is customary to employ an excess consisting of about 5 Cc. of the indicator for each titration. The addition of this colors the solution slightly, which, however, disappears upon acidifying with nitric acid.

(*d*) Nitric Acid C. P.

The nitric acid employed must be free from nitrous acid or the lower oxides of nitrogen, which may be removed by diluting the sample with about one-fourth its volume of water and boiling until colorless. Excepting in the case of iodides, the quantity of nitric acid added exerts no material influence upon the accuracy of the process; usually just sufficient is added to remove the yellow color of the solution produced by the indicator. The acid should be preserved away from the light.

The titrations must take place in *cold* solution, and the total volume may vary between 100 and 200 Cc. The solutions should be free from all traces of nitrous acid, which may be removed by evaporation.

Volhard's method for the determination of silver is especially advantageous, owing to the fact that the presence of other metals, with the exception of mercury, does not exert any disturbing influence on the reaction. These estimations are best carried out in a flask of from 150 to 250 Cc. capacity, placed on a sheet of white paper or a porcelain tile.

Estimation of Halogens.

In the estimation of chlorine and bromine, as well as their acids and soluble salts, 5 Cc. of the indicator are added to the solution of the substance, followed by sufficient nitric acid to effect decolorization; then, after adding the measured excess of standard silver solution, the titration is begun with the standard thiocyanide. On the other hand, in the estimation of iodides, the indicator is added *after* the precipitation of the iodine by the standard silver solution, owing to the fact that ferric salts liberate iodine from alkali iodides which reacts very slowly with the silver solution. Also excessive quantities of nitric acid should be avoided in the estimation of iodides.

In titrating back the excess of uncombined silver with thiocyanide solution, the mixture should be frequently shaken and the operation carried rapidly to completion. An interruption of the titration should be avoided owing to the slight reaction which takes place between the haloid silver salt and the silver thiocyanide. The addition of the standard thiocyanide V. S. to the mixture of the standard silver V. S. and substance being examined produces a reddish-brown cloud, which immediately disappears upon shaking, leaving a milk-like mixture; as the reaction nears its termination the precipitate becomes more flocculent and readily settles, when, upon its completion, the solution takes on a reddish-brown tint, which, after shaking, remains unchanged. The color lasts for about ten minutes.

The quantity of salt selected for analysis should weigh from 0.2 to 0.4 Gm. according to the comparative high or low molecular equivalence of the salt in question. Calculations may be avoided by employing a fractional molecular equivalent quantity of the haloid salt, wherein the number of cubic centimeters of the $\frac{N}{10}$ $AgNO_3$ V. S. consumed expresses directly the percentage of absolute salt present. However, this applies only to those haloid salts and acids which are practically free from other interfering halogens. As already explained (page 144), the bromides and iodides of potassium, sodium, ammonium, calcium, and strontium usually contain appreciable quantities of chlorides, which must be taken into consideration in the final calculations. Direct estimations are made in the following examples: If $\frac{1}{400}$ part of the molecular equivalent weight of such salts as NH_4Cl (0.13278 Gm.), KCl (0.185 Gm.), NaCl (0.14515 Gm.), or $\frac{1}{800}$ part of the molecular equivalent weight of the salts of bibasic metals, as $CaCl_2$ (0.1377 Gm.), $SrBr_2$ (0.30704 Gm.), SrI_2 dry (0.4234 Gm.), $ZnCl_2$ (0.1691 Gm.), $ZnBr_2$ (0.2795 Gm.), ZnI_2 (0.39585 Gm.), is taken, each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. consumed in titrating the given quantity will represent 4 per cent. purity or 25 Cc., an absolutely pure salt.

With solutions of halogen salts or acids which usually contain from 10 to 25 per cent. of active substance, $\frac{1}{100}$ part of the molecular equivalent weight of this in fluid is taken for analysis, and each 1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. consumed represents 1 per cent. of absolute pure salt or acid present; thus, HCl (0.3618 Gm.), HBr 10 per cent. sol. (0.8304 Gm.), HI 10 per cent. sol. (1.2689 Gm.), HI 1 per cent. sol. (12.689), and $\frac{1}{200}$ part of the molecular equivalent weight of the salts of diabasic metals, as $FeBr_2$ 10 per cent. sol. (1.071 Gm.), FeI_2 10 per cent. sol. (1.5364 Gm.), FeI_2 20 per cent. dry (1.5364 Gm.).

Such quantities of the salt or solution should be selected so as to avoid an excessive and unnecessary waste of silver solution. Where it is desirable to estimate very small amounts of a salt,—as, for example, 0.14515 Gm. of sodium chloride,—it is best to weigh off and dissolve 14.515 Gm. in distilled water, making the volume up to exactly 100 Cc.; of this solution, 1 Cc. is then accurately measured by means of a 1 Cc. pipette and transferred to the assay flask containing from 50 to 100 Cc. of distilled water. Like quantities of a fluid to be examined may be measured off as directed on page 72.

Example: 5 Cc. of *Hydrochloric Acid* of sp. gr. 1.150 were diluted to measure exactly 100 Cc.; 5 Cc. of this solution, representing 0.2875 Gm., were transferred to a flask (200 Cc.) containing about 50 Cc. of distilled water; and, after adding 5 Cc. of the indicator, sufficient nitric acid was added to decolorize the solution; this was followed by exactly 40 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S., which was slowly run in from a burette, shaking thoroughly. The unprecipitated excess of silver solution was then determined by adding $\frac{N}{10}$ KSCN V. S. in small portions at a time, shaking after each addition until the fluid retained a permanent reddish-brown tint; to accomplish this, 15 Cc. were consumed.

40 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., the added excess.
15 Cc. $\frac{N}{10}$ KSCN V. S. corresponding to unconsumed $\frac{N}{10}$ $AgNO_3$ V. S.
25 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., consumed by the 5 Cc. or 0.2875 Gm. of HCl.

Since 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. = 0.003618 Gm. of absolute HCl, 25 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. = 25 × 0.003618 or 0.09045 Gm. of absolute HCl contained in the 0.2875 Gm. of the sample, which would correspond to 31.46 per cent. strength. For:

$$\underset{\text{HCl}}{0.09045} : \underset{\text{Solution.}}{0.2875} :: x : 100 ;\ x = 31.46$$

The reactions are as follows:

$$(a)\ \underset{168.68}{AgNO_3} + \underset{36.18}{HCl} = AgCl + HNO_3.$$

If 168.68 parts of $AgNO_3$ correspond to 36.18 parts of absolute HCl,
16.868 Gm. " " (1000 Cc. $\frac{N}{10}$ V. S.) = 3.618 Gm. of absolute HCl
1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (0.016868 Gm.) = 0.003618 Gm. of absolute HCl.

$$(b)\ \underset{168.68}{AgNO_3} + \underset{96.48.}{KSCN} = AgSCN + KNO_3.$$

If 168.68 parts of $AgNO_3$ correspond to 96.48 parts of KSCN,
16.868 Gm. " " (1000 Cc. $\frac{N}{10}$ V. S.) = 9.648 Gm. or 1000 Cc. $\frac{N}{10}$ KSCN V. S.
1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (0.016868 Gm.) = 1 Cc. $\frac{N}{10}$ KSCN V. S. (0.009648 Gm.).

Example: An equivalent molecular quantity consisting of 2.795 Gm. of *Zinc Bromide* was dissolved in distilled water and the volume made up to measure 100 Cc.; 10 Cc. of this solution, representing 0.2795 Gm., were added to about 50 Cc. of water, followed by 5 Cc. of the indicator and sufficient nitric acid to decolorize. After adding a measured excess consisting of 30 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. and thoroughly shaking, 5.5 Cc. of $\frac{N}{10}$ KSCN V. S. were required to produce a permanent reddish-brown tint. Then

30 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., the added excess.
5.2 Cc. $\frac{N}{10}$ KSCN V. S., corresponding to unconsumed $\frac{N}{10}$ $AgNO_3$ V. S.
24.8 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., consumed by the $ZnBr_2$.

As a control over this titration, 5 Cc. more of the standard silver solution were added, whereby decolorization of the mixture took place; and for the restoration of the terminal color reaction 4.9 Cc. of the standard thiocyanide solution were required. Then

30 Cc. + 5 Cc. = 35 Cc. total $\frac{N}{10}$ $AgNO_3$ V. S.
5.2 Cc. + 4.9 Cc. = 10.1 Cc. " $\frac{N}{10}$ KSCN V. S.
24.9 Cc. " $\frac{N}{10}$ $AgNO_3$ V. S. consumed.

The average of these two estimations would be 24.8 + 24.9 ÷ 2 = 24.85 Cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Since each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents 4 per cent. of absolute $ZnBr_2$, then 24.85 Cc. would correspond to 4 × 24.85 or 99.4 per cent. purity.

The reaction and calculation are as follows:

$$\underset{2 \times 168.68}{2AgNO_3} + \underset{223.58.}{ZnBr_2} = 2AgBr + Zn(NO_3)_2.$$

If 2 × 168.68 parts of $AgNO_3$ represent 223.58 parts of $ZnBr_2$,
168.68 " " " " 111.79 " " "
1000 Cc. $\frac{N}{10}$ V. S. or 16.868 Gm. of $AgNO_3$ represent 11.179 Gm. of $ZnBr_2$
100 Cc. " " " 1.6868 Gm. " " " 1.1179 Gm. " "

Owing to the large volume of $\frac{N}{10}$ $AgNO_3$ V. S. which would be required for precipitation if 1.1179 Gm. of the zinc salt were taken, one-fourth of this amount, that is, 0.2795* Gm., suffices; and for the precipitation of this, 0.4217 Gm. $\left(\frac{1.6868}{4}\right)$ or 25 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. is necessary.

If the 0.2795 Gm. of zinc bromide was absolutely pure (100 per cent.), 25 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. would be required for complete precipitation ($25 \times 0.011179 = 0.2795$). Each 1 Cc. of the silver solution would then represent $\frac{100}{25}$, or 4 per cent., of absolute zinc bromide.

Example: A sample of syrup of *Ferrous Iodide* weighing 18.55 Gm. was diluted with distilled water to 100 Cc.; 10 Cc. of this, representing 1.855 Gm., were transferred to a flask containing 100 Cc. of water and $\frac{N}{10}$ $AgNO_3$ V. S. added in portions from a burette, with constant agitation, until the precipitate coagulated, showing that the silver was in excess; 15 Cc. were consumed. To this mixture 5 Cc. of the indicator were added, followed by just sufficient nitric acid to decolorize; then $\frac{N}{10}$ KSCN V. S. was slowly added from a burette, shaking constantly, until the mixture assumed a permanent reddish-brown tint; 5 Cc. of the standard sulphocyanide were consumed in the operation. Then 15 Cc. — 5 Cc. = 10 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. required for the precipitation of the iodine of the ferrous iodide. Since 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.015364 Gm. of FeI_2, 10 Cc. $= 10 \times 0.015364$ or 0.15364 Gm. of absolute ferrous iodide contained in 1.855 Gm. of the syrup, which corresponds to 8.37+ per cent. for:

$$\overset{FeI_2.}{0.15364\ \text{Gm.}} : \overset{\text{Syrup.}}{1.835\ \text{Gm.}} :: x : 100; \qquad x = 8.37+$$

The reaction is as follows:

$$\underset{2 \times 168.68}{2AgNO_3} + \underset{307.28}{FeI_2} = 2AgI + Fe(NO_3)_2.$$

If 2×168.68 parts of $AgNO_3$ represent 307.28 parts of FeI_2,
168.68 " " " 153.64 " " "
16.868 Gm. $AgNO_3$ (1000 Cc. $\frac{N}{10}$ V. S.) = 15.364 Gm. " "
1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. containing 0.016868 Gm. = 0.015364 Gm. FeI_2

Estimation of Metallic Silver (Ag = 107.11).

Volhard's method is adapted for the estimation of either pure silver or alloys of the same, provided that not more than 70 per cent. of copper is present, owing to the formation of a black cupric thiocyanide, which would mask the terminal color reaction. The presence of such metals as Pb, Cd, Bi, Zn, Fe, and Mn, which yield colorless solutions, does not interfere with the determination. Should nickel or cobalt be present in sufficient amount to impart a decided color to the solution of the alloy, it is best to proceed as directed under the analysis of silver alloy, page 154. The only metal which interferes with the determination of silver is mercury, which can be readily removed by heating to a sufficiently high temperature. The procedure is as follows: A quantity of the metal or alloy weighing between 0.3 and 0.4 Gm. is dissolved in about 8 Cc. of pure nitric acid (1.20 sp. gr.), and, after solution has taken place,

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* Rounded from 0.279475 Gm.

the fluid is heated sufficiently to remove all traces of nitrous acid. After cooling the solution is diluted with from 100 to 150 Cc. of water and 5 Cc. of the ferric indicator added; should this produce a coloration, nitric acid is added drop by drop, stirring, until this disappears. To the solution $\frac{N}{10}$ KSCN V. S. is slowly added from a burette, with constant agitation; each drop of the added reagent produces a red brown color, which disappears on shaking; as the reaction nears completion the precipitate of silver thiocyanide coagulates more readily, until finally the clear supernatant fluid takes on a permanent pale reddish-brown tint. Each 1 Cc. of the $\frac{N}{10}$ KSCN V. S. consumed is equivalent to 0.010711 Gm. of metallic silver.

Example: A piece of silver alloy weighing 0.351 Gm. was dissolved in pure nitric acid, boiled, and diluted to 150 Cc.; then 5 Cc. of ferric indicator were added and 8 Cc. of nitric acid for decolorization. For the complete precipitation of the silver 30 Cc. of $\frac{N}{10}$ KSCN V. S. were required. Since 1 Cc. of the thiocyanide solution represents 0.010711 Gm. of metallic silver, 30 Cc. would be equivalent to 30 × 0.010711 or 0.32133 Gm., or 91.54+ per cent. of silver in the alloy.

In the estimation of a copper silver alloy which contains more than the 70 per cent. limit of copper, a silver solution of known strength is added to the solution of the alloy until the percentage of copper has been reduced below the limit; then the titration is carried on with the standard thiocyanide in the usual manner. Allowance is made for the added silver by calculating it into cubic centimeters of standard thiocyanide solution, which is then deducted from the total volume of the latter consumed; the difference corresponds to the metallic silver in the original sample.

Estimation involving an Empirical Solution: A piece of silver alloy (containing an excess of copper) weighing 0.436 Gm., after dissolving and diluting as already directed, was treated with 15 Cc. of a silver solution (each 1 Cc. = 0.01748 Gm. $AgNO_3$ or 0.0111 Gm. Ag). After thoroughly mixing, a $\frac{N}{10}$ KSCN V. S. (1 Cc. = 0.010711 Gm. Ag) was added until a permanent reddish-brown tint was produced, 20.60 Cc. being consumed for this purpose. The 15 Cc. of silver solution added (1 Cc. = 0.0111 Gm. Ag) correponds to $\frac{15 \times 0.0111}{0.010711} = 15.55$ Cc. of $\frac{N}{10}$ KSCN V. S. (1 Cc. = 0.010711 Gm. Ag); then for the precipitation of the original silver (of the alloy) there has been consumed 20.60 — 15.55 = 5.05 Cc. of decinormal thiocyanide V. S.

Since 1 Cc. of $\frac{N}{10}$ KSCN V. S. = 0.010711 Gm. Ag, 5.05 Cc. would represent 5.05 × 0.010711 or 0.05409 Gm., corresponding to 12.4 per cent. of metallic silver in the sample.

Estimation of Metallic Copper (Cu = 63.1).

This method is based upon the observation that potassium thiocyanide precipitates copper quantitatively from its boiling solution in the presence of a reducing agent (SO_2) as cuprous thiocyanide according to the following equation:

$$\underset{\substack{2 \times 158.45 \\ (2 \times 63.1\ Cu)}}{2CuSO_4} + \underset{2 \times 96.48}{2KSCN} + SO_2 + 2H_2O = Cu_2(SCN)_2 + K_2SO_4 + 2H_2SO_4.$$

An accurately measured excess of the $\frac{N}{10}$ KSCN V. S. is added to the copper solution and the uncombined excess estimated by titrating back with a $\frac{N}{10}$ $AgNO_3$ V. S. Each 1 Cc. of $\frac{N}{10}$ KSCN V. S. consumed represents 0.00631 Gm. of metallic copper. The equivalence calculation is, according to the above equation:

2 × 96.48 parts of KSCN represents 2 × 63.1 parts of Cu.
96.48 " " " " 63.1 " " "
1000 Cc. $\frac{N}{10}$ V. S. containing 9.648 Gm. KSCN = 6.31 Gm. Cu.
1 Cc. $\frac{N}{10}$ KSCN V. S. containing 0.009648 Gm. = 0.00631 Gm. Cu.

If halogens, silver, or mercury are present, this method is not available. The operation is carried out as follows:

A sample of metallic copper or an alloy weighing from 0.3 to 0.5 Gm. is dissolved in pure nitric (or H_2SO_4) acid; the resulting solution is heated sufficiently to remove the excess of acid and nitrous oxides; then, after diluting with about 100 Cc. of water, it is rinsed into a flask the neck of which is graduated at 500 Cc. This solution is carefully neutralized with sodium carbonate (free from chloride) until a slight precipitate of basic copper salt begins to form; to this sufficient sulphurous acid solution is now added to impart, after shaking, a strong odor to the fluid; the precipitated copper is thereby redissolved. This solution is heated to boiling and an excess of $\frac{N}{10}$ KSCN V. S. slowly added, each addition producing a dark green coloration, due to the formation of cupric thiocyanide, which disappears upon agitation, with the formation of a white precipitate of cupr*ous* thiocyanide. The addition of the standard thiocyanide solution is continued until no further coloration * is produced at the point of contact of the reagent and the fluid; then a few more cubic centimeters are added in order to constitute an excess, and the volume of thiocyanide solution consumed is accurately noted. The solution with precipitate is allowed to cool, and is then diluted to measure exactly 500 Cc. After thoroughly shaking, this is filtered through a dry plaited filter into a dry flask, and an aliquot portion—for example, 100 Cc. (representing one-fifth of the total quantity of the metal taken)—is transferred to a flask or beaker for final titration. To the clear solution, 10 Cc. of the ferric indicator are added, and some nitric acid, followed by $\frac{N}{10}$ $AgNO_3$ V. S., added slowly, with frequent agitation, until the solution has become colorless—that is, until it is in slight *excess;* the volume consumed is noted; finally the excess of added

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* Should iron be present in the alloy, it will cause a like coloration, even after the complete precipitation of the copper. In such a case a few drops of the clear fluid are transferred to a test-tube, and, after adding a drop of the standard thiocyanide solution, the mixture is warmed; any fresh precipitation may then be readily noted. The tested fluid is then rinsed back into the original solution.

silver solution is determined by titrating back with $\frac{N}{10}$ KSCN V. S. until a permanent brownish-red tint is produced.

The volume of silver solution added, less the unprecipitated excess, corresponding to the Cc. of $\frac{N}{10}$ KSCN V. S. finally added, is deducted from the volume of thiocyanide solution originally added; the difference represents the volume of the latter required for the precipitation of the copper. The result, multiplied by 5, will represent the total pure copper present.

Example: 0.201 Gm. of a copper nickel alloy (a nickel coin) was dissolved in nitric acid, boiled, diluted, neutralized, treated with sulphurous acid, and an excess consisting of 30 Cc. of $\frac{N}{10}$ KSCN V. S. added; after diluting to 500 Cc., one-fifth, or 100 Cc., of the filtrate were taken for titration. For the precipitation of the excess of the thiocyanide solution an excess consisting of 4.3 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. was added; and for titrating back the excess of this latter, 2.5 Cc. of $\frac{N}{10}$ KSCN V. S. were consumed.

Thus:
4.3 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., excess added.
2.5 Cc. $\frac{N}{10}$ KSCN V. S., corresponding to unconsumed excess of silver solution.
1.8 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. represent the excess of $\frac{N}{10}$ KSCN V. S. which has not been consumed by the copper.
6.0 Cc. $\frac{N}{10}$ KSCN V. S., one-fifth of total original volume added.
1.8 Cc. $\frac{N}{10}$ $AgNO_3$ V. S., representing excess of $\frac{N}{10}$ KSCN V. S.
4.2 Cc. $\frac{N}{10}$ KSCN V. S., corresponding to Cu in 100 Cc. solution.
4.2 Cc. × 5 = 21 Cc. " " " " 500 Cc. "

If 1 Cc. $\frac{N}{10}$ KSCN V. S. represents 0.00631 Gm. Cu, 21 Cc. would represent 21 × 0.00631, or 0.13251 Gm., corresponding to 65.9+ per cent. of metallic copper in the alloy.

Estimation involving Empirical Solutions: To the neutralized solution of 0.253 Gm. of a copper nickel alloy, an excess consisting of 40 Cc. of a potassium sulphocyanide solution (1 Cc. = 0.0103 Gm. Ag) was added. After diluting the mixture to 500 Cc., and filtering, 100 Cc. of the filtrate were taken for assay; to this, 4 Cc. of a silver nitrate solution (1 Cc. = 0.0111 Gm. Ag) were added, and for titrating back the unconsumed excess of this silver solution, 1.7 Cc. of the above-mentioned potassium thiocyanide solution were required. The 4 Cc. of silver solution added to the filtrate (100 Cc.) correspond to $\frac{4 \times 0.0111}{103} = 4.31$ Cc. of the thiocyanide solution; then for the precipitation of the excess of the thiocyanide in the 100 Cc. of filtrate 4.31 — 1.7 = 2.61 Cc. of a thiocyanide solution, corresponding to a silver solution of like titer, were necessary. The total excess of KSCN solution for the 500 Cc. would be 5 × 2.61, or 13.05 Cc.; then for the precipitation of the total copper present 40 — 13.05 = 26.95 Cc. of thiocyanide solution were consumed, which represent $\frac{26.95 \times 0.0103 \times 63.1}{107.11} = 0.1635+$ Gm., or 64.3+ per cent., of metallic copper present in the sample.

Copper Sulphate ($CuSO_4 + 5H_2O$).—For the estimation of this salt 0.5 Gm. is dissolved in about 100 Cc. of water, which is heated to boiling and sulphurous acid added until in excess. A measured excess of $\frac{N}{10}$ KSCN V. S. is now added to the hot solution and the analysis continued as directed on page 154.

According to the equation on page 154, each 1 Cc. of $\frac{N}{10}$ KSCN V. S. (containing 0.009648 Gm.) is equivalent to 0.00631 Gm. Cu, or 0.024785 Gm. of $CuSO_4 + 5H_2O$.

ESTIMATION OF HYDROCYANIC ACID OR ALKALI CYANIDES.

Volhard's method is also applicable to the estimation of hydrocyanic acid and soluble cyanides; however, owing to the readiness with which the precipitated cyanide and thiocyanide of silver react upon one another during the titration, it is necessary to remove the precipitate of silver cyanide by filtration before titrating back the excess of uncombined silver. This inconvenience is avoided in the direct method of Liebig or that of Vielhaber with the chromate indicator.

(A) Titration to First Formation of a Precipitate.

$$1\text{ Cc. }\frac{N}{10}\ AgNO_3\text{ V. S. is equivalent to }\left\{\begin{array}{l}0.01293\text{ Gm. KCN.}\\ 0.009742\text{ Gm. NaCN.}\\ 0.005366\text{ Gm. HCN.}\end{array}\right.$$

This method of Liebig is based on the fact that when a standard solution of silver nitrate is added to an *alkaline* solution of a cyanide or hydrocyanic acid, the precipitate which first forms redissolves on stirring so long as any traces of unchanged cyanide remain; the alkali cyanide and silver nitrate react, with the formation of a soluble double cyanide of silver and alkali.

$$\begin{array}{ccccccc} 2KCN & + & AgNO_3 & = & AgCN\,.\,KCN & + & KNO_3. \\ \text{Potassium Cyanide.} & & \text{Silver Nitrate.} & & \text{Double Cyanide of Silver} & & \\ 2 \times 64.65 & & 168.68 & & \text{and Potassium.} & & \\ (2 \times 26.83\ HCN) & & & & & & \end{array}$$

The instant the last trace of cyanide has been converted into a double salt, the slightest excess of silver causes a decomposition of this, with the formation of a precipitate of silver cyanide which constitutes the terminal point in the reaction. Thus:

$$AgCN\,.\,KCN + AgNO_3 = 2AgCN + KNO_3.$$

According to the preceding equation this terminal point is reached when *two* molecules of the alkali cyanide have reacted with *one* molecule of silver nitrate.

168.68 parts of $AgNO_3$ represent 129.3 p. KCN, or 97.42 p. NaCN, or 53.66 p. HCN.
16.868 Gm. " " (1000 Cc. $\frac{N}{10}$ V. S.) = 12.93 Gm. KCN, or 9.742 Gm. NaCN, or 5.366 Gm. HCN.
1 Cc. $\frac{N}{10}$ $AgNO_3$ (containing 0.016868 Gm.) = 0.01293 Gm. KCN, or 0.009742 Gm. NaCN, or 0.005366 Gm. HCN.

If quantities representing an aliquot ($\frac{1}{100}$) part of each salt in question are weighed off for analysis (for example, 1.293 Gm. KCN, or 0.9742 Gm. NaCN), then each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. consumed would represent the $\frac{1}{100}$ part, or 1 per cent., of absolute salt. But in order to avoid the unnecessary waste of silver solution, half of these quantities are taken—namely, 0.6465 Gm. KCN, or 0.4871 Gm. NaCN; then each 1 Cc. of the silver solution consumed will represent 2 per cent. of absolute salt present.

The solution of the salt to be estimated should show an alkaline reaction to litmus paper; also during the titration the solution should be tested from time to time, for should it assume an acid reaction, sodium hydroxide solution must be added until alkaline. This is necessary owing to the liberation of nitric acid, which, from its solvent action, prevents the precipitation of the silver cyanide.

Example: 6.465 Gm. of *potassium cyanide* were dissolved in water and the volume made up to 100 Cc.; 10 Cc. of this solution, representing 0.6465 Gm., after diluting with a little water, were transferred to a flask (100 Cc.) and $\frac{N}{10}$ $AgNO_3$ V. S. slowly added, with constant agitation, until the precipitate, which at first redissolved on agitation, became permanent; 45 Cc. were required. Since each 1 Cc. of the standard silver represents 2 per cent. of pure KCN, then 45 Cc. would represent (2 × 45) 90 per cent. purity

Hydrocyanic Acid: Owing to the poisonous characters of this solution, also in order to avoid loss through handling, it is advisable to pour from 5 to 10 Cc. from the accurately tared vial and contents direct into a flask containing a solution of sodium hydroxide; after again weighing, the quantity of added acid is accurately fixed. The volume of alkali employed should be sufficient to neutralize the acid and leave the solution slightly (not excessively) alkaline. This is now diluted to measure 100 Cc., and 10 Cc., representing one-tenth of the added quantity of acid, is measured into about 100 Cc. of water contained in a flask and $\frac{N}{10}$ $AgNO_3$ V. S. slowly added, under agitation, occasionally testing the solution so as to preserve its alkalinity, until a slight permanent precipitate remains after agitation. The number of cubic centimeters of the $\frac{N}{10}$ $AgNO_3$ V. S. consumed, multiplied by 0.005366 × 10, will indicate the weight of absolute HCN contained in the original sample taken. The method of Vielhaber is generally preferred as being more convenient of application.

(B) Titration with Indicator (Vielhaber).

$$1 \text{ Cc. } \frac{N}{10} AgNO_3 \text{ V. S. is equivalent to } \begin{cases} 0.006465 \text{ Gm. KCN.} \\ 0.004871 \text{ Gm. NaCN.} \\ 0.002683 \text{ Gm. HCN.} \end{cases}$$

This method, which is especially adapted for the examination of hydrocyanic acid or solutions containing it,—as bitter almond water, cherry laurel water, bitter almond oil (natural), etc.,—consists in adding sufficient magnesia paste * to impart an opaque milkiness to the solution of the substance; this is followed by a few drops of potassium chromate indicator; then $\frac{N}{10}$ $AgNO_3$ V. S. is added, with constant agitation, until the mixture assumes a permanent red tint. The magnesia paste serves to neutralize the hydrocyanic acid as

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* Prepared by triturating heavy magnesia (calcined) with sufficient water to form a thick paste.

well as to afford the operator, because of its milky opacity, a ready means of distinguishing the end-reaction.

Each 1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. is equivalent to 0.006465 Gm. KCN, or 0.004871 Gm. NaCN, or 0.002683 Gm. HCN. It will be seen that the equivalence of the standard silver solution, when employed in conjunction with an indicator, is *one-half* that of Liebig's method (A).

The reactions are the same as in the preceding method, but the terminal point is reached only after the *completion* of the decomposition of the double cyanides of potassium * and silver, when the next drop of silver solution, which is in excess, reacts with the potassium chromate with the formation of the red silver chromate.

$$\underset{\substack{2 \times 64.65 \\ (2 \times 26.83\ HCN)}}{2KCN} + \underset{168.68}{AgNO_3} = AgCN \, . \, KCN + KNO_3.$$

$$AgCN \, . \, KCN + AgNO_3 = 2AgCN + KNO_3.$$

2 mol. $AgNO_3$ or 2 × 168.68 parts are equivalent to 2 mol. or 2 × 64.65 parts of KCN (or 2 × 26.83 parts of HCN or 2 × 48.71 parts of NaCN).

1 mol. $AgNO_3$ or 168.68 parts = KCN 64.65 parts = HCN 26.83 parts = NaCN 48.71 parts.

1000 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (containing 16.868 Gm.) = KCN 6.465 Gm. = HCN 2.683 Gm. = NaCN 4.871 Gm.

1 Cc. $\frac{N}{10}$ $AgNO_3$ V. S. (containing 0.016868 Gm.) = KCN 0.006465 Gm. = HCN 0.002683 Gm. = NaCN 0.004871 Gm.

Example: A volume of *hydrocyanic acid* measuring approximately 2 Cc. was poured from its container into a graduated and stoppered cylinder containing about 80 Cc. of water; after mixing, the volume was made up to exactly 100 Cc. The vial containing the hydrocyanic acid was accurately weighed before and after pouring out the desired quantity; the difference amounted to 2.173 Gm. Of this diluted solution, 10 Cc., representing 0.2173 Gm. of the sample, were measured by means of a pipette directly into a flask (100 Cc.) containing about 10 Cc. of magnesia paste; then, after adding 2 or 3 drops of potassium chromate solution, $\frac{N}{10}$ $AgNO_3$ V. S. was slowly added, with constant shaking, until the mixture assumed a permanent red tint; 16 Cc. of the standard solution were consumed in this instance.

If 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. is equivalent to 0.002683 Gm. of absolute HCN, 16 Cc. would represent 16 × 0.002683, or 0.042928 Gm., or 1.97+ per cent.

The sample contains, therefore, 1.97+ per cent. of absolute hydrocyanic acid.

Potassium and sodium cyanides may be estimated in the same manner, employing the magnesia mixture only for keeping the solution neutral during the titration. If 0.32325 Gm. of KCN and 0.2436 Gm. of NaCN are taken for analysis, then each 1 Cc. of $\frac{N}{10}$ $AgNO_3$ V. S. consumed will represent 2 per cent. purity.

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* For the sake of uniformity and clearness, potassium is retained in the explanatory formulæ instead of magnesium.

CHAPTER V.

ESTIMATION OF PHENOL AND VOLUMETRIC ESTIMATION OF FERMENTABLE SUGARS.

ESTIMATION OF PHENOL (Koppeschaar).

This method for the quantitative volumetric estimation of phenol is based upon the fact that when an excess of bromine is added to an aqueous or weak hydro-alcoholic solution of phenol, the latter is precipitated as an insoluble tri-brom-phenol; thus:

$$\underset{\text{Bromine.}}{6Br} + \underset{\text{Phenol.}}{C_6H_5OH} = \underset{\text{Tri-brom-phenol.}}{C_6H_2Br_3OH} + \underset{\text{Hydrobromic Acid.}}{3HBr.}$$

The operation in general consists in adding a measured excess of standard bromine solution to the solution of the phenol to be estimated; the excess of the standard solution which has *not* combined with the phenol is then ascertained by adding potassium iodide and titrating the free iodine, which has been liberated through the action of the bromine, by means of a standard decinormal sodium thiosulphate.

Owing to the loss in titer which would occur in handling a standardized bromine water from a burette, Koppeschaar devised a method for preparing this in which bromine is liberated in the nascent condition through interaction between solutions of sodium bromate, bromide, and hydrochloric acid according to the equation:

$$\underset{\substack{\text{Sodium}\\\text{Bromide.}}}{5NaBr} + \underset{\substack{\text{Sodium}\\\text{Bromate.}}}{NaBrO_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{6HCl} = 6NaCl + 3H_2O + \underset{\text{Bromine.}}{3Br_2.}$$

In order to standardize this extemporaneously prepared bromine solution, potassium iodide is added to the solution, whereby a molecular equivalent quantity of iodine is liberated for each molecule of bromine present; thus:

$$2KI + \underset{2 \times 79.34}{Br_2} = 2KBr + \underset{2 \times 125.89.}{I_2.}$$

The quantity of iodine liberated is now estimated by means of $\frac{N}{10}$ $Na_2S_2O_3$ V. S., each cubic centimeter of which represents 0.012589 Gm. of iodine, which, in turn, has been liberated by an equivalent molecular quantity of bromine—that is, 0.007934 Gm.

Thus:

Br_2 is equivalent to I_2, which is equivalent to $2(Na_2S_2O_3.5H_2O)$.
2 × 79.34 parts are equivalent to 2 × 125.89 parts, equivalent to 2 × 246.46 parts.
79.34 " " " " 125.89 " " " 246.46 "

1000 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S. containing 24.646 Gm. represents 12.589 Gm. of Iodine, which, in turn, represents 7 934 Gm. of Bromine (1000 Cc. of $\frac{N}{10}$ Bromine V. S.).
Then 1 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. (containing 0.024646 Gm.) will represent 0.007934 Gm. or 1 Cc. of $\frac{N}{10}$ Bromine V. S.

Decinormal Bromine Volumetric Solution.

(Koppeschaar's Solution.)

Br = 79.34.
1000 Cc. $\frac{N}{10}$ Bromine V. S. contains 7.934 Gm. of Bromine.

This is prepared as directed by the U. S. P. as follows:

"Dissolve 3 Gm. of sodium bromate and 50 Gm. of sodium bromide (or 3.2 Gm. of potassium bromate and 50 Gm. of potassium bromide) in enough water to make, at or near 15° C. (59° F.), 900 Cc. Of this solution transfer 20 Cc., by means of a pipette, into a bottle having a capacity of about 250 Cc., provided with a glass stopper; add 75 Cc. of water, next 5 Cc. of pure hydrochloric acid, and immediately insert the stopper. Shake the bottle a few times, then remove the stopper just sufficiently to quickly introduce 5 Cc. of potassium iodide T. S., taking care that no bromine vapor escape, and immediately stopper the bottle. Agitate the bottle thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water so that the washings flow into the bottle, and then add from a burette decinormal sodium hyposulphite V. S. until the iodine tint is exactly discharged, using toward the end a few drops of starch T. S. as indicator. Note the number of cubic centimeters of the sodium hyposulphite V. S. thus consumed, and then dilute the bromine solution so that equal volumes of it and of decinormal sodium hyposulphite V. S. will exactly correspond to each other under the conditions mentioned above.

"*Example:* Assuming that the 20 Cc. of the bromine solution have required 25.2 Cc. of the hyposulphite to completely discharge the iodine tint, the bromine solution must be diluted in the proportion of 20 to 25.2. Thus, if 850 Cc. of it are remaining, they must be diluted with water to measure 1071 Cc.

"After the solution is thus diluted, a new trial should be made in the manner above described, in which 25 Cc. of the decinormal sodium hyposulphite V. S. should exactly discharge the tint of the iodine liberated by the bromine set free from the 25 Cc. of bromine solution.

"Keep the solution in dark amber-colored, glass-stoppered bottles."

One Cubic Centimeter of Decinormal Bromine Solution V. S. is the equivalent of:

	GRAMME.
Bromine, Br,	0.007934
Carbolic Acid, C_6H_5OH,	0.0015547

For, according to the equation:

$$\underset{6 \times 79.34}{6Br} + \underset{93.28}{C_6H_5OH} = C_6H_3Br_3OH + 3HBr.$$

If 6 × 79.34 parts of Bromine are equivalent to 93.28 parts of Phenol,
79.34 " " " " " 15.547 " "
7.934 Gm. Br (1000 Cc. $\frac{N}{10}$ V.S.) " " " 1.5547 Gm. "
1 Cc. $\frac{N}{10}$ Bromine V. S. (0.007934 Gm.) = 0.0015547 Gm. of Phenol.

As an example illustrating the application of this method the following valuation of the U. S. Pharmacopœia is given: "Dissolve 1.555 Gm. (1.5547) of the Carbolic Acid to be valued in a sufficient quantity of water to make 1000 Cc. Transfer 25 Cc. of this solution (containing 0.03888 Gm. of the acid) to a glass-stoppered bottle having a capacity of about 200 Cc., add 30 Cc. of bromine decinormal volumetric solution (which is 5 Cc. more than would be required if the carbolic acid in the solution were absolute phenol, the excess being added to promote the formation and separation of tri-brom-phenol), then 5 Cc. of hydrochloric acid, and immediately insert the stopper. Shake the bottle repeatedly in the course of half an hour, then remove the stopper just sufficiently to introduce quickly 5 Cc. of a 20 per cent. aqueous solution of potassium iodide, being careful that no bromine vapor escapes, and immediately stopper the bottle. Shake the latter thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water, so that the washings may flow into the bottle, and then add, from a burette, sodium thiosulphate decinormal V. S., until the iodine tint is exactly discharged, using toward the end a few drops of starch test-solution as indicator. Note the number of cubic centimeters of sodium thiosulphate decinormal V. S. consumed. Deduct this from 30 (the number of cubic centimeters of bromine volumetric solution originally added), and multiply the remainder by 4. The product will approximately represent the percentage of absolute Phenol in the Carbolic Acid tested." Each cubic centimeter of the volumetric solution corresponds to 4 per cent. of absolute Phenol.

Example: A few drops of a sample of Phenol weighing 1.84 Gm. were dissolved in 1000 Cc. of water, and, after thoroughly mixing, 25 Cc. containing 0.046 Gm. of the sample were placed in a glass-stoppered vial and 30 Cc. of $\frac{N}{10}$ Bromine V. S. added, followed by 5 Cc. of hydrochloric acid; after introducing the KI solution, 3.2 Cc. of $\frac{N}{10}$ $Na_2S_2O_3$ V. S. were required for the decolorization of the liberated iodine, then :

30 Cc. $\frac{N}{10}$ Bromine V. S., the added excess.
3.2 Cc. $\frac{N}{10}$ $Na_2S_2O_3$ V. S., corresponding to the unconsumed excess of $\frac{N}{10}$ Bromine V. S.
26.8 Cc. $\frac{N}{10}$ Bromine V. S. consumed by the Phenol.

Since 1 Cc. $\frac{N}{10}$ Bromine V. S. is equivalent to 0.0015547 Gm. Phenol, 26.8 Cc. would represent 26.8 × 0.0015547, or 0.04166+ Gm., of absolute Phenol in the sample of 0.046 Gm., which corresponds to 90.58 per cent. purity.

VOLUMETRIC ESTIMATION OF FERMENTABLE SUGARS.

The following method of Pavy is adapted for the rapid and accurate estimation of lactose (milk-sugar), glucose, maltose, invert sugar, and glucose in diabetic urine.

Owing to the difficulty encountered in accurately fixing the end-point reaction and the experience necessary in fulfilling all conditions required for exact determinations, the original Fehling's volumetric method has been largely replaced by Pavy's modification, which is based on the decolorizing power of sugar solutions on an ammoniacal cupric tartrate solution. The end-point is very sharp and cannot be overrun.

Pavy's Standard Ammoniacal Cupric Tartrate V. S.

This may be prepared either by mixing 120 Cc. of Fehling's solution with 300 Cc. of aqua ammonia (sp. gr. 0.880) adding 100 Cc. of a 10 per cent. solution of sodium hydroxide, and diluting to one liter; or—

A cold solution of 21.6 Gm. of cryst. Rochelle Salt, and 18.4 Gm. of sodium hydroxide (or 25.8 Gm. of KOH) in about 300 Cc. of distilled water, are added to a solution of 4.157 Gm. of pure cryst. cupric sulphate in about 200 Cc. of distilled water; then 300 Cc. of aqua ammonia (sp. gr. 0.880) and sufficient water are added to bring the volume up to exactly 1000 Cc.

100 Cc. of Pavy's Solution (Equivalent to 10 Cc. Fehling's Solution) are completely reduced by:

Glucose,	0.0500 Gm.	(Levulose).
Cane-sugar,	0.0475 Gm.	(after inversion).
Milk-sugar,	0.0678 Gm.	(Lactose).
Maltose,	0.0807 Gm.	
Starch,	0.0450 Gm.	(after inversion).

Owing to the readiness with which the ammoniacal copper solution undergoes oxidation from contact with the air, the titration is carried out in a short wide-necked flask which contains 100 Cc. of the standard solution; the surface of this is then covered with a layer (about 5 mm. deep) of fused paraffin. To this standard solution, which is kept at boiling temperature while titrating, the solution of the sugar to be examined is added from a burette in portions of about 1 Cc. at a time, waiting a short interval before adding a second portion; this procedure is continued until the blue color of the standard solution has been discharged. A second estimation should be made and nearly the entire volume of the sugar added at once; then in small portions until decolorization is complete. The volume of sugar solution added contains 0.05 Gm. of glucose or a corresponding equivalent amount of any of the above-mentioned sugars. The saccharine solutions to be examined must be of neutral or alkaline reaction; if not they should be rendered so by the addition of a solution of sodium hydroxide. In estimating the *lactose* of milk the albuminoids must first be removed, which may be accomplished by either of the following methods: (*a*) The method of Ritthausen consists in adding about 10 Cc. of a 10 per cent. solution of cupric sulphate to 10 Cc. of the milk, which has been diluted to about 200 Cc.; this is followed by a solution of sodium hydroxide the quantity of which added is somewhat *less* than that necessary to precipitate the entire copper as hydroxide. The precipitate of cupric hydroxide and albuminoids is filtered off and thoroughly washed with water until all traces of sugar have been removed from the precipitate; the filtrate and washings, which should contain some free copper, are made up to a definite volume (400 to 500 Cc.) and an aliquot volume (100 Cc.) taken for analysis. (*b*) This method consists in precipitating 10 Cc. of the sample, diluted to 200 Cc., with a solution of lead acetate, removing the excess of lead (with albuminoids) by the addition of a solution of sodium sulphate. The precipitate is thoroughly washed with water until all traces of sugar have been removed, then the filtrate and washings are diluted to the volume of 300 to 400 Cc. and an aliquot volume (100 Cc.) taken for analysis.

For the estimation of sugar in diabetic *urine* 10 Cc. of a clear sample of the latter are diluted with water to 200 Cc.; a burette is filled with this solution, which is slowly added to the boiling Pavy-Fehling solution until the color is discharged. For example, 50 Cc. of the diluted urine were required to reduce the 100 Cc. of standard copper solution equivalent to 0.05 Gm. of glucose. Since the urine was diluted twenty times its volume, the 50 Cc. would have contained 2.5 Cc. of the original samples; therefore 2.5 Cc. contained 0.05 Gm. of sugar, or 20 parts are contained in 1000.

APPENDIX.

TABLE OF ATOMIC WEIGHTS.

Including Only the More Important Elements in Common Use Based on H = 1.000.

Aluminum,	Al,	26.9
Antimony,	Sb,	119.5
Arsenic,	As,	74.45
Barium,	Ba,	136.4
Bismuth,	Bi,	206.5
Boron,	B,	10.9
Bromine,	Br,	79.34
Cadmium,	Cd,	111.55
Calcium,	Ca,	39.8
Carbon,	C,	11.9
Chlorine,	Cl,	35.18
Chromium,	Cr,	51.7
Cobalt,	Co,	58.55
Copper,	Cu,	63.1
Fluorine,	F,	18.9
Gold,	Au,	195.7
Hydrogen,	H,	1.000
Iodine,	I,	125.89
Iron,	Fe,	55.5
Lead,	Pb,	205.36
Lithium,	Li,	6.97
Magnesium,	Mg,	24.1
Manganese,	Mn,	54.6
Mercury,	Hg,	198.5
Molybdenum,	Mo,	95.3
Nickel,	Ni,	58.25
Nitrogen,	N,	13.93
Oxygen,	O,	15.88
Phosphorus,	P,	30.75
Platinum,	Pt,	193.4
Potassium,	K,	38.82
Selenium,	Se,	78.6
Silicon,	Si,	28.2
Silver,	Ag,	107.11
Sodium,	Na,	22.88
Strontium,	Sr,	86.95
Sulphur,	S,	31.83
Tin,	Sn,	118.1
Zinc,	Zn,	64.9

MULTIPLES OF SOME ATOMIC AND MOLECULAR WEIGHTS IN FREQUENT USE. (H = 1.)

H	1	2	3	4	5	6	7	8	9	H
O	15.88	31.76	47.64	63.52	79.40	95.28	111.16	127.04	142.92	O
OH	16.88	33.76	50.64	67.52	84.40	101.28	118.16	135.04	151.92	OH
H_2O	17.88	35.76	53.64	71.52	89.40	107.28	125.16	143.04	160.92	H_2O
N	13.93	27.86	41.79	55.72	69.65	83.58	97.51	111.44	125.37	N
NH_2	15.93	31.86	47.79	63.72	79.65	95.58	111.51	127.44	143.37	NH_2
NH_3	16.93	33.86	50.79	67.72	84.65	101.58	118.51	135.44	152.37	NH_3
NH_4	17.93	35.86	53.79	71.72	89.65	107.58	125.51	143.44	161.37	NH_4
NO_2	45.69	91.38	137.07	182.76	228.45	274.14	319.83	365.52	411.21	NO_2
NO_3	61.57	123.14	184.71	246.28	307.85	369.42	430.99	492.56	554.13	NO_3
C	11.9	23.8	35.7	47.6	59.5	71.4	83.3	95.2	107.1	C
CO_3	59.54	119.08	178.62	238.16	297.70	357.24	416.78	476.32	535.86	CO_3
CN	25.83	51.66	77.49	103.32	129.15	154.98	180.81	206.64	232.47	CN
Cl	35.18	70.36	105.54	140.72	175.90	211.08	246.26	281.44	316.62	Cl
Br	79.34	158.68	238.02	317.36	396.70	476.04	555.38	634.72	714.06	Br
I	125.89	251.78	377.67	503.56	629.45	755.34	881.23	1007.12	1133.01	I
S	31.83	63.66	95.49	127.32	159.15	190.98	222.81	254.64	286.47	S
SO_4	95.35	190.70	286.05	381.40	476.75	572.10	667.45	762.80	858.15	SO_4
PO_4	94.27	188.54	282.71	377.08	471.35	565.62	659.89	754.16	848.43	PO_4
Na	22.88	45.76	68.64	91.52	114.40	137.28	160.16	183.04	205.92	Na
K	38.82	77.64	116.46	155.28	194.10	232.92	271.74	310.56	349.38	K
H	1	2	3	4	5	6	7	8	9	H

LIST

OF THE

MORE IMPORTANT ELEMENTS AND CHEMICALS EMPLOYED IN VOLUMETRIC ANALYSIS

TOGETHER WITH THEIR

ATOMIC OR MOLECULAR WEIGHTS.

		H = 1.
Acid, Acetic,	$HC_2H_3O_2$,	59.56
" Arsenous,	As_2O_3,	196.54
" Benzoic,	$HC_7H_5O_2$,	121.06
" Boric,	H_3BO_3,	61.54
" Carbolic,	C_6H_5OH,	93.28
" Carbonic (anhydride),	CO_2,	43.66
" Chromic,	CrO_3,	99.34
" Citric,	$H_3C_6H_5O_7 + H_2O$,	208.44
" " dry,	$H_3C_6H_5O_7$,	190.56
" Gallic,	$HC_7H_5O_5 + H_2O$,	186.58
" " dry,	$HC_7H_5O_5$,	168.70
" Hydriodic,	HI,	126.89
" Hydrobromic,	HBr,	80.34
" Hydrochloric,	HCl,	36.18
" Hydrocyanic,	HCN,	26.83
" Hydrofluoric,	HF,	19.9
" Hydrosulphuric. (See Hydrogen Sulphide.)		
" Hypophosphorous,	HPH_2O_2,	65.51
" Lactic,	$HC_3H_5O_3$,	89.34
" Nitric,	HNO_3,	62.57
" Oleic,	$HC_{18}H_{33}O_2$,	279.96
" Oxalic,	$H_2C_2O_4 + 2H_2O$,	125.08
" " dry,	$H_2C_2O_4$,	89.32
" Phosphoric,	H_3PO_4,	97.27
" Salicylic,	$HC_7H_5O_3$,	136.94
" Stearic,	$HC_{18}H_{35}O_2$,	281.96
" Sulphuric,	H_2SO_4,	97.35
" Sulphurous,	H_2SO_3,	81.47
" Tannic,	$HC_{14}H_9O_9$,	319.52
" Tartaric,	$H_2C_4H_4O_6$,	148.88
Aluminum,	**Al,**	26.9
Ammonia,	NH_3,	16.93
Ammonium Acetate,	$NH_4C_2H_3O_2$,	76.49
" Benzoate,	$NH_4C_7H_5O_2$,	137.99
" Bromide,	NH_4Br,	97.27
" Carbonate (Normal),	$(NH_4)_2CO_3$,	95.40
" " (U. S. P.),	$NH_4HCO_3.NH_4NH_2CO_2$,	155.99
" Chloride,	NH_4Cl,	53.11
" Citrate,	$(NH_4)_3C_6H_5O_7$,	241.35
" Iodide,	NH_4I,	143.82
" Lactate,	$NH_4C_3H_5O_8$,	106.27

		H = 1.
Ammonium Oxalate,	$(NH_4)_2C_2O_4 + H_2O$,	141.06
" " dry,	$(NH_4)_2C_2O_4$,	123.18
" Salicylate,	$NH_4C_7H_5O_3$,	153.87
" Sulphate,	$(NH_4)_2SO_4$,	131.21
" Tartrate,	$(NH_4)_2C_4H_4O_6$,	182.74
Antimony,	**Sb,**	119.5
Antimony Oxide (Trioxide),	Sb_2O_3,	286.64
" and Potassium Tartrate,	$2K(SbO)C_4H_4O_6 + H_2O$,	660.04
" " " " dry,	$K(SbO)C_4H_4O_6$,	321.08
" Tri-Sulphide,	Sb_2S_3,	334.49
" Penta-Sulphide,	Sb_2S_5,	318.40
Arsenic,	**As,**	74.45
Arsenic Iodide,	AsI_3,	452.12
" (Penta-) Sulphide,	As_2S_5,	308.05
" Trioxide. (See Acid, Arsenous.)		
Atropine,	$C_{17}H_{23}NO_3$,	286.87
" Sulphate,	$(C_{17}H_{23}NO_3)_2H_2SO_4$,	671.09
Barium,	**Ba,**	136.4
Barium Carbonate,	$BaCO_3$,	195.94
" Chloride,	$BaCl_2 + 2H_2O$,	242.52
" " dry,	$BaCl_2$,	206.76
" Chromate,	$BaCrO_4$,	251.62
" Dioxide,	BaO_2,	168.16
" Hydroxide,	$Ba(OH)_2$,	170.16
" Nitrate,	$Ba(NO_3)_2$,	259.54
" Sulphate,	$BaSO_4$,	231.75
" Sulphide,	BaS,	168.23
Bismuth,	**Bi,**	206.5
Bismuth Citrate,	$BiC_6H_5O_7$,	394.06
" Nitrate (Normal),	$Bi(NO_3)_3 + 5H_2O$,	480.61
" Salicylate,	$Bi(OH)_2C_7H_5O_3$,	376.20
Boron,	**B,**	10.9
Boron Trioxide,	B_2O_3,	69.44
Bromine,	**Br,**	79.34
Brucine,	$C_{23}H_{26}N_2O_4 + 4H_2O$,	462.60
" dry,	$C_{23}H_{26}N_2O_4$,	391.08
Cadmium,	**Cd,**	111.55
Cadmium Sulphate,	$3CdSO_4 + 8H_2O$,	763.74
" Sulphide,	CdS,	143.38
Cæsium,	**Cs,**	131.9
Caffeine,	$C_8H_{10}N_4O_2 + H_2O$,	210.56
" dry,	$C_8H_{10}N_4O_2$,	192.68
Calcium,	**Ca,**	39.8
Calcium Bromide,	$CaBr_2$,	198.48
" Carbonate,	$CaCO_3$,	99.34
" Chloride,	$CaCl_2 + 6H_2O$,	217.44
" " dry,	$CaCl_2$,	110.16
" Fluoride,	CaF_2,	76.6
" Hydroxide,	$Ca(OH)_2$,	73.56
" Hypophosphite,	$Ca(PH_2O_2)_2$,	168.82
" Oxalate,	$CaC_2O_4 + 2H_2O$,	162.88
" Oxide,	CaO,	55.68
" Sulphate (Gypsum),	$CaSO_4 + 2H_2O$,	170.91
" " dry,	$CaSO_4$,	135.15
" Sulphide (Monosulphide),	CaS,	71.63
Carbon,	**C,**	11.9
Cerium,	**Ce,**	138.0
Cerium Oxalate,	$Ce_2(C_2O_4)_3 + 10H_2O$,	716.76
" Oxalate, dry,	$Ce_2(C_2O_4)_3$,	537.96
Chlorine,	**Cl,**	35.18
Chromium,	**Cr,**	51.7
Chromium Oxide,	Cr_2O_3,	151.04
Cinchonidine,	$C_{19}H_{22}N_2O$,	291.84
" Salicylate,	$C_{19}H_{22}N_2OC_7H_6O_3$,	428.78

		H = 1.
Cinchonidine Sulphate,	$(C_{19}H_{22}N_2O)_2H_2SO_4 + 3H_2O$,	734.67
“ “ dry,	$(C_{19}H_{22}N_2O)_2H_2SO_4$,	681.03
Cinchonine,	$C_{19}H_{22}N_2O$,	291.84
“ Sulphate,	$(C_{19}H_{22}N_2O)_2H_2SO + 2H_2O$,	716.79
“ “ dry,	$(C_{19}H_{22}N_2O)_2H_2SO_4$,	681.03
Cobalt,	**Co,**	58.55
Cocaine Hydrochloride,	$C_{17}H_{21}NO_4HCl$,	336.93
Codeine,	$C_{18}H_{21}NO_3 + H_2O$,	314.65
“ dry,	$C_{18}H_{21}NO_3$,	296.77
“ Phosphate,	$C_{18}H_{21}NO_3H_3PO_4 + 2H_2O$,	429.80
“ “ dry,	$C_{18}H_{21}NO_3H_3PO_4$,	394.04
“ Sulphate,	$(C_{18}H_{21}NO_3)_2H_2SO_4 + 5H_2O$,	780.29
“ “ dry,	$(C_{18}H_{21}NO_3)_2H_2SO_4$,	690.89
Colchicine,	$C_{22}H_{25}NO_6$,	396.01
Copper,	**Cu,**	63.1
Cupric Ammonium Sulphate,	$Cu(NH_3)_4SO_4 + H_2O$,	244.05
“ Sulphate,	$CuSO_4 + 5H_2O$,	247.85
“ “ dry,	$CuSO_4$,	158.45
“ Sulphide,	CuS,	94.93
“ Tartrate,	$CuC_4H_4O_6 + 3H_2O$,	263.62
Ferric Acetate,	$Fe_2(C_2H_3O_2)_6$,	462.36
“ Ammonium Sulphate,	$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$,	957.38
“ “ “ dry,	$Fe_2(NH_4)_2(SO_4)_4$,	528.26
“ Chloride,	$Fe_2Cl_6 + 12H_2O$,	536.64
“ “ dry,	Fe_2Cl_6,	322.08
“ Hydroxide,	$Fe_2(OH)_6$,	212.28
“ Hypophosphite,	$Fe_2(PH_2O_2)_6$,	498.06
“ Nitrate,	$Fe_2(NO_3)_6$,	480.42
“ Oxide,	Fe_2O_3,	158.64
“ Sulphate,	$Fe_2(SO_4)_3$,	397.05
Ferrous Bromide,	$FeBr_2$,	214.18
“ Carbonate,	$FeCO_3$,	115.04
“ Iodide,	FeI_2,	307.28
“ Lactate,	$Fe(C_3H_5O_3)_2 + 3H_2O$,	285.82
“ Sulphate,	$FeSO_4 + 7H_2O$,	276.01
“ “ dry,	$FeSO_4$,	150.85
“ Sulphide,	FeS,	87.33
Fluorine,	**F,**	18.9
Glucose. (See Sugar, Grape.)		
Gold,	**Au,**	195.7
Gold Chloride,	$AuCl_3$,	301.24
Heroine Hydrochloride,	$C_{17}H_{17}(C_2H_3O_2)_2NOHCl$,	402.41
Homatropine Hydrobromide,	$C_{16}H_{21}NO_3HBr$,	353.31
Hydrastine Hydrochloride,	$C_{21}H_{21}NO_6HCl$,	416.29
Hydrastinine Hydrochloride,	$C_{11}H_{11}NO_2HCl$,	223.77
Hydrogen,	**H,**	1.00
Hydrogen Dioxide,	H_2O_2,	33.76
“ Sulphide,	H_2S,	33.83
Hyoscine Hydrobromide,	$C_{17}H_{21}NO_4HBr + 3H_2O$,	434.73
“ “ dry,	$C_{17}H_{21}NO_4HBr$,	381.09
Hyoscyamine Hydrobromide,	$C_{17}H_{23}NO_3HBr$,	367.21
“ Sulphate,	$(C_{17}H_{23}NO_3)_2H_2SO_4$,	671.09
Iodine,	**I,**	125.89
Iron,	**Fe,**	55.5
Iron Salts. See under *Ferric* and *Ferrous*.		
Lead,	**Pb,**	205.36
Lead Acetate,	$Pb(C_2H_3O_2)_2 + 3H_2O$,	376.12
“ “ dry,	$Pb(C_2H_2O_2)_2$,	322.48
Lead Carbonate,	$(PBCO_3)_2Pb(OH)_2$,	768.92
“ Chloride,	$PbCl_2$,	275.72
“ Chromate,	$PbCrO_4$,	320.58
“ Iodide,	PbI_2,	457.14
“ Nitrate,	$Pb(NO_3)_2$,	328.50
“ Oxide,	PbO,	221.24

		H = 1.
Lead Subacetate (approximately),	$Pb_2O(C_2H_3O_2)_2$,	543.72
“ Sulphate,	$PbSO_4$,	300.71
“ Sulphide,	PbS,	237.19
Lime. (See Calcium Oxide.)		
Lithium,	**Li,**	6.97
Lithium Benzoate,	$LiC_7H_5O_2$,	127.03
“ Bromide,	$LiBr$,	86.31
“ Carbonate,	Li_2CO_3,	73.48
“ Citrate,	$Li_3C_6H_5O_7$,	208.47
“ Salicylate,	$LiC_7H_5O_3$,	142.91
Magnesia. (See Magnesium Oxide.)		
Magnesium,	**Mg,**	24.1
Magnesium Carbonate (approximately),	$(MgCO_3)_4Mg(OH)_2 + 5H_2O$,	481.82
“ Oxide,	MgO,	39.98
“ Sulphate,	$MgSO_4 + 7H_2O$,	244.61
“ “ dry,	$MgSO_4$,	119.45
Manganese,	**Mn,**	54.6
Manganese Dioxide,	MnO_2,	86.36
Manganous Sulphate,	$MnSO_4 + 4H_2O$,	221.47
“ “ dry,	$MnSO_4$,	149.95
Mercuric Ammonium Chloride,	$HgClNH_2$,	249.61
“ Chloride,	$HgCl_2$,	268.86
“ Cyanide,	$Hg(CN)_2$,	250.16
“ Iodide,	HgI_2,	450.28
“ Nitrate,	$Hg(NO_3)_2 + 4H_2O$,	393.16
“ “ dry,	$Hg(NO_3)_2$,	321.64
“ Oxide,	HgO,	214.38
“ Potassium Iodide,	$HgI_2 + 2KI$,	779.70
“ Subsulphate,	$Hg(HgO)_2SO_4$,	722.61
“ Sulphate,	$HgSO_4$,	293.85
“ Sulphide,	HgS,	230.33
Mercurous Chloride,	Hg_2Cl_2,	467.36
“ Iodide,	Hg_2I_2,	648.78
“ Nitrate,	$Hg_2(NO_3)_2 + H_2O$,	538.02
“ Sulphate,	Hg_2SO_4,	492.35
Mercury,	**Hg,**	198.50
Molybdenum,	**Mo,**	95.3
Morphine,	$C_{17}H_{19}NO_3 + H_2O$,	300.75
“ dry,	$C_{17}H_{19}NO_3$,	282.87
“ Acetate (variable),	$C_{17}H_{19}NO_3C_2H_4O_2 + 3H_2O$,	396.07
“ Hydrochloride,	$C_{17}H_{19}NO_3HCl + 3H_2O$,	372.69
“ “ dry,	$C_{17}H_{19}NO_3HCl$,	319.05
“ Sulphate,	$(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$,	752.49
“ “ dry,	$(C_{17}H_{19}NO_3)_2H_2SO_4$,	663.09
Nickel,	**Ni,**	58.25
Nickelous Oxide,	NiO,	74.13
“ Sulphate,	$NiSO_4 + 7H_2O$,	278.76
Nitrogen,	**N,**	13.93
Oxygen,	**O,**	15.88
Phenol. (See Acid, Carbolic.)		
Phosphorus,	**P,**	30.75
Physostigmine Salicylate,	$C_{15}H_{21}N_3O_2C_7H_6O_3$,	409.99
“ Sulphate,	$(C_{15}H_{21}N_3O_2)_2H_2SO_4$,	643.45
Picrotoxin,	$C_{30}H_{34}O_{13}$,	597.44
Pilocarpine Hydrochloride,	$C_{11}H_{16}N_2O_2HCl$,	242.70
“ Nitrate,	$C_{11}H_{16}N_2O_2HNO_3$,	269.09
Platinic Chloride,	$PtCl_4$,	334.12
Platinum,	**Pt,**	193.4
Potassa. (See Potassium Hydroxide.)		
Potassium,	**K,**	38.82
Potassium Acetate,	$KC_2H_3O_2$,	97.38
“ Arsenite (Metarsenite),	$KAsO_2$,	145.03
“ Benzoate,	$KC_7H_5O_2 + 3H_2O$,	212.52
“ “ dry,	$KC_7H_5O_2$,	158.88

		H = 1.
Potassium Bicarbonate,	$KHCO_3$,	99.36
“ Bichromate. (See Dichromate.)		
“ Bisulphate,	$KHSO_4$,	135.17
“ Bitartrate,	$KHC_4H_4O_6$,	186.70
“ Bromate,	$KBrO_3$,	165.80
“ Bromide,	KBr,	118.16
“ Carbonate,	K_2CO_3,	137.18
“ Chlorate,	$KClO_3$,	121.64
“ Chloride,	KCl,	74.00
“ Chromate,	K_2CrO_4,	192.86
“ Citrate,	$K_3C_6H_5O_7 + H_2O$,	321.90
“ “ dry,	$K_3C_6H_5O_7$,	304.02
“ Cyanide,	KCN,	64.65
“ Dichromate,	$K_2Cr_2O_7$,	292.20
“ Ferricyanide,	$K_6Fe_2(CN)_{12}$,	653.88
“ Ferrocyanide,	$K_4Fe(CN)_6 + 3H_2O$,	419.40
“ “ dry,	$K_4Fe(CN)_6$,	365.76
“ Hydroxide,	KOH,	55.70
“ Hypophosphite,	KPH_2O_2,	103.33
“ Iodide,	KI,	164.71
“ Lactate,	$KC_3H_5O_3$,	127.16
“ Nitrate,	KNO_3,	100.39
“ Permanganate,	$KMnO_4$,	156.94
“ Phosphate,	K_2HPO_4,	172.91
“ Salicylate,	$KC_7H_5O_3$,	174.76
“ and Sodium Tartrate,	$KNaC_4H_4O_6 + 4H_2O$,	280.10
“ “ “ “ dry,	$KNaC_4H_4O_6$,	208.58
“ Sulphate,	K_2SO_4,	172.99
“ Sulphite,	$K_2SO_3 + 2H_2O$,	192.87
“ “ dry,	K_2SO_3,	157.11
“ Thiocyanate,	$KSCN$,	96.48
“ Tartrate,	$2K_2C_4H_4O_6 + H_2O$,	466.92
“ “ dry,	$K_2C_4H_4O_6$,	224.52
Quinidine Sulphate,	$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 2H_2O$,	776.35
“ “ dry,	$(C_{20}H_{24}N_2O_2)_2H_2SO_4$,	740.59
Quinine,	$C_{20}H_{24}N_2O_2 + 3H_2O$,	375.26
“ dry,	$C_{20}H_{24}N_2O_2$,	321.62
“ Bisulphate,	$C_{20}H_{24}N_2O_2H_2SO_4 + 7H_2O$,	544.13
“ “ dry,	$C_{20}H_{24}N_2O_2H_2SO_4$,	418.97
“ Hydrobromide,	$C_{20}H_{24}N_2O_2HBr + H_2O$,	419.84
“ “ dry,	$C_{20}H_{24}N_2O_2HBr$,	401.96
“ Hydrochloride,	$C_{20}H_{24}N_2O_2HCl + 2H_2O$,	393.56
“ “ dry,	$C_{20}H_{24}N_2O_2HCl$,	357.80
“ Salicylate,	$C_{20}H_{24}N_2O_2C_7H_6O_3$,	458.56
“ Sulphate,	$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 7H_2O$,	865.75
“ “ dry,	$(C_{20}H_{24}N_2O_2)_2H_2SO_4$,	740.59
“ Valerianate,	$C_{20}H_{24}N_2O_2C_5H_{10}O_2 + H_2O$,	440.76
Selenium,	**Se,**	78.6
Silicon,	**Si,**	28.2
Silicon Oxide (Silica),	SiO_2,	59.96
Silver,	**Ag,**	107.11
Silver Chloride,	$AgCl$,	142.29
“ Cyanide,	$AgCN$,	132.94
“ Iodide,	AgI,	233.00
“ Nitrate,	$AgNO_3$,	168.68
“ Oxide,	Ag_2O,	230.10
“ Sulphate,	Ag_2SO_4,	309.57
“ Sulphide,	Ag_2S,	246.05
Soda. (See Sodium Hydroxide.)		
Sodium,	**Na,**	22.88
Sodium Acetate,	$NaC_2H_3O_2 + 3H_2O$,	135.08
“ “ dry,	$NaC_2H_3O_2$,	81.44
“ Arsenate,	$Na_2HAsO_4 + 7H_2O$,	309.89
“ “ dry,	Na_2HAsO_4,	184.73

		H = 1.
Sodium Arsenite (Metarsenite),	$NaAsO_2$,	129.09
“ Benzoate,	$NaC_7H_5O_2$,	142.94
“ Bicarbonate,	$NaHCO_3$,	83.42
“ Bisulphite,	$NaHSO_3$,	103.35
“ Bitartrate,	$NaHC_4H_4O_6 + H_2O$,	188.64
“ Borate,	$Na_2B_4O_7 + 10H_2O$,	379.32
“ “ dry,	$Na_2B_4O_7$,	200.52
“ Bromate,	$NaBrO_3$,	149.86
“ Bromide,	$NaBr$,	102.22
“ Carbonate,	$Na_2CO_3 + 10H_2O$,	284.10
“ “ dry,	Na_2CO_3,	105.30
“ Chlorate,	$NaClO_3$,	105.70
“ Chloride,	$NaCl$,	58.06
“ Citrate,	$2Na_3C_6H_5O_7 + 11H_2O$,	709.06
“ “ dry,	$Na_3C_6H_5O_7$,	256.20
“ Cobaltic Nitrite,	$Co_2(NO_2)_6 6NaNO_2 + H_2O$,	820.54
“ Hydroxide,	$NaOH$,	39.76
“ Hypophosphite,	$NaPH_2O_2 + H_2O$,	105.27
“ Hyposulphite. (See Thiosulphate.)		
“ Iodide,	NaI,	148.77
“ Lactate,	$NaC_3H_5O_3$,	111.22
“ Nitrate,	$NaNO_3$,	84.45
“ Nitrite,	$NaNO_2$,	68.57
“ Nitroprusside,	$Na_2Fe(NO)(CN)_5 + 2H_2O$,	295.98
“ Phosphate,	$Na_2HPO_4 + 12H_2O$,	355.59
“ “ dry,	Na_2HPO_4,	141.03
“ Pyrophosphate,	$Na_4P_2O_7 + 10H_2O$,	442.98
“ “ dry,	$Na_4P_2O_7$,	264.18
“ Salicylate,	$NaC_7H_5O_3$,	158.82
“ Sulphate,	$Na_2SO_4 + 10H_2O$,	319.91
“ “ dry,	Na_2SO_4,	141.11
“ Sulphite,	$Na_2SO_3 + 7H_2O$,	250.39
“ “ dry,	Na_2SO_3,	125.23
“ Tartrate,	$Na_2C_4H_4O_6 + 2H_2O$,	228.40
“ Thiosulphate,	$Na_2S_2O_3 + 5H_2O$,	246.46
“ “ dry,	$Na_2S_2O_3$,	157.06
Sparteine Sulphate,	$C_{15}H_{26}N_2H_2SO_4 + 4H_2O$,	401.23
“ “ dry,	$C_{15}H_{26}N_2H_2SO_4$,	329.71
Stannic Chloride,	$SnCl_4$,	258.52
Stannous Chloride,	$SnCl_2 + 2H_2O$,	224.22
Strontium,	**Sr,**	86.95
Strontium Bromide,	$SrBr_2 + 6H_2O$,	352.91
“ “ dry,	$SrBr_2$,	245.63
“ Carbonate,	$SrCO_3$,	146.49
“ Iodide,	$SrI_2 + 6H_2O$,	446.01
“ “ dry,	SrI_2,	338.73
“ Lactate,	$Sr(C_3H_5O_3)_2 + 3H_2O$,	317.27
“ “ dry,	$Sr(C_3H_5O_3)_2$,	263.63
“ Salicylate,	$Sr(C_7H_5O_3)_2 + 2H_2O$,	394.59
“ Sulphate,	$SrSO_4$,	182.30
Strychnine,	$C_{21}H_{22}N_2O_2$,	331.52
“ Nitrate,	$C_{21}H_{22}N_2O_2HNO_3$,	394.09
“ Sulphate,	$(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 5H_2O$	849.79
“ “ dry,	$(C_{21}H_{22}N_2O_2)_2H_2SO_4$,	760.39
Sugar, Cane,	$C_{12}H_{22}O_{11}$,	339.48
“ Grape,	$C_6H_{12}O_6$,	178.68
“ Milk,	$C_{12}H_{22}O_{11} + H_2O$,	357.36
Sulphur,	**S,**	31.83
Sulphur Dioxide,	SO_2,	63.59
Tellurium,	**Te,**	126.5
Tin,	**Sn,**	118.1
Tin-Salts. (See under *Stannic* and *Stannous.*)		
Uranium,	**U,**	237.8
Water,	H_2O,	17.88

		H = 1.
Zinc,	**Zn,**	64.9
Zinc Acetate,	$Zn(C_2H_3O_2)_2 + 2H_2O$,	217.78
“ “ dry,	$Zn(C_2H_3O_2)_2$,	182.02
“ Bromide,	$ZnBr_2$,	223.58
“ Carbonate (normal, not U.S.P.),	$ZnCO_3$,	124.44
“ Chloride,	$ZnCl_2$,	135.26
“ Iodide,	ZnI_2,	316.68
“ Oxide,	ZnO,	80.78
“ Phosphide,	Zn_3P_2,	256.20
“ Sulphate,	$ZnSO_4 + 7H_2O$,	285.41
“ “ dry,	$ZnSO_4$,	160.25
“ Sulphide,	ZnS,	96.73
“ Sulphocarbolate,	$Zn(C_6H_4(OH)SO_3)_2 + 8H_2O$,	551.44
“ Valerianate,	$Zn(C_5H_9O_2)_2 + 2H_2O$,	301.18

INDEX.

The heavy-faced type references indicate those pages which, among others, contain the more important subject-matter or practical exercises.