A TEXT-BOOK

OF

VOLUMETRIC ANALYSIS

WITH SPECIAL REFERENCE TO

THE VOLUMETRIC PROCESSES OF THE PHARMACOPŒIA OF THE UNITED STATES.

Designed for the Use of Pharmacists and Pharmaceutical Students.

BY

HENRY W. SCHIMPF, PH.G., M.D.,

Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy; Member of the American Chemical Society; of the American Association for the Advancement of Science; of the American Pharmaceutical Association; of the New York State Pharmaceutical Association; of the Kings County Pharmaceutical Society; of the German Apothecaries' Society of New York City; Honorary Member of the Alumni Association of the Brooklyn College of Pharmacy, etc., etc.

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THIRD EDITION, REVISED AND ENLARGED.

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PREFACE TO THE THIRD EDITION.

IN submitting this new edition to the profession, the author hopes that the same generous reception will be given it as was accorded its predecessor.

The main features of the latter have been retained in the present edition and much new matter added, which is intended to increase the usefulness of the book for the practical pharmacist and for the student.

The present edition is divided into four parts.

Part I is a systematic arrangement of volumetric processes and includes the pharmacopœial methods for inorganic substances. This part has been revised and enlarged.

In the chapter on apparatus used in volumetric analysis some new forms of apparatus are described and illustrated.

The chapter on the use of apparatus has been enlarged, several new cuts introduced, and methods for the calibration of graduated instruments described. There is also some additional matter concerning weights and measures.

In the sixth chapter some unusual volumetric methods are described, and under alkalimetry several meth-

PREFACE TO THE FIRST EDITION.

THIS book is designed for the use of pharmacists, and especially as a text-book for students in pharmacy.

In the first portion of the book the author has attempted, in explaining the principles of volumetric analysis, to combine thoroughness with simplicity of expression.

The United States Pharmacopœia has been taken as the basis of the work, and the volumetric processes therein given are followed throughout, each step being carefully explained, and chemical equations inserted, wherever deemed necessary.

The author has also added descriptions of processes not given in the Pharmacopœia, but which are worthy of consideration.

In teaching volumetric analysis to students in pharmacy the author discovered the necessity for a work especially designed for this class of students.

Moreover, the requirements of the new edition of the United States Pharmacopœia, in which many volumetric processes are given, necessitate on the part of the careful pharmacist a knowledge of this branch of analytical chemistry; and no work that has as yet fallen into the hands of the author has seemed to be exactly suited to the needs of the practical pharmacist. Consequently the necessity for a book based upon the Pharmacopœia and free from technicality is apparent.

The latter portion of the book is devoted to descriptions of such special analytical processes as the pharmacist may be called upon to use, and such as are taught in the pharmaceutical colleges.

The author has selected such processes as can be easily and quickly executed, and has given the gravimetric only where volumetric processes cannot be employed.

In the subject-matter of the book little originality is claimed, but the author has used his own judgment in its selection and arrangement.

He has endeavored in the text to give credit wherever it was due, and especially acknowledges his indebtedness to the United States Pharmacopœia; Sutton's Volumetric Analysis; Bartley's, Simon's, and Attfield's text-books; Blythe's Food Analysis; Prescott's Organic Analysis; Muter's Analytical Chemistry (*American edition*); Lefmann and Beam's Milk and Water Analysis; and Witthaus' and Holland's Urine Analysis.

He wishes to express his thanks to Dr. J. F. Golding for the valued assistance he has rendered during the preparation of the book. He is also indebted to Richards & Co., of 41 Barclay Street, N. Y. City, manufacturers of chemical apparatus, from whom several of the cuts were borrowed.

The author submits this work to the consideration of pharmacists, trusting its reception will be at least commensurate with the labor expended in its preparation.

HENRY W. SCHIMPF.

365 FRANKLIN AVE., BROOKLYN, N. Y.

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A LIST OF ELEMENTS OCCURRING IN VOLUMETRIC METHODS, THEIR SYMBOLS, AND ATOMIC WEIGHTS.

Name.		Exact Atomic Weights according to Meyer and Seubert, adopted by the U. S. P.	Approximate Atomic Weights.
Aluminium	Al	27.04	27.0
Antimony	Sb	119.6	120.0
Arsenic	As	74.9	75.0
Barium	Ba	136.9	136.9
Bismuth	Bi	208.9	208.0
Boron	B	10.9	11.0
Bromine	Br	79.76	80.0
Cadmium	Cd	111.5	111.5
Calcium	Ca	39.91	40.0
Carbon	C	11.97	12.0
Chlorine	Cl	35.37	35.4
Chromium	Cr	52.0	52.0
Copper	Cu	62.18	63.0
Gold	Au	196.7	196.7
Hydrogen	H	1.0	1.0
Iodine	I	126.53	126 5
Iron	Fe	55.88	56.0
Lead	Pb	206.4	206.4
Lithium	Li	7.01	7.0
Magnesium	Mg	24.3	24.0
Manganese	Mn	54.8	55.0
Mercury	Hg	199.8	200.0
Nitrogen	N	14.01	14.0
Oxygen	O	15.96	16.0
Phosphorus	P	30.96	31.0
Platinum	Pt	194.3	194.3
Potassium	K	39.03	39.0
Silver	Ag	107.66	107.7
Sodium	Na	23.0	23.0
Strontium	Sr	87.3	87.3
Sulphur	S	31.98	32.0
Tin	Sn	118.8	118.0
Zinc	Zn	65.1	65.0

ABBREVIATIONS AND SIGNS.

Cc. . . . . cubic centimetre.
Gm . . . . . gramme, 15.43235 grains.
Gr. . . . . grain.
At. wt. . . . atomic weight.
V. S . . . . . volumetric solution.
T. S . . . . . test solution, according to U. S. P.
U. S. P. . . . United States Pharmacopœia.
$\frac{N}{1}$ . . . . . normal.
$\frac{N}{10}$ . . . . . decinormal.
$\frac{N}{100}$ . . . . . centinormal.
$\frac{N}{2}$ . . . . . semi-normal.
$\frac{2}{N}$ or 2N . . double-normal.
* means that the figure is approximate.

A TEXT-BOOK

OF

VOLUMETRIC ANALYSIS.

PART I.

CHAPTER I.

INTRODUCTION.

In a chemical analysis the aim is to determine the nature of the chemical substances contained in a given compound or to ascertain their quantities. In the former case the analysis is a *qualitative*, in the latter a *quantitative*, one.

The quantitative analysis of a substance may be made either by the *gravimetric* or the *volumetric* method.

The Gravimetric Method consists in separating and weighing the constituents either in their natural states or in the form of new and definite compounds, the composition of which is known to the analyst. From the weights of these new compounds the analyst can calculate the quantities of the original constituents.

Example.—To determine the quantity of silver in a solution by the gravimetric method we proceed as follows:

Add hydrochloric acid to the solution in slight but distinct excess, i.e., sufficient to cause the precipitation of all the silver in the form of silver chloride. The precipitate is thoroughly washed, dried, and then carefully weighed. 143.03 grammes of silver chloride represent 107.66 grammes of silver.

The Volumetric Method.—In this method the quantity of the substance analyzed is ascertained by paying attention to the volume of a solution of known strength (*standard solution*) which must be added to it to perform a certain reaction.

Example.—If a silver solution is to be analyzed by this method it is treated with a standard solution of sodium chloride, added slowly from a burette until no more silver chloride is precipitated. Each cc. of this standard solution will precipitate a certain weight of silver as silver chloride, and hence by noting the number of cc. used to complete the precipitation, the weight of the silver in the solution analyzed is easily ascertained.

The $\frac{N}{10}$ sodium chloride solution is generally used for this purpose. It is made by dissolving $\frac{1}{10}$ of the molecular weight of the salt (in grammes) (5.837 gms.) in water sufficient to make 1000 cc. 1000 cc. of this solution will precipitate $\frac{1}{10}$ of the atomic weight of silver (in grammes) (10.766 gms.), and hence each cc. of the sodium chloride solution represents 0.010766 gramme of metallic silver, and by multiplying this figure by the number of cc. used, the quantity of silver in the solution is found. If in the above analysis 100 cc. of the $\frac{N}{10}$ sodium chloride solution were used,

then $0.010766 \times 100 = 1.0766$ gms. of metallic silver.

The reaction is illustrated by this equation:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

$$\begin{array}{lll} 10)107.66 & 10)58.37 & \\ 1000)\ 10.766\ \text{gms.} & 1000)5.837\ \text{gms.} & = 1000\ \text{cc.}\ \frac{N}{10}\ \text{V. S.} \\ 0.010766\ \text{gm.} & 0.005837\ \text{gm.} & = 1\ \text{“}\ \text{“}\ \text{“} \end{array}$$

From the examples given it will be seen that the gravimetric operations consume no little time, and require the exercise of considerable skill. The washing of the precipitate must be thoroughly performed in order that it be freed from all adhering matter. The drying also is a matter of some consequence and must be performed in such a manner as to prevent the admixture of dust or the decomposition of the precipitate by excessive heat. A very accurate balance is also required.

The volumetric operations, on the other hand, do not require that the substance to be determined be separated in the form of a compound of known composition and weighed in the dry state; in fact, the substance may be accurately estimated when mixed with many others. It therefore obviates the necessity for the frequent separations and weighings which the gravimetric method demands, and enables the analyst to do the work in a very short time.

The instruments needed for volumetric work are few and simple, and comparatively little skill is required. Furthermore the results obtained are in most instances more accurate.

CHAPTER II.

GENERAL PRINCIPLES OF CHEMICAL COMBINATION UPON WHICH VOLUMETRIC ANALYSIS IS BASED.

1. When substances unite chemically the union always takes place in definite and invariable proportions. Thus when silver nitrate and sodium chloride are brought together, 169.55 parts (by weight) of silver nitrate and 58.37 parts (by weight) of sodium chloride will react with each other, producing 143.05 parts of a curdy white precipitate (silver chloride).

These substances will react with each other in these proportions only.

If a greater proportion of silver nitrate than that above stated be added to the sodium chloride, only the above proportion will react, the excess remaining unchanged.

The same is true if sodium chloride be added in excess of the above proportions. For instance, if 200 parts of silver nitrate be mixed with 58.37 parts of sodium chloride 169.55 parts only will react with the sodium chloride, while 30 45 parts of silver nitrate will remain unchanged. Again, when potassium hydroxide and sulphuric acid are mixed potassium sulphate is formed, 111.98 parts of potassium hydroxide and 97.82 parts of sulphuric acid being required for complete neutralization. These two substances unite chemically in these proportions only.

The equation is

$$\underbrace{2KOH}_{111.98} + \underbrace{H_2SO_4}_{97.82} = K_2SO_4 + 2H_2O.$$

In other words, 111.98 parts of KOH will neutralize 97.82 parts of H_2SO_4, and consequently 97.82 parts of H_2SO_4 will neutralize 111.98 parts of KOH.

Oxalic acid and sodium carbonate react upon each other in the proportions shown in the equation

$$\underbrace{H_2C_2O_4 \cdot 2H_2O}_{125.7} + \underbrace{Na_2CO_3}_{105.85} = Na_2C_2O_4 + CO_2 + 3H_2O$$

125.7 parts of crystallized oxalic acid are neutralized by 105.85 parts of anhydrous sodium carbonate.

2. Definite chemical compounds always contain the same elements in exactly the same proportions, the proportions being those of their atomic weights, or some multiple of these weights.

Thus sodium chloride (NaCl) contains 23 parts of metallic sodium and 35.37 parts of chlorine, these being the atomic weights of sodium and chlorine, respectively.

Potassium sulphate (K_2SO_4) contains twice 39.03 = 78.06 parts of potassium, 31.98 parts of sulphur, and four times 15.96 = 63.84 parts of oxygen.

Potassium hydroxide (KOH) contains 39.03 parts of potassium, 15.96 parts of oxygen, and one part of hydrogen. Hydrochloric acid (HCl) contains one part of hydrogen and 35.37 parts of chlorine.

Upon these facts the volumetric methods of analysis are based.

It has been shown that 97.82 grammes of sulphuric acid will neutralize 111.98 grammes of potassium hy-

droxide; it is therefore evident that if a solution of sulphuric acid be made containing 48.91 grammes of the pure acid in 1000 cc. that one cc. of this solution will neutralize 0.056 gm. of potassium hydroxide. In estimating alkalies with this acid solution the latter is added from a burette, in small portions, until the alkali is neutralized, as shown by its reaction with some indicator.

Each cc. of the acid solution required before neutralization is complete indicates 0.056 gm. of KOH, and the number of cc. used multiplied by 0.056 gm. gives the quantity of pure KOH in the sample analyzed.

One cc. of the same solution will neutralize 0.03996 gm. of sodium hydroxide (NaOH), 0.052925 gm. of anhydrous sodium carbonate (Na_2CO_3), etc.

If a solution of crystallized oxalic acid be made by dissolving 62.85 gm. in sufficient water to make 1000 cc., we will have a normal solution, the neutralizing power of which is exactly equivalent to the above-mentioned normal sulphuric-acid solution.

The strength of acids is estimated by alkali volumetric solutions. A normal solution of potassium hydroxide containing 55.99 gm. in the litre will neutralize exactly 1 litre of the normal acid solution; 1 cc. of this normal alkali will neutralize 0.03637 gm. of HCl, 0.06285 gm. of $H_2C_2O_4$, or 0.04891 gm. of H_2SO_4, etc.

CHAPTER III.

APPARATUS USED IN VOLUMETRIC ANALYSES.

The Burette is a graduated glass tube which holds from 25 to 100 cc. and is graduated in fifths or tenths of a cc., and provided at the lower end with a rubber tube and pinch-cock. The use of this instrument is to accurately measure quantities of standard solutions used in an analysis. It is in an upright position when in use, and the flow of the solution can be regulated so as to run out in a stream or flow in drops by pressing the pinch-cock between the thumb and forefinger. The quantity of solution used can be read from the graduation on the outside of the tube. This is the simplest and most common form of burette, and is known as *Mohr's* (Fig. 1).

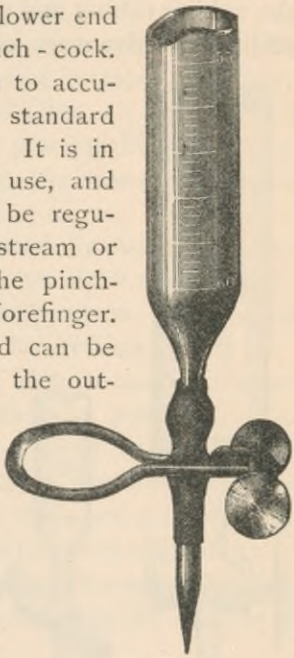

FIG. 1.

The use of the pinch-cock in Mohr's burette may be dispensed with by introducing into the rubber tube a small piece of glass rod, which must not fit too tightly. By firmly squeezing the rubber tube surrounding the glass rod a small canal is opened, through which the liquid escapes. A very delicate action can in this way be obtained, and the

flow of the liquid is completely under the control of the operator. (See Fig. 2.)

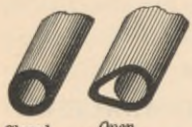

FIG. 2.

The greatest drawback to this burette is that it cannot be used for permanganate or other solutions that act upon the rubber.

This defect can be overcome by the use of a burette having a glass stop-cock in place of the rubber tubing and pinch-cock. This form has the additional advantage of being capable of delivering

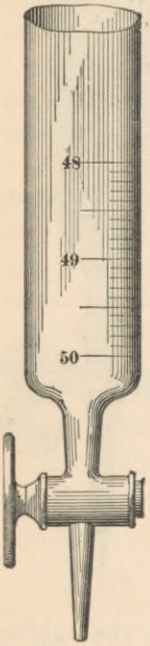

FIG. 3.

FIG. 4.

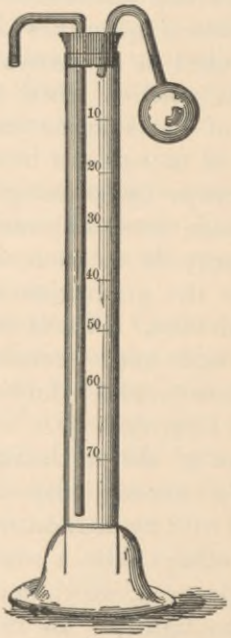

FIG. 5.

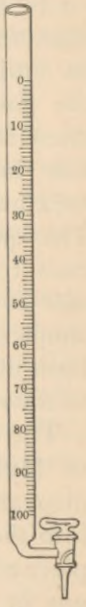

FIG. 6.

the solution in drops while both hands of the operator are disengaged (Fig. 3).

Another good arrangement is that in which the tap is placed in an oblique position, so that it will not easily drop out of place (Fig. 4).

These glass stop-cock burettes should be emptied and washed immediately after use, especially if soda or potassa solution has been used; for these act upon the glass, and often cause the stopper to stick so firmly that it cannot be turned or removed without danger of breaking the instrument.

The most satisfactory form of glass stop-cock is that shown in Fig. 6. Other forms of burettes are *Mohr's Foot Burette*, with rubber ball (Fig. 5). There is a hole in the rubber ball, and by placing the thumb over the hole and gently squeezing, the flow of the liquid may be regulated.

Bink's Burette (Fig. 7) is used by holding in the hand and inclining sufficiently to allow the liquid to flow, then placing in an upright position, and reading when the surface of the liquid has settled.

Gay-Lussac's (Fig. 8) must also be inclined when used. A wooden foot is generally provided, into which this burette is placed to rest in an upright position. By inserting a tightly fitting cork into the open end and passing through this cork a small bent glass tube, the flow of the solution from the exit-tube can be nicely regulated by blowing through the small glass tube. The necessity for inclining the burette is thus obviated. See Fig. 9.

The burette shown in Fig. 10 with the spindle-shaped spout is used in the same manner as Bink's. It is claimed for the dilated spout that it more readily admits of the delivery of single drops and prevents

the too sudden back-dropping of the solution upon returning the burette to the upright position.

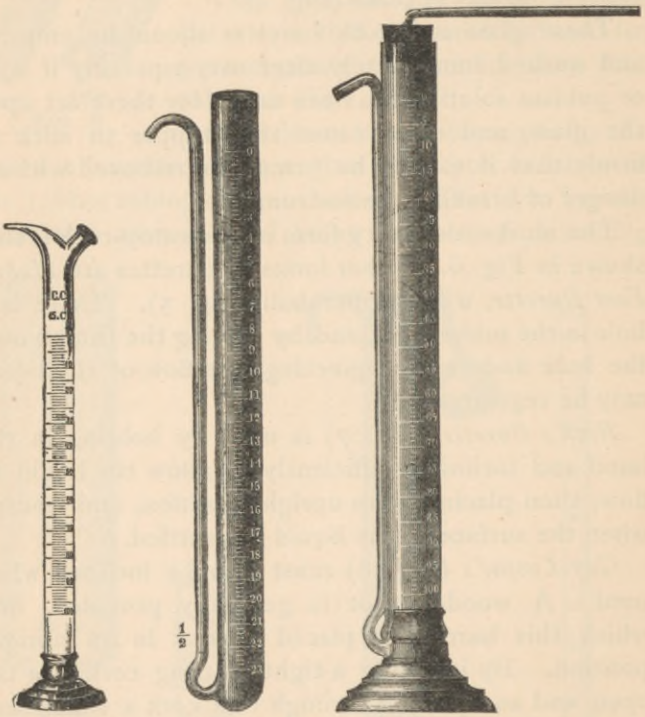

FIG. 7. FIG. 8. FIG. 9.

Casamajor's Burette (Fig. 11), described in *American Chemist*, vol. VII. p. 213, has the advantage of portability and may be handled without heating the liquid. In using it the tube is grasped at the top and inclined; then by turning it the flow may be nicely controlled.

The four latter burettes being held in the hand when in use, there is a chance of increasing the bulk

of the fluid by the heat of the hand, thus leading to errors in measurement.

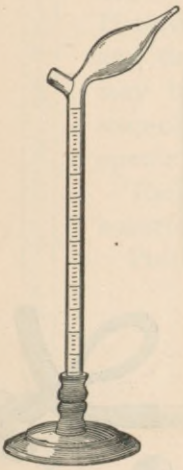

FIG. 10.

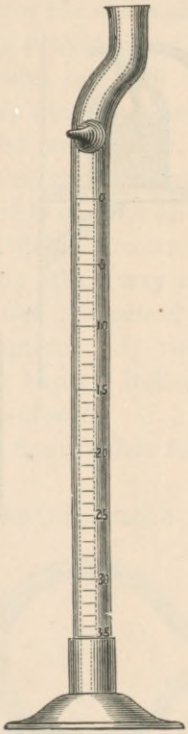

FIG. 11.

FIG. 12.

Geissler's Foot Burette (Fig. 12) needs no further description.

When a number of estimations are to be made in which the same volumetric solution is employed, the arrangement shown in Figs. 13 and 14 is very serviceable.

A T-shaped glass tube is inserted between the lower

end of the burette and the pinck-cock and connected by a rubber tube with a reservoir containing the volumetric solution. The tube which communicates with

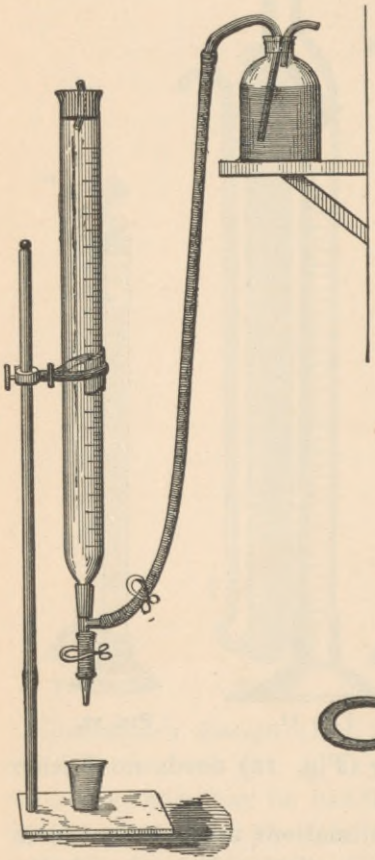

FIG. 13.

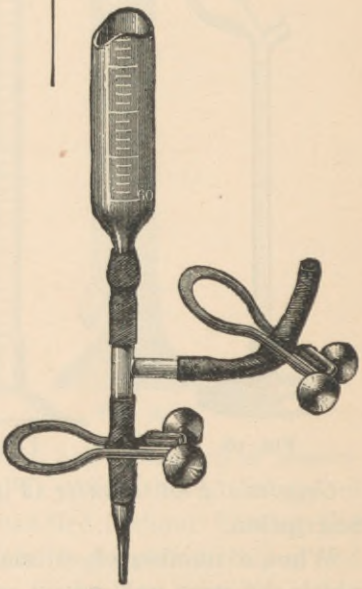

FIG. 14.

the reservoir is provided with a pinch-cock, which when open allows the solution to flow into and fill the

burette in so gradual a manner that no bubbles are formed. The burette is emptied in the usual manner.

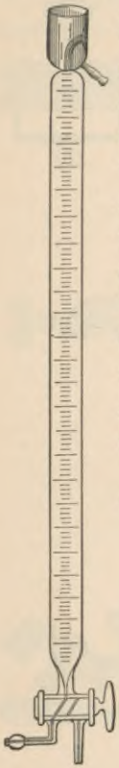

FIG. 15.

E. & A. Automatic Burette (Fig. 15). This is used for the same purpose as the foregoing. It is provided with a side tube for connection with reservoir, and has an overflow reservoir which prevents its being filled to above the zero mark. The three-way stop-cock is so arranged that if turned one way the inlet is opened and the liquid from the reservoir flows into and fills the burette. If turned the other way the inlet is closed and the outlet is opened and the burette may be emptied. If the handle of the stop-cock is turned half-way round, both openings are closed.

There are many other forms of automatic burettes.

Pinch-cocks used with Mohr's burettes

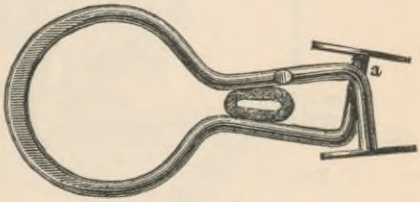

FIG. 16.

are of various kinds (see Figs. 16 and 17). That shown in Fig. 16 is to be preferred.

Burette-supports are of various forms; one of the best for one or two burettes is shown in Fig. 18. It is made of iron, can stand firmly upon an uneven surface, and does not easily tip over. The burettes are

fastened to it by means of clamps, illustrated in Figs. 19 and 20.

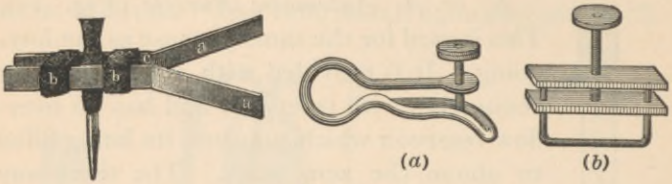

FIG. 17.

FIG. 18.

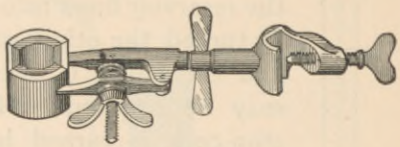

FIG. 19.

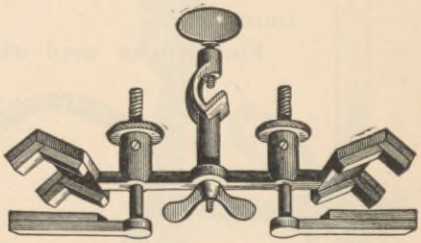

FIG. 20.

A revolving burette-holder for eight burettes is shown in Fig. 21. Burette-supports are also made with white porcelain base which enables the operator the more readily to see the change of color in the liquid titrated.

Pipettes are of two kinds—those which are marked to deliver one quantity only, and those which are

graduated on the stem like burettes. Their use is to measure out portions of solutions with exactness.

Pipettes are filled by applying the mouth to the upper end and sucking the liquid up to the mark, then

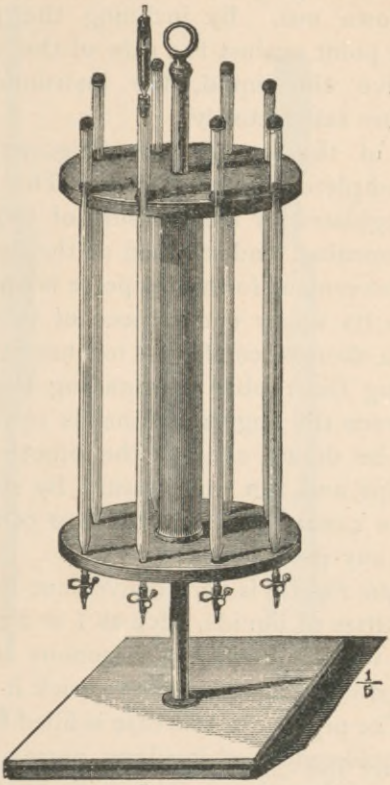

FIG. 21.

by closing the upper opening with the forefinger the liquid is prevented from running out, but may be delivered in drops or allowed to run out to any mark by lessening the pressure of the finger over the opening.

In using the pipettes of the first class (Fig. 22) the finger is raised and the instrument allowed to empty itself entirely. A drop or two, however, usually remains in the lower portion of the instrument, which may be blown out. By inclining the pipette and placing the point against the side of the vessel which is to receive the liquid, the instrument may be emptied more satisfactorily.

Pipettes of the second class (Fig. 23) are never emptied completely when in use. The flow of the liquid is regulated by the pressure of the finger over the upper opening, and stopped at the desired point.

A very convenient form of pipette is one which has attached to its upper end a piece of rubber tubing, into which a short piece of glass rod has been inserted. By squeezing the rubber surrounding the glass bead firmly between the fingers, a canal is opened and the liquid can be drawn up into the pipette by suction with the lips and run out again. By removing the pressure the canal closes and the flow of the liquid is stopped at any point (Fig. 24).

The Nipple Pipette is very convenient for measuring small quantities of liquids, such as 1 or 2 cc. (Fig. 25).

When a volatile or highly poisonous solution is to be measured it is not advisable to suck it up with the mouth. The pipette in this case is filled by dipping it into the liquid contained in a long, narrow vessel, until the liquid reaches the proper mark on the pipette, then closing the upper opening and withdrawing. When this is done the liquid which adheres to the outside of the pipette should be dried off before the measured liquid is delivered.

The Measuring-flask is a vessel made of thin glass

having a narrow neck, and so constructed as to hold a definite amount of liquid when filled up to the mark on the neck. These flasks are of various sizes, hold-

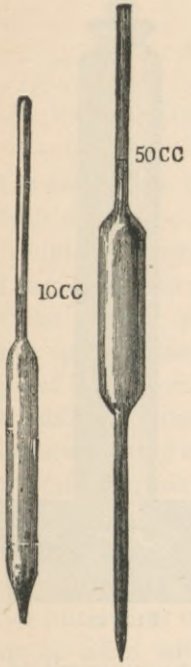

FIG. 22.

FIG. 23.

FIG. 24.

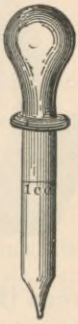

FIG. 25.

ing 100, 250, 500, 1000 cc., etc., but are generally called "*Litre Flasks.*" (Fig. 26.)

They are used for making volumetric solutions.

Those which have the mark below the middle of the neck are to be preferred, because the contents can be more easily shaken.

Litre flasks are sometimes made with two marks

on the neck very near together; the lower one is the litre mark. If the flask is required to deliver a litre, it must be filled to the upper mark; the difference

FIG. 26.

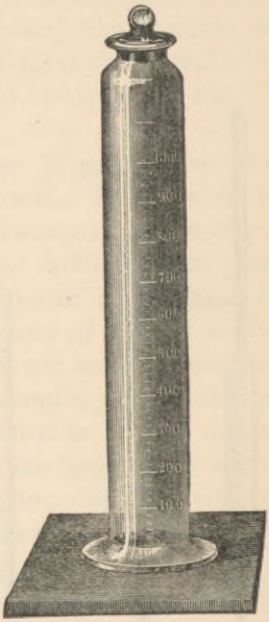

FIG. 27.

between the two measures being the equivalent of the liquid which remains in the flask, adhering to the sides.

The Test Mixer, or **Graduated Cylinder** (Fig. 27), is for measuring and mixing smaller quantities of solutions. They are made of different sizes, holding 100, 250, 500, and 1000 cc., and graduated in fifths or tenths of a cc.

CHAPTER IV.

ON THE USE OF APPARATUS.

It is important that all apparatus used in volumetric analysis should be perfectly clean. Even new apparatus should be cleansed by passing dilute hydrochloric acid through them and then rinsing with distilled water.

If the burette, pipette, or other instrument is even slightly greasy, the liquid will not flow smoothly, and drops of the liquid will remain adhering to the sides, thus leading to inaccurate results.

Greasiness may be removed with dilute soda solution. If this fails the instrument should be allowed to remain for some little time in a solution containing sulphuric acid and potassium dichromate, which will radically remove all traces of grease.

The burette or other measuring instruments should never be filled with volumetric solution without first rinsing, even if the burette be perfectly dry.

It is well to wash the inside of the instrument with two or three small portions of the solution with which it is to be filled.

The burette may be filled with the aid of a funnel, the stem of which should be placed against the inner wall of the burette so that the solution will flow down the side and thus prevent the formation of bubbles.

The burette should be filled to above the zero mark,

and the air-bubbles, if there are any, removed by gently tapping with the finger.

A portion of the liquid should then be allowed to run out in a stream so that no air-bubbles remain in the lower part of the burette. In the glass tap burette it can be easily seen if any air is present, but in the pinch-cock burette it is sometimes necessary to take hold of the rubber tube between the thumb and fore-finger and gently stroke upward. Or the glass nip at the lower end of the burette may be pointed upward, and the pinch-cock opened wide so that a stream of the liquid will pass through and force out any air that may be inclosed.

If the titration is to be conducted at a high temperature, as in the estimation of carbonates, when litmus is used as the indicator, or in the estimation of sugar by copper solution, a long rubber tube should be attached to the lower end of the burette. The boiling can then be done at a little distance, and the expansion of the liquid in the burette avoided. The pinch-cock is fixed about midway on the tube.

Hart calls attention to the fact that if the fluid in a burette or pipette be run out rapidly at one time and slowly at another, different amounts of fluid are obtained.

This is due to the adhesion of the fluid to the inner sides of the instrument, and reading before it has settled down. It is therefore advisable always to deliver burettes slowly, as more constant results are obtained.

Solutions which are measured by means of pipettes should be dilute, since concentrated solutions adhere to glass with different degrees of tenacity, and hence

the amount of fluid delivered is slightly less than that measured.

The temperature of the solutions measured should be taken into account, since all liquids are affected by change of temperature, expanding and contracting as the temperature is increased or reduced.

This change of volume in the case of standard solutions does not exactly correspond to that in pure water; in fact some of them differ widely. The correction of the volume of a standard solution for the temperature by the expansion coefficient of water is not entirely satisfactory, but in the case of very dilute solutions this may be done.

Casamajor (C. N., XXXV. 160) gives the following figures showing the relative contraction and expansion of water below and above 15° C.:

Degree C.	Degree C.
8 — .000590	17 + .000305
9 — .000550	18 + .000473
10 — .000492	19 + .000652
11 — .000420	20 + .000841
12 — .000334	21 + .001039
13 — .000236	22 + .001246
14 — .000124	23 + .001462
15 — normal	24 + .001686
16 + .000147	25 + .001919

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature between 8° C. and 25° C. If 25 cc. of solution had been used at 20° C., the table shows that 1 cc. of water passing from 15° to 20° is increased to 1.000841 cc. Therefore, by dividing

25 cc. by 1.000841, the quotient, 24.97 cc., is obtained, which represents the volume at 15° C. corresponding to 25 cc. at 20° C.

These corrections are of value only for very dilute solutions and for water, but useless for concentrated solutions. Slight variations of atmospheric pressure may be disregarded.

ON THE READING OF INSTRUMENTS.

In narrow vessels the surfaces of liquids are never level. This is owing to the capillary attraction exerted by the sides of the vessel upon the liquid, drawing the edge up and forming a saucerlike concavity (Fig. 28). All liquids present this concave surface except mercury, the surface of which is convex.

FIG. 28.

This behavior of liquids makes it difficult to find a distinct level, and in reading the measure either the upper meniscus (*a*) or the lower meniscus (*b*) may be used (Fig. 29).

The most satisfactory results are obtained if the lowest point of the curve (*b*) is used, especially with light-colored solutions. But if dark-colored or opaque solutions are measured, it is necessary to use the upper meniscus (*a*) for reading.

In all cases the eye should be brought on a level with the surface of the liquid in reading the graduation.

The eye is very much assisted by using a small card, the lower half of which is black and the upper half white. This card is held behind the burette, the dividing line between white and black being about an

eighth of an inch below the surface of the liquid. The eye is then brought on a level with it, and the lower meniscus can be distinctly seen as a sharply defined black line against the white background (Fig. 30).

Erdman's Float, Fig. 31, is an elongated glass bulb, which is weighted at its lower end with mercury, to keep it in an upright position when floating. It is of

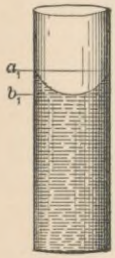

FIG. 29.

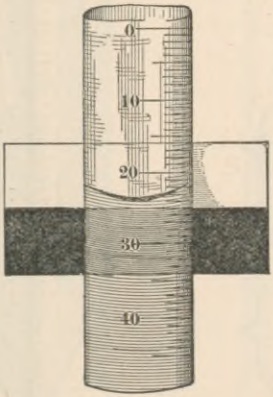

FIG. 30.

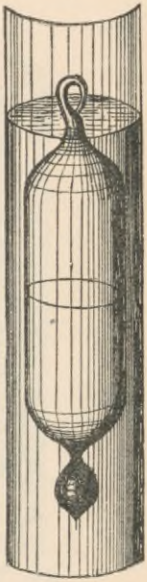

FIG. 31.

such diameter that it will slide easily up and down inside of a burette. There is a ring at the top by which it can be lifted in or out by means of a bent wire. Around its centre a line is marked. At this line instead of at the meniscus the reading is taken.

These floats are sometimes provided with a ther-

mometer, and they then register the temperature as well as the volume.

Others are provided with projecting points along the sides, the object of which is to prevent adhering to the walls of the burette. See Fig. 32.

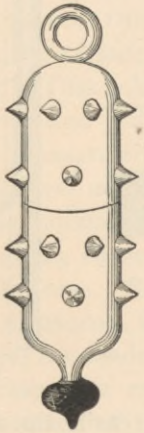

FIG. 32.

FIG. 33.

For the purpose of facilitating the reading, special forms of burettes are constructed which are provided with a dark longitudinal stripe on a white enamelled

background (Fig. 33); the reflection of the dark stripe with the meniscus produces the peculiar appearance shown in Fig. 34. The narrowest point is at the middle of the meniscus, and by reading from this point very accurate measurements are obtained. The same effect can be produced by holding behind an

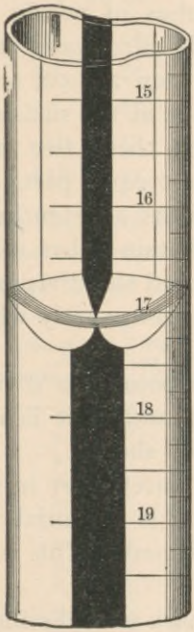

FIG. 34.

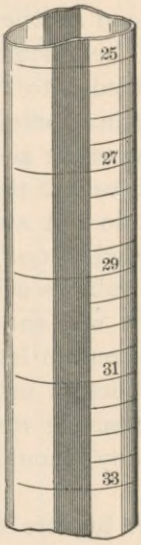

FIG. 35.

ordinary burette a white flexible card having a heavy black longitudinal stripe, about one-eighth inch in width.

Another form of burette designed for the purpose of facilitating reading is that provided with white

enamelled sides, leaving a strip of clear glass in front and back (Fig. 35). This form is especially adapted for use with dark-colored liquids such as iodine and permanganate.

CALIBRATION OF INSTRUMENTS.

Burettes are made from tubes of nearly uniform width. They are filled with distilled water at 15° C. (59° F.) to the 0° mark, and then 25, 50, or 100 cc. run out, and another mark made at the surface of the liquid. The distance between these two marks is then divided into 25, 50, or 100 equal parts, and the spaces again subdivided into fifths and tenths. Now it is very rarely possible to obtain tubes of exactly the same calibre throughout, and the divisions made as above do not always represent exactly what they are intended to do.

If the tube is wider at one point the divisions at that point will contain more, and if it is narrower they will contain less, than they should.

Hence before using a new burette, or in fact any other measuring instrument, it is essential that the error, if any, should be determined. This is done as follows:

Fill the burette to the 0 mark with distilled water at 15° C. (59° F.) and run out 10 cc. at a time into a small weighed flask, and weigh after each addition of 10 cc.

Each 10 cc. should weigh exactly 10 gms., and every deviation found should be noted and taken into consideration in using the instrument.

Example.

Flask		weighed	20.0000 grammes.
"	+ 10 cc.	"	30.1005 "
"	+ 20 cc.	"	40.0499 "
"	+ 30 cc.	"	49.8000 "
"	+ 40 cc.	"	59.9700 "
"	+ 50 cc.	"	70.0100 "
Thus the 1st	10 cc.	weighed	10.1005 grammes.
2d	10 cc.	"	9.9494 "
3d	10 cc.	"	9.7501 "
4th	10 cc.	"	10.1700 "
5th	10 cc.	"	10.0400 "

Having obtained these data, a table like the following may be constructed and kept in some convenient place where it can be readily consulted whenever the

No. of cc. as read on Burette.	No. of cc. as Corrected.	No. of cc. as read on Burette.	No. of cc. as Corrected.	No. of cc. as read on Burette.	No. of cc. as Corrected.
1	1.01	14	14.06	27	26.79
2	2.02	15	15.05	28	27.76
3	3.03	16	16.04	29	28.73
4	4.04	17	17.03	30	29.70
5	5.05	18	18.02	31	30.71
6	6.06	19	19.01	32	31.72
7	7.07	20	20.00	33	32.73
8	8.08	21	20.97	34	33.74
9	9.09	22	21.94	35	34.75
10	10.10	23	22.91	36	35.76
11	11.09	24	23.88	37	36.77
12	12.08	25	24.85	38	37.78
13	13.07	26	25.82	39	38.79

burette it represents is being used. It is not necessary to carry the figure beyond the second decimal place.

A burette which deviates as much as is represented

by the foregoing table is best not used. There should be no greater deviation than 0.15 cc. In the foregoing table there is a deviation of 0.30 cc. at one point.

In order to test the accuracy of a pipette, fill to the mark with distilled water at 15° C. (59° F.); empty into a previously weighed flask, weigh again and thus determine the weight of the water measured. 1 gramme is equal to 1 cc.

Litre flasks are tested as follows:

The flask, perfectly dry and clean, is counterpoised on a balance capable of turning with .005 when carrying about 2000 grammes; it is then filled to the mark with distilled water at 15° C. (59° F.), and the increase in weight should be exactly the number of grammes as the cc. indicated at the mark.

CHAPTER V.

WEIGHTS AND MEASURES USED IN VOLUMETRIC ANALYSIS.

THE metric or decimal system is used in this country and on the continent in Europe, but in England the grain system is used.

The unit of weight in the metric system is the gramme (gm.).

A gramme of distilled water at its maximum density, 4° C. (39° F.), measures one cubic centimetre (cc.).

A kilogram is 1000 gms.

A litre is 1000 cubic centimetres.

Volumetric instruments are graduated in the metric system, but not at 4° C. If they were, it would necessitate the carrying out of all volumetric operations at that temperature, and it would be impossible to do careful volumetric work except for two or three months of the year, unless troublesome calculations for the correction of volume were made.

For this reason the temperature of 15° C. (59° F.) was taken as the standard, and at this temperature most volumetric instruments are graduated. In making very careful examinations the work should be done at this temperature.

One gramme of distilled water at 15° C. measures one cc. as used in volumetric analysis.

The true cc. weighs at 15° C. only 0.999 gm. In the grain system used in England, 10,000 grains is

taken as the standard of measurement. Sutton in his Handbook of Volumetric Analysis proposes that ten-grain measures be called a decem, or for shortness dm.; this term corresponding to the cubic centimetre, and bearing the same relation to the 10,000-grain measure that the cubic centimetre does to the litre. A 10,000-grain measure contains 10,000 fluid grains, or 1000 decems. The flasks used in working by this system are graduated to hold 10,000, 5000, 2500, and 1000 grain measures. Burettes are graduated in 300-grain measures with 1-grain divisions, 600 grains in 1 or 2 grain divisions, 1100 grains in 5 or 10 grain divisions, etc.

The system based upon the imperial-gallon measure of 70,000 grains is still to some extent in use. In this the decimillem (7 grains) bears the same relation to the pound (7000 grains) that the cubic centimetre does to the litre, or the decem to the 10,000-grain measure.

CHAPTER VI.

SOME UNUSUAL VOLUMETRIC METHODS.

VOLUMETRIC ANALYSIS WITHOUT WEIGHTS AND STANDARD SOLUTIONS.

THIS is a matter of curiosity rather than of value, but under certain circumstances it might prove useful. The way in which this is carried out is best explained by an example.

Suppose we wish to determine the proportion of pure sodium chloride in an impure specimen of salt. A portion of the latter is placed upon one pan of a balance and exactly counterpoised by placing on the other pan sufficient of the pure sodium chloride. The samples are then dissolved in water and each titrated with a solution of silver nitrate of unknown strength and the calculation made as follows:

If the pure salt required 60 cc. of the silver solution, and the impure specimen 45 cc., then

$$60 : 45 :: 100 : x; \quad x = 75,$$

the percentage of pure sodium chloride in the salt analyzed.

This process it will be seen can be applied only to such substances of which pure specimens can be had, though in some instances a pure specimen of some

other salt may be used as a substitute, and the result obtained by calculation.

For instance, suppose it is required to estimate sodium carbonate, and we have only pure calcium carbonate on hand to use as a weight. Equal weights are taken, and each titrated with an acid solution. It is now necessary to find out how many cc. of acid solution would be required if pure sodium carbonate were used, instead of pure calcium carbonate, as a counterpoise. The molecular weights of calcium carbonate and sodium carbonate are 100 and 106 respectively, and thus sodium carbonate would require $\frac{100}{106}$, the amount of acid solution as calcium carbonate.

We will assume that the calcium carbonate required 60 cc. of the acid solution and the impure sal soda 40 cc. $60 \times \frac{100}{106} = 56.6$, the number of cc. which an equal weight of sodium carbonate will require. Then

$$56.6 : 40 :: 100 : x; \quad x = 70.67,$$

the percentage of pure sodium carbonate in the specimen analyzed.

With the exercise of a little ingenuity the method may be extended to a number of substances.

Koningh and Peacock have devised a method by which the same end is attained without the aid of a pure substance as a standard.

If impure sodium chloride is to be examined, an equal weight of silver nitrate is taken and dissolved in sufficient water to make 100 cc. of solution; this is placed in a burette, and the sodium chloride titrated after the latter is dissolved.

Assuming that 10 cc. of the silver solution were required, then

$$169.7 : 58.4 :: 10 : x; \quad x = 3.44\%.$$

In the estimation of sodium carbonate an equal weight of oxalic acid is taken and used in the same manner.

VOLUMETRIC ANALYSIS WITHOUT A BURETTE.

The standard solutions are weighed instead of measured. This method is often resorted to where great accuracy is desired, for variations in temperature do not influence the result. It is, however, a slow process.

The standard solution is placed in a suitable flask (see Fig. 36), and the whole weighed on a delicate balance. The solution is then carefully run into the beaker containing the substance to be analyzed, and when the end reaction is obtained the flask is again weighed, and the difference in weight is the amount of solution used. The standard solution should of course be standardized by weight.

FIG. 36.

CHAPTER VII.

Standard and Normal Solutions.—When volumetric analysis first came into use the solutions were so made that each substance to be estimated had its own special volumetric solution, and this was generally of such strength as to give the result in percentages.

Thus a certain strength of solution was used for testing soda, another for potassa, and a third for ammonia.

These solutions were known as normal solutions, and since they are still to some extent in use it is important that no misconception should exist as to what a normal solution is. It is to be regretted that some authors define a normal solution as one having the molecular weight in grammes of the active reagent in a litre.

A Normal Solution is one which contains in a litre a quantity of the active reagent, expressed in grammes, and chemically equivalent to one atom of hydrogen.

According to the U. S. P., Normal solutions $\left(\frac{N}{1}\right)$ are those which contain in one litre (1000 cc.) the molecular weight of the active reagent in grammes, and reduced to the valence corresponding to one atom of replaceable hydrogen or its equivalent.

Thus oxalic acid $H_2C_2O_4 + 2H_2O = 125.7$, having two replaceable H atoms. One half of its molecular weight in grammes is contained in a litre of its normal

solution, while hydrochloric acid HCl = 36.37, which has but one replaceable H atom, has its full molecular weight in grammes in a litre of its normal solution. Sulphuric acid H_2SO_4 has two replaceable H atoms, so its normal solution contains one half of its molecular weight in grammes in a litre. NaOH and KOH being monobasic, a litre of a normal solution of either contains the full molecular weight of the salt in grammes.

Decinormal Solutions, $\frac{N}{10}$, are one tenth the strength of normal solutions.

Centinormal Solutions, $\frac{N}{100}$, are one hundredth the strength of normal solutions.

Seminormal Solutions, $\frac{N}{2}$, are one half the strength of normal solutions.

Double-normal Solutions, $\frac{2}{N}$, are twice the strength of the normal.

Empirical Solutions are those which do not contain an exact atomic proportion of reagent, but are generally of such strength that 1 cc. = 0.01 gm. of the substance upon which it acts.

A Standard Solution is any solution employed in volumetric analysis for the purpose of estimating the strength of substances—that is, any solution the strength or chemical power of which has been determined. It may be normal, decinormal, or of any strength so long as its strength is known. Such a solution is said to be "titrated" (French *titre* = title or power), sometimes called a "set" solution or "standardized" solution.

Standard solutions for use in volumetric analysis are usually solutions of acids, bases, or salts, and in two cases elements, namely, iodine and bromine.

A standard solution of a base is usually used for the estimation of free acids.

A standard solution of an acid is usually used for the estimation of a free base, or the basic part of a salt, the acid of which can be completely expelled by the acid used in the standard solution. Example, carbonates.

A standard solution of a salt may be used, as a precipitant, or it may be used as an oxidizing or reducing agent.

That part of the reagent in a standard solution which reacts with the substance under analysis is the active constituent of the solution. As Ag in $AgNO_3$ is the active constituent of the standard solution of silver nitrate,

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

or Cl in NaCl, is the active constituent of the standard solution of sodium chloride.

If the reagent is a base, as KOH, the basic part K is the active constituent. If the reagent is an acid, the active constituent is the acidulous part, as SO_4 in H_2SO_4.

If the action of the reagent is oxidizing, then that part of the reagent which produces the oxidation is the active constituent.

The valence of an acid is shown by the number of replaceable hydrogen atoms it contains. Thus, HCl is univalent, H_2SO_4 is bivalent; which means that a molecule of HCl is chemically equivalent to one atom of

hydrogen, and a molecule of H_2SO_4 is chemically equivalent to two atoms of hydrogen.

The valence of a base is shown by the number of hydroxyls it is combined with. As KOH is univalent, $Ca(OH)_2$ is bivalent.

The valence of a salt is shown by the equivalent of base which has replaced the hydrogen of the corresponding acid.

Thus NaCl, in which Na has replaced H of HCl, is univalent.

K_2SO_4, in which K_2 has replaced H_2 of H_2SO_4, is bivalent.

If a normal solution is to be made for a special purpose, its reaction in that special case is to be considered. As, when $K_2Cr_2O_7$ is to be used as a precipitating agent its reaction is as follows:

$$2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

It is thus seen that one molecule of $K_2Cr_2O_7$ will cause the precipitation of two atoms of barium in the form of chromate. Each atom of barium is chemically equivalent to two atoms of hydrogen; therefore one fourth of a molecule of $K_2Cr_2O_7$ is equivalent to one atom of hydrogen. And therefore a normal solution of this salt when used as a precipitating agent must contain in one litre one fourth of its molecular weight in grammes.

If $K_2Cr_2O_7$ is to be used as an oxidizing agent, the three atoms of oxygen which it yields for oxidizing purposes must be taken into account. When this salt oxidizes it splits up into $K_2O + Cr_2O_3 + O_3$. The three atoms of oxygen combine with and oxidize the

salt acted upon, or they combine with an equivalent quantity of the hydrogen of an acid and liberate the acidulous part, which then combines with the salt. As the equations show,

$$6FeO + K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3Fe_2O_3;$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 7H_2O + K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3;$$

$$7H_2SO_4 + K_2Cr_2O_7 = 3SO_4 + 7H_2O + K_2SO_4 + Cr_2(SO_4)_3.$$

Each of these atoms of oxygen are equivalent to two atoms of hydrogen. Thus O_3 is equivalent to H_6.

Hence a litre of a normal solution of $K_2Cr_2O_7$, when used as an oxidizing agent, contains one sixth of its molecular weight in grammes.

The same may be said of potassium permanganate when used as an oxidizing agent.

$2KMnO_4$ has five atoms of oxygen which are available for oxidizing purposes, and each of these is capable of taking two atoms of hydrogen from an acid and liberating the acidulous part. The hydrogen equivalent of this salt may therefore be said to be one tenth of the weight of $2KMnO_4$, and a normal solution of this salt contains 31.534 gm. in a litre.

Sodium Thiosulphate (Hyposulphite), $Na_2S_2O_3$, is another instance. The molecule of this salt has two atoms of sodium, which have replaced two atoms of hydrogen of thiosulphuric acid. Thus it would seem that a normal solution should contain one half of the molecular weight in grammes. But the particular reaction of this salt with iodine is taken into account.

One molecule reacts with one atom of iodine, as seen by the equation

$$2Na_2S_2O_3, 5H_2O + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Since iodine is univalent, a molecule of the salt is equivalent to one atom of hydrogen.

A normal solution of this salt therefore contains the molecular weight in grammes in a litre.

To Titrate a substance means to test it volumetrically for the amount of pure substance it contains. The term is used in preference to "tested" or "analyzed," because these terms may relate to qualitative examinations as well as quantitative, whereas titration applies only to volumetric analysis.

Residual Titration, Re-titration, sometimes called Back Titration, consists in treating the substance under examination with standard solution in a quantity known to be in excess of that actually required; the excess (or residue) is then ascertained by residual titration with another standard solution.

Thus the quantity of the first solution which went into combination is found.

Example.—Ammonium carbonate is treated first with $\frac{N}{1}H_2SO_4$ in excess, and the excess then found by titration with $\frac{N}{1}$ KOH.

The quantity of the $\frac{N}{1}KOH$ used is then deducted from the quantity of $\frac{N}{1}H_2SO_4$ added, which gives the quantity of the latter which was neutralized by the ammonium carbonate.

In preparing standard solutions it must be remembered that most salts when dissolved in water reduce the temperature, while some, for instance sulphuric acid and alkaline hydroxides, cause a rise in temperature. Therefore the solutions should be allowed to stand a while so that they may attain the temperature of the air before being measured.

Furthermore, most salts cause a condensation in volume when dissolved in water; this must also be borne in mind.

It is always best to weigh out a little more of the salt than the amount required by theory; dissolve in water less than required for the finished solution, determine its strength, and then dilute to the proper strength. After dilution it should always be again carefully titrated, and proved normal.

To prepare solutions of exactly normal or decinormal strength is a tedious process and often inconvenient.

A solution may be made of approximately normal strength and, its exact strength having been determined, used as it is. For instance, an approximately normal solution of potassium hydroxide is made and its strength determined as follows:

10 cc. of normal oxalic acid are put into a beaker, and after having added a suitable indicator the potassium hydroxide solution is run in from a burette, and we will assume that 10.4 cc. of the latter are required. Then we calculate thus: 10 cc. of normal oxalic acid solution contain 0.63 gramme of the acid; hence 10.4 cc. of the hydroxide solution are equivalent to 0.63 gramme of the acid, and 1 cc. is equivalent to 0.0605 gramme.

Then in estimating the strength of any solution of oxalic acid with this hydroxide solution, the number of cc. of the latter used must be multiplied by the factor 0.0605 gm.

A handier way is as follows: A normal hydroxide solution will neutralize an equal volume of $\frac{N}{1}$ oxalic acid solution. In the case of the approximate solution, it was shown that 10.4 cc. were required for 10 cc. of $\frac{N}{1}$ oxalic acid solution; hence its strength is $\frac{100}{104}$ or 0.9615 that of the strictly normal solution, and the number of cc. used of it in any estimation must be multiplied by $\frac{100}{104}$ or 0.9615, and then by the normal factor for the substance analyzed.

It is a good plan to have the factor marked on the label of the bottle containing such an approximate solution. In this case it would be $\times$ 0.9615 = normal.

CHAPTER VIII.

INDICATORS.

IN volumetric analysis the substance to be analyzed in the state of solution is placed in a beaker and the standard solution is added from a burette until a certain reaction is produced. The exact moment when a sufficient quantity of the standard solution has been added is known by certain visible changes, which differ according to the substance analyzed and the standard solution used. When such a visible change occurs the "end reaction" is reached.

The end reaction manifests itself in various ways, as follows:

1. Cessation of precipitation.
2. First appearance of a precipitate.
3. Change of color.

In some cases, however, the addition of the standard solution to the substance under analysis does not produce either a precipitate or a change of color; in such cases we must resort to the use of an indicator.

An indicator is a substance which is used in volumetric analysis, and which indicates by change of color, or some other visible effect, the exact point at which a given reaction is complete.

Generally the indicator is added to the substance under examination, but in a few cases it is used alongside, a drop of the substance being occasionally brought in contact with a drop of the indicator.

Thus in estimating an alkali with an acid-volumetric solution the alkali is shown to be completely neutralized when the litmus tincture which was added becomes faintly red or the phenolphthalein colorless. Again, when haloid salts are estimated with nitrate-of-silver solution, chromate of potassium is added as indicator. A white precipitate is produced as long as any halogen is present to combine with the silver, and when all is precipitated the chromate of potassium acts upon the silver nitrate, forming the red-silver chromate, this color thus showing that all the halogen has been precipitated.

INDICATORS COMMONLY USED.

The principal indicators used are:

Tincture of Litmus, which shows acidity by turning red and alkalinity by becoming blue.

Phenolphthalein Solution, which is colorless in acid solutions and red in alkaline solutions, but is not reliable for alkaline phosphates, bicarbonates, or ammonia.

Methyl-orange Solution turns red with acids and yellow with alkalies. It is not affected by carbonic acid, and is therefore adapted for the titration of alkaline carbonates.

Rosolic-acid Solution is yellow with acids and violet-red with alkalies. It is very sensitive to ammonia.

Tincture of Turmeric turns brown with alkalies, and the yellow color is restored by acids.

Cochineal Solution turns violet with alkalies and yellowish with acids. It is used chiefly in the presence of ammonia or alkaline earths.

Eosin Solution is red by transmitted light, and shows a strong green fluorescence by reflected light. Acids destroy this fluorescence and alkalies restore it.

Brazilwood Test-solution turns purplish red with alkalies and yellow with acids.

Fluorescein Test-solution shows a strong green fluorescence by reflected light in the presence of the least excess of an alkali.

Neutral Potassium-chromate Test-solution is used in the titration of haloid salts with silver-nitrate solution. It indicates that all the halogen has combined with the silver by producing a red-colored precipitate (silver chromate).

Potassium-ferricyanide Test-solution is used in the estimation of ferrous salts with potassium-dichromate solution. It gives a blue color to a drop of the solution on a white slab as long as any iron salt is present which has not been oxidized to ferric.

Many other indicators are also used.

PRECISION IN DETERMINING END REACTIONS.

In most volumetric precipitation processes no direct reading of the end-point is possible; filtration and trial with small quantities of the clear filtrate being usually necessary. P. N. Rakow (*Chem. Zeit.*) has found that many precipitates which remain obstinately suspended under ordinary conditions, and cause, in the liquid being titrated, an unmanageable turbidity, can be induced to collect and subside by the addition of some immiscible liquid heavier than water; for example, carbon disulphide or chloroform. Such liquids, although exerting no solvent action on the

precipitate, mix intimately with it and carry it down, leaving the supernatant liquid sufficiently clear for the observation of any turbidity produced by the addition of a further quantity of the precipitating solution. Carbon disulphide and chloroform are usually but not invariably effective. Thus the former carries down silver chloride rapidly and completely, but has no influence on the precipitation of barium sulphate. The author has found the method to work fairly well in the few cases he tried.

In the titration of chlorides by means of silver nitrate with neutral chromate as indicator, the end reaction is more distinctly seen by gaslight than by daylight; and if very dilute solutions of chloride are estimated the titration is best performed by gaslight, and even then the change of color from yellow to red is not easily perceived.

In order to overcome this difficulty Dupré suggests the following simple method:

The chloride solution is placed in a white porcelain dish, a small quantity of neutral chromate added (sufficient to make the liquid yellow). Then the titration is begun and watched by looking through a flat glass cell containing some of the neutral chromate.

If the solution in the cell corresponds fairly with the tint of the liquid in the porcelain dish, the latter will appear to be perfectly colorless, like pure water, and the first faint appearance of red becomes strikingly manifest, and no mistake can be made.

The same plan may be followed in other titrations, where the end reaction depends upon the perception of color changes.

CHAPTER IX.

METHODS OF CALCULATING RESULTS.

EACH cc. of a $\frac{N}{1}$ un.valent volumetric solution contains $\frac{1}{1000}$ of the molecular weight in grammes of its reagent, and will neutralize $\frac{1}{1000}$ of the molecular weight of a univalent substance, or $\frac{1}{2000}$ of the molecular weight of a bivalent substance.

Each cc. of a $\frac{N}{1}$ bivalent volumetric solution contains $\frac{1}{2000}$ of the molecular weight in grammes of its reagent, and will neutralize or combine with $\frac{1}{2000}$ of the molecular weight of a bivalent salt, or $\frac{1}{1000}$ of the molecular weight of a univalent salt.

A $\frac{N}{10}$ is only $\frac{1}{10}$ the strength of a normal solution and will neutralize only $\frac{1}{10}$ the quantity of salt, etc.

Normal and decinormal solutions of acids should neutralize normal and decinormal solutions of alkalis, volume for volume. Decinormal solution of silver nitrate and decinormal solution of hydrochloric acid or sodium chloride should combine volume for volume, etc.

The Rules for Obtaining the Percentage of pure substance in any commercial article, such as acids, alkalis, and various salts, are:

1. With normal solutions $\frac{1}{1}$ or $\frac{1}{2}$ (according to its atomicity) of the molecular weight in grammes of the substance is weighed for titration, and the number of cc. of the V. S. required to produce the desired reaction is the percentage of the substance whose molecular weight has been used.

Thus, if sodium hydroxide (NaOH) is to be examined by titration with a normal acid solution $\frac{1}{1}$ of its molecular weight in grammes, 4 gms. is weighed out, and each cc. of the acid solution required represents 1% of the pure salt.

If sodium carbonate (Na_2CO_3) is to be tritated $\frac{1}{2}$ of its molecular weight in grammes, 5.3 gms. is taken.

2. With decinormal solutions $\frac{1}{10}$ or $\frac{1}{20}$ of the molecular weight in grammes of the substance to be analyzed is taken, and the number of cc. will, in like manner, give the percentage.

The following equations will serve to explain more fully:

Sodium hydroxide with $\frac{N}{1}$ *sulphuric acid:*

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

$2 \times 40 = 80$ $\qquad$ 2)98

10)40 $\qquad$ 49 = to 1000 cc.

4.0 gms $\qquad$ = to 100 cc.

Sodium carbonate with $\frac{N}{1}$ *sulphuric acid:*

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

2)98

20)106 $\qquad$ 49 = to 1000 cc.

5.3 gms. $\qquad$ = to 100 cc.

With $\frac{N}{10}$ *sulphuric acid:*

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

$2 \times 40 = 80$ $2)98$

$100)\ 40$ 49 = to 1000 cc.

0.40 gms. = to 100 cc.

3. *Factors or coefficients for calculating the analyses.*—It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed.

The best way to proceed in such a case is to find the factor.

The first step in all cases is to write the equation for the reaction which takes place between the substance under analysis and the solution used.

For instance, a solution of caustic potash is to be examined, a $\frac{N}{1}$ solution of sulphuric acid being used.

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

$2)112$ $2)98$

56 49 = to 1000 cc. $\frac{N}{1}$ acid.

0.56 gm. .049 = to 1 cc. $\frac{N}{1}$ acid.

The factor for KOH when $\frac{N}{1}$ solution is used is .056 gm., that being the quantity neutralized by each cc. of the $\frac{N}{1}$ acid. If $\frac{N}{10}$ acid were used the factor would be .0056 gm.

The number of cc. of the acid used to produce the desired result, when multiplied by the factor gives the quantity in grammes of KOH in the solution taken.

Example.—If 10 grammes of caustic-potash solution were taken, and 40 cc. of $\frac{N}{1}$ acid were required, the 10 gms. of solution contained .056 gm. $\times$ 40 = 2.24 gms. of pure KOH.

To find the percentage, the following formula may be used.

$$\frac{Q \times 100}{W} = \%.$$

Q = the quantity of pure substance found by calculation;

W = weight of substance taken.

If the above example is taken, we have

$$\frac{2.24 \times 100}{10} = 22.4\%.$$

Or the calculation may be made by proportion.

The quantity of the substance taken is always the first term, and the quantity of pure substance found, the second term.

The following rule is easily remembered: *As the quantity taken is to the quantity found, so is* 100 *to* x, *the percentage of pure substance in the sample.*

Three terms of the equation being given, the fourth is found by multiplying the means and dividing the product by the given extreme. By applying this rule to the above case we have

$$10 : 2.24 :: 100 : x. \qquad x = 22.4\%.$$

TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., OF THE ALKALIES, ALKALINE EARTHS, AND ACIDS.

Substance.	Formula.	Molecular Weight.	Normal Factor.*
Sodium hydroxide	$NaOH$	40	0.040
Sodium carbonate	Na_2CO_3	106	0.053
Sodium bicarbonate	$NaHCO_3$	84	0.084
Potassium hydroxide	KOH	56	0.056
Potassium carbonate	K_2CO_3	138	0.069
Potassium bicarbonate	$KHCO_3$	100	0.100
Ammonia (gas)	NH_3	17	0.017
Ammonium carbonate, normal	$(NH_4)_2CO_3$	96	0.048
Ammonium carbonate, commercial	$N_2H_{11}C_2O_5$	157	$0.052\frac{1}{8}$
Lime	CaO	56	0.028
Calcium hydroxide	$Ca(OH)_2$	74	0.037
Calcium carbonate	$CaCO_3$	100	0.050
Nitric acid	HNO_3	63	0.063
Hydrochloric acid	HCl	36.4	0.0364
Sulphuric acid	H_2SO_4	98	0.049
Oxalic acid, crystallized	$H_2C_2O_4.2H_2O$	126	0.063
Acetic acid	$HC_2H_3O_2$	60	0.060

* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure substance present in the material examined.

CHAPTER X.

ANALYSIS BY NEUTRALIZATION.

THIS is based upon the fact that acids are neutralized by alkalies and alkalies by acids.

The strength of an acid is estimated by the quantity of alkali that is required to neutralize it. This process is called *acidimetry.*

The strength of an alkali is found by the quantity of an acid that is required to neutralize it. This process is called *alkalimetry.* The stronger the acid, the more alkali is required, and *vice versa.*

A substance is said to be *alkaline* when it turns red litmus blue; phenolphthalein, red; turmeric, brown; etc. *Acid,* when it turns blue litmus red; red phenolphthalein, colorless, etc.

The principal alkaline substances are the hydroxides and carbonates of sodium, potassium, and ammonium, and the hydroxides and oxides of calcium, barium, and strontium, and the alkaloids.

When an acid is brought in contact with an alkali combination takes place, and a neutral salt is formed. This combination takes place in definite and invariable proportions; thus: If 112 parts of potassium hydroxide are mixed with 98 parts of absolute sulphuric acid the alkali as well as the acid will be neutralized. If only 80 parts of the acid have been added the mixture would still be alkaline, for it requires 98 parts of the

acid to neutralize it. If more than 98 of the acid have been added the mixture would consist of potassium sulphate and free sulphuric acid. The reaction is thus illustrated:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

$K_2 = 78$	$H_2 = 2$	Potassium sulphate.
$O_2 = 32$	$S = 32$	
$H_2 = 2$	$O_4 = 64$	
112	98	

Sodium hydroxide will unite with oxalic, and form a neutral compound in the proportion of 80 parts by weight of the former and 126 parts by weight of the latter, as the equation shows:

$$2NaOH + H_2C_2O_4 . 2H_2O = Na_2C_2O_4 + 4H_2O.$$

$2Na = 46$	$6H = 6$
$2O = 32$	$2C = 24$
$2H = 2$	$6O = 96$
80	126

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

$N = 14$	$H = 1.$	
$5H = 5$	$Cl = 35.4$	
$O = 16$		
35	36.4	
Ammonium hydroxide.	Hydrochloric acid.	

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

106 72.8

Sodium carbonate.

Upon a careful perusal of the foregoing equations it will be seen that since definite weights of acids neutralize definite weights of alkalies the quantity of a certain alkali in solution can be easily determined by the quantity of an acid solution of known strength required to neutralize it, and *vice versa*.

If we make a solution of oxalic acid of such strength that 1000 cc. of it contains 63 gms. of the crystallized acid, 1 cc. of it will neutralize .056 gm. of KOH, .040 gm. of NaOH, or .035 gm. of NH_4OH.

Thus if 10 gms. of solution of KOH be treated with this oxalic-acid solution and it is found that 25 cc. of it are required to neutralize the alkali, the alkali solution contains $25 \times .056 = 1.4$ gms. of pure KOH.

Since the acid and alkali as well as the neutral salt which is formed are colorless, and no visible change takes place during the reaction, it is necessary to add some substance which by change of color will show when the neutralization is complete. Such a substance is known as an indicator. A number of these are spoken of on page 43.

Neutralization is sometimes called saturation.

ALKALIMETRY.

Preparation of Acid Volumetric Solutions.—It is possible to carry out the titration of most alkalies with only one standard acid solution, but the standard acids are frequently required in other processes besides mere saturation, and it is therefore advisable to have a variety.

The standard oxalic acid is preferred by some because of the ease with which it may be prepared, pro-

vided a pure acid can be had. It does not, however, keep very long, and when used for titrating carbonates with methyl orange as an indicator the end reaction is not very distinct. Oxalic acid cannot very well be used for the titration of alkaline earths, since it forms insoluble compounds with these metals.

Sulphuric acid V. S. is preferred by others. A pure acid can be gotten without difficulty, and the standard solution made with it is totally unaffected by boiling, which cannot be said of either nitric or hydrochloric acid. Sulphuric acid, however, forms with alkaline earths insoluble compounds. For this reason standard solution of hydrochloric acid must frequently be employed.

Normal Oxalic Acid V. S., U. S. P.—$H_2C_2O_4 + 2H_2O = 125.7$. $\left.\begin{matrix} 62.85 \\ *63. \end{matrix}\right\}$ gms. in 1 litre.

Dissolve 62.85 gms. (*63 gms.) of pure oxalic acid (see below) in enough water to make, at or near 15° C., exactly 1000 cc.

Pure oxalic acid, crystallized, is in the form of colorless, transparent, clinorhombic crystals, which should leave no residue when ignited upon platinum foil. It is completely soluble in 14 parts of water at 15° C. If the acid leaves a residue on ignition it should be purified by recrystallization, as directed by the U. S. P.

1 cc. of $\frac{\frac{54}{N}}{1}$ oxalic acid V. S. is the equivalent of NaOH, 0.03996; KOH, 0.05599; NH_3, 0.01701.

Decinormal Oxalic Acid V. S., U. S. P.—$H_2C_2O_4 + 2H_2O = 125.7$. $\left.\begin{matrix} 6.285 \\ *6.3 \end{matrix}\right\}$ gms. in 1 litre.

Dissolve 6.285 gms. (*6.3 gms.) of pure oxalic acid in enough water to make, at or near 15° C., exactly 1000 cc.

Normal Hydrochloric Acid V. S., U. S. P. — $HCl = 36.37$. $\left.\begin{matrix}36.37\\36.4\end{matrix}\right\}$ gms. in 1 litre.

Mix 130 cc. of hydrochloric acid of sp. gr. 1.163 with enough water to measure, at or near 15° C., 1000 cc.

Of this liquid (which is still too concentrated) measure carefully into a flask or beaker 10 cc., add a few drops of phenolphthalein T. S., and gradually add from a burette $\frac{N}{1}$ potassium hydroxide V. S. until a permanent pale pink tint is produced. Note the number of cc. of $\frac{N}{1}$ potassium hydroxide solution consumed, and then dilute the acid so that equal volumes of this and the $\frac{N}{1}$ KOH V. S. neutralize each other.

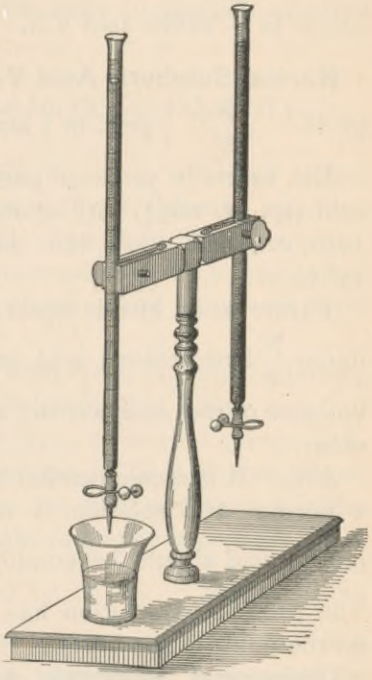

FIG. 37.

Example.—Assuming that the 10 cc. of the acid solution required 12 cc. of the $\frac{N}{1}$ KOH, each 10 cc. of

the acid must be diluted to 12 cc., or the whole of the remaining acid in the same proportion.

After the dilution a new trial should be made. 10 cc. of the acid V. S. should require exactly 10 cc. of the alkali.

This solution is exactly equivalent in neutralizing power to $\frac{N}{1}$ oxalic acid V.S.

Normal Sulphuric Acid V. S., U. S. P.—$H_2SO_4 = 97.82$. $\left.\begin{matrix} 48.91 \\ *49. \end{matrix}\right\}$ gms. in 1 litre.

Mix carefully 30 cc. of pure concentrated sulphuric acid (sp. gr. 1.835) with enough water to make about 1050 cc., and allow the liquid to cool to about 15° C.

Titrate 10 cc. of this liquid in the manner described under $\frac{N}{1}$ hydrochloric acid, and dilute it so that equal volumes of the acid and the alkali will neutralize each other.

Note.—It is recommended in the U. S. P. that when a normal acid solution is required the normal sulphuric acid should be employed in place of $\frac{N}{1}$ oxalic. The oxalic-acid solution has a tendency to crystallize on the point of the burette.

Decinormal Sulphuric Acid V. S., U. S. P.—$H_2SO_4 = 97.82$. $\left.\begin{matrix} 4.891 \\ 4.9 \end{matrix}\right\}$ gms. in a litre.

Dilute 10 cc. of the normal sulphuric-acid solution with enough water to make 100 cc.

The standardization of normal acid solutions may

also be effected by the use of pure anhydrous sodium carbonate.

Pure anhydrous sodium carbonate may be obtained by heating to dull redness a few grammes of *pure* sodium bicarbonate for about 15 minutes. The resulting carbonate is practically free from impurity.

The sodium bicarbonate loses on ignition one half of its carbonic acid gas:

$$2NaHCO_3 + \text{Heat} = Na_2CO_3 + CO_2 + H_2O.$$

The bicarbonate should, however, be tested before igniting, and if more than traces of chloride, sulphate, or thiosulphate are found, these may be removed by washing a few hundred grammes, first with a saturated solution of sodium bicarbonate, and afterward with distilled water.

0.53 gm. of the pure anhydrous sodium carbonate is accurately weighed and dissolved in about 20 cc. of water in a flask and a few drops of methyl orange T. S. added as indicator. The acid to be "set" or "standardized" is then run into the sodium-carbonate solution until a permanent light-red color is produced. It should require exactly 10 cc. of the $\frac{N}{1}$ acid solution. If 8 cc. of the acid solution are consumed to bring about the required result, then every 8 cc. must be diluted to 10 cc., or the whole of the remaining solution must be diluted in this proportion:

$$\underset{\substack{2)106 \\ 53 \text{ gms.} \\ 0.53 \text{ gm.}}}{Na_2CO_3} + \underset{\substack{2)98 \\ 49}}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

$$= \text{to } 1000 \text{ cc. } \frac{N}{1} \text{ V. S.;}$$

$$= \text{to } 10 \text{ cc. } \frac{N}{1}$$

Instead of methyl orange, litmus tincture may be used. The carbonic-acid gas which is liberated in this reaction turns litmus red; the contents of the flask should therefore be boiled for a few minutes to drive off the CO_2, when the blue color will return. More acid is then run in until the mixture after boiling remains of a neutral color; indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

ESTIMATION OF ALKALINE HYDROXIDES.

A definite quantity of the substance is taken (generally weighed), and diluted with or dissolved in a little water in a flask or beaker. A few drops of a suitable indicator are now added, and the standard acid solution allowed to flow in until the last drop added just causes the color to change, the flask being agitated after each addition of the acid solution.

The proper method of titrating is shown in Fig. 38.

Potassa. $KOH = \frac{55.99}{56}$ U. S. P.—Weigh carefully 1 gm. of potassa, dissolve it in a small quantity of water, add a drop of phenolphtalein solution as indicator, and titrate with $\frac{N}{1}$ sulphuric acid V. S. until the red color just disappears. Each cc. of the normal acid solution used represents .056 gm. of pure potassa. To find percentage, multiply the factor (.056) by the number of cc. of $\frac{N}{1}$ V. S. used, and then multiply the product by 100. Potassium hydroxide having great affinity for carbonic-acid gas, which it absorbs out of the air, generally contains small quantities of carbonate. There-

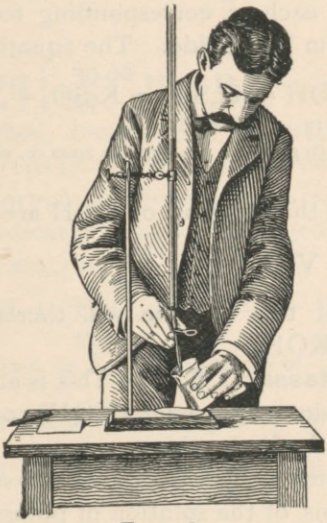

FIG. 38.

fore in titrating as above described it should be boiled once or twice toward the end of the reaction in order to drive off any CO_2 which may be present. This gas, which has an acid reaction with phenolphtalein, would otherwise cause an incorrect estimation. This precaution should be taken with the other alkaline hydroxides.

The U. S. P. requirement is that 0.56 gm. of potassa be neutralized by not less than 9 cc. of the normal acid solution, each cc. corresponding to 10 per cent of pure potassium hydroxide. The equation is

$$\underset{2)112}{2KOH} + \underset{2)98}{H_2SO_4} = K_2SO_4 + {}_2H_2O.$$
$$\underset{56 \text{ gms.}}{} = \underset{49 \text{ gms. in 1000 cc. of } \frac{N}{1} \text{ V. S.}}{}$$

This shows that 56 gms. of KOH are neutralized by 1000 cc. of $\frac{N}{1}$ V. S.

Each cc. of this solution will therefore neutralize 0.056 gm. of KOH.

Liquor Potassa, U. S. P.—This is an aqueous solution of potassium hydroxide (KOH) containing about 5 per cent of the hydroxide.

It is estimated volumetrically in the same manner as potassa, 10 gms. of the solution of potassa being taken, each cc. of the $\frac{N}{1}$ V. S. representing 0.056 gm. of KOH.

By multiplying the factor by the number of cc. of $\frac{N}{1}$ V. S. used, the quantity of absolute KOH in the 10 gms. of liquor taken is obtained.

The percentage is then found by multiplying the quantity so obtained by 100 and dividing by the number of grammes of the liquor taken.

Thus if 9 cc. of the $\frac{N}{1}$ V. S. were used, the 10 gms. taken contained $9 \times 0.056 = 0.504$ gm. Then

$$10 \text{ gms.} : 0.504 :: 100 : x. \qquad x = 5.04\%.$$

28 gms. of the U. S. P. liquor potassa should require about 25 cc. of the $\frac{N}{1}$ acid V. S., each cc. representing 0.2% of KOH.

Soda, ($NaOH \left\{ \begin{matrix} \\ * \frac{39.96}{40} \end{matrix} \right.$ **U. S. P.**).—1 gm. of soda is carefully weighed, dissolved in a small quantity of water, a few drops of phenolphthalein added, and then titrated with normal sulphuric acid V. S. until the red color of the indicator is just discharged. This equation shows the reaction :

$$2NaOH + H_2SO_4 = Na_2SO_4 + H_2O.$$
$$\underset{40 \text{ gms.}}{\overset{2)80}{}} = \underset{49 \text{ gms. or } 1000 \text{ cc. of } \frac{N}{1} \text{ V. S.}}{\overset{2)98}{}}$$

Thus each cc. represents 0.040 gm. of NaOH. 1 gm. should require 22.5 cc. of $\frac{N}{1}$ acid V. S., which indicates 90%.

$$.040 \times 22.5 = .900$$
$$\frac{.900 \times 100}{1} = 90\%$$

Liquor Soda, U. S. P.—This is an aqueous solution, containing about 5% of the hydroxide (NaOH). 10 grammes of liquor soda are taken mixed with a little water, a few drops of phenolphthalein are added, and then from a burette the $\frac{N}{1}$ sulphuric acid V. S. in the

manner described above. Each cc. required represents 0.040 gm. of NaOH. If 12.5 cc. were required, then $0.040 \times 12.5 = .500$.

$$\frac{.500 \times 100}{10} = 5\%$$

Aqua Ammoniæ, U. S. P.—An aqueous solution of ammonia ($NH_3 = 17.01$) containing 10% by weight of the gas.

Three grammes of ammonia water are diluted with a little water, a few drops of rosolic acid T. S. are added, and then $\frac{N}{1}$ sulphuric acid V. S. slowly from a burette until the yellow color indicates that all the alkali is neutralized. Phenolphthalein is not suitable as an indicator for ammonia. Litmus may be used, but it is not as delicate an indicator as rosolic acid.

Each cc. of $\frac{N}{1}$ acid V. S. used represents 0.017 gm. NH_3 or *0.035 gm. NH_4OH, as shown by the equation

$$\left.\begin{matrix} 2NH_4OH \\ 2NH_3 . H_2O \end{matrix}\right\} + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

$$\underbrace{2NH_4OH}_{\frac{2)70}{35}} \quad \underbrace{2NH_3 . H_2O}_{\frac{2)34}{17}} \quad \frac{2)98}{49} = \text{to 1000 cc. } \frac{N}{1} \text{ acid V. S.}$$

If the 3 gms. required 17.8 cc. $\frac{N}{1}$ acid V. S., then it contained $17.8 \times .017$ gm. = 0.3026 gm.

$$\frac{.3026 \times 100}{3} = 10.08\% \text{ of } NH_3.$$

According to the U. S. P., 3.4 gms. should require 20 cc. of normal acid V. S.

Aqua Ammoniæ Fortior, U. S. P. (Stronger Ammonia Water).—An aqueous solution of ammonia (NH_3) containing about 28% by weight of the gas. This is estimated in the same manner as aqua ammonia, two grammes of the stronger ammonia water being taken instead of three.

Spiritus Ammoniæ (Spirit of Ammonia).—This is an alcoholic solution of NH_3, containing 10% by weight of the gas.

3.4 grammes (or 4.2 cc.) of the spirit are diluted with water and treated with $\frac{N}{1}$ sulphuric V. S. Each cc. of the $\frac{N}{1}$ acid solution used represents .017 gm. of NH_3 or 0.5%. 20 cc. should be required. Rosolic acid is the indicator.

ESTIMATION OF ALKALINE CARBONATES.

When carbonates are treated with acids carbonic-acid gas is liberated. This gas shows an acid reaction with most indicators, and the reaction will seem to be completed before the alkali is entirely neutralized. To avoid this the process is conducted at a boiling temperature in order to drive off the CO_2. The standard acid being added until two minutes' boiling fails to restore the color indicating alkalinity. If the titration is conducted at a boiling temperature it is advisable to attach to the lower end of the burette a long rubber tube with a pinch-cock fixed about midway on the tube.

The boiling can then be done at a little distance

from the burette and the expansion of the standard solution therein thus prevented.

Another and better method is to use methyl orange as an indicator, and conduct the process by simple titration without the use of heat.

Methyl orange is not affected by CO_2. When methyl orange is used as an indicator, standard sulphuric acid, and not oxalic acid, should be employed. The reaction of the latter with this indicator is not very sharp.

Potassium Carbonate, $K_2CO_3 = \left\{ \begin{matrix} 137.91 \\ *138 \end{matrix} \right.$.—Weigh carefully one gramme of the salt, dissolve in a small quantity of water in a beaker or flask, add a few drops of methyl orange T. S., and titrate with normal sulphuric acid until a faint orange-red color appears.

$$\underset{\underset{69}{2)138}}{K_2CO_3} + \underset{\underset{49}{2)98}}{H_2SO_4} = K_2SO_4 + H_2O + CO_2.$$

= grammes in 1000 cc. $\frac{N}{1}$ V. S.

Each cc. of $\frac{N}{1}$ H_2SO_4, therefore, represents 0.069 gramme (more accurately 0.068955 gramme) of pure dry potassium carbonate.

Thus if 14.4 cc. of the normal acid were required, the salt contained $14.4 \times .069 = .9936$ grammes of pure K_2CO_3, or 99.36 per cent. The U. S. P. requirement is that 0.69 grammes of the salt be neutralized by not less than 9.5 cc. of normal acid, corresponding to 95% of the pure salt.*

When methyl orange is used the end reaction is not very well defined, and practice is required to obtain good results. If it is desired to use litmus or phenol-

phthalein, it will be necessary to boil the solution as described above.

$$*.069 \times 9.5 = 0.6555$$
$$\frac{0.6555 \times 100}{0.69} = 95\%$$

Potassium Bicarbonate, $KHCO_3 = \left\{ \begin{matrix} 99.88 \\ *100 \end{matrix} \right.$.—
The process is exactly the same as that for the carbonate.

$$\underset{\substack{2)200 \\ 100}}{2KHCO_3} + \underset{\substack{2)98 \\ 49 = \text{to grammes in 1000 cc. of } \frac{N}{1} \text{ acid.}}}{H_2SO_4} = K_2SO_4 + 2H_2O + 2CO_2.$$

Each cc. of $\frac{N}{1}$ acid represents 0.1 gramme (more exactly 0.09988 gramme) of pure $KHCO_3$.

The U. S. P. requirement is that 1 gramme of the salt be neutralized by not less than 10 cc. of normal acid (corresponding to 100 per cent of the pure salt).

Sodium Carbonate, $Na_2CO_3 + 10H_2O = \left\{ \begin{matrix} 285.45 \\ *286 \end{matrix} \right.$.—
Dissolve two grammes of sodium carbonate in sufficient water, add a few drops of methyl orange, and titrate as described under potassium carbonate.

$$\underbrace{Na_2CO_3 + 10H_2O}_{\substack{2)286 \\ 143}} + \underset{\substack{2)98 \\ 49 = \text{grammes in 1000 cc. } \frac{N}{1} \text{ acid V. S.}}}{H_2SO_4} = Na_2SO_4 + 11H_2O + CO_2.$$

Each cc. of $\frac{N}{1}$ acid V. S. represents 0.143 gramme of crystallized sodium carbonate.

The U. S. P. directs that the salt be deprived of its water of crystallization by heat immediately before being weighed, and that 1 gramme of the anhydrous carbonate should neutralize not less than 18.7 cc. of $\frac{N}{1}$ sulphuric acid, corresponding to 98.9%.

Sodium Carbonate (exsiccated).—Operate upon 1 gramme of the salt as described.

$$\underset{2)106}{Na_2CO_3} + \underset{2)98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$
$$53 \qquad 49 = \text{grammes in 1000 cc. } \frac{N}{1} \text{ acid.}$$

Each cc. of the $\frac{N}{1}$ acid represents .053 gramme of anhydrous sodium carbonate. The U. S. P. requirement is that not less than 13.8 cc. of normal sulphuric acid should neutralize 1 gramme of the salt, corresponding to about 73 per cent of anhydrous sodium carbonate.

$$.053 \times 13.8 = .7314 \quad \text{or} \quad 73.14\%$$

Sodium Bicarbonate, $NaHCO_3 = \begin{cases} 83.85 \\ *84 \end{cases}$.—Operate upon 1 gramme of the salt, and proceed in the usual way.

$$\underset{2)168}{2NaHCO_3} + \underset{2)98}{H_2SO_4} = Na_2SO_4 + 2H_2O + 2CO_2.$$
$$84 \qquad 49 = \text{to grammes in 1000 cc. } \frac{N}{1} \text{ acid.}$$

Thus each cc. of $\frac{N}{1}$ acid represents .084 gramme of pure sodium carbonate.

According to the U. S. P., 0.85 gramme of sodium

bicarbonate should require not less than 10 cc. of normal sulphuric acid, which corresponds to at least 98.6% of the pure salt.

$$.084 \times 10 = .84$$

$$\frac{.84 \times 100}{.85} = 98.6\%$$

Lithium Carbonate, $Li_2CO_3 = \begin{cases} 73.87 \\ *74 \end{cases}$.—

$$\underset{2)74}{\underset{37}{Li_2CO_3}} + H_2SO_4 = Li_2SO_4 + H_2O + CO_2.$$
$$\underset{2)98}{49} = \text{grammes in 1000 cc. } \frac{N}{1} \text{ acid.}$$

Each cc. of $\frac{N}{1}$ acid represents 0.037 gramme of lithium carbonate (more accurately .03693). 0.5 gm. of dry lithium carbonate are mixed with about 20 cc. of water in a beaker, a few drops of methyl orange T. S. added, and titration proceeded with until a faint orange-red color of the solution indicates the complete neutralization of the lithium carbonate.

To comply with the U. S. P. test, 0.5 gm. should require for complete neutralization not less than 13.4 cc. of normal sulphuric acid, corresponding to at least 98.98 per cent of the pure salt.

$$0.03693 \times 13.4 = 0.494862 \text{ gm.}$$

$$\frac{0.494862 \times 100}{0.5} = 98.98\%$$

Ammonium Carbonate, $N_2H_{11}C_2O_5 = \begin{cases} 156.77 \\ *157 \end{cases}$.

— Normal ammonium carbonate has the formula

$(NH_4)_2CO_3$, but the normal salt loses upon exposure NH_3 and H_2O. The commercial salt, therefore, generally is a mixture of carbamate and bicarbonate.

$$(NH_4)_2CO_3 - NH_3 = NH_4HCO_3;$$
$$(NH_4)_2CO_3 - H_2O = NH_4NH_2CO_2.$$

The commercial carbonate is therefore generally expressed thus:

$$NH_4HCO_3 . NH_4NH_2CO_2 \quad \text{or} \quad N_2H_{11}C_2O_5.$$

For estimating the ammonium carbonate the U. S. P. recommends the following procedure: Dissolve 7.84 gms. of unaltered ammonium carbonate in water to the volume of 90 cc. Take 30 cc. of this solution (which contains 2.613 gms. of the salt), add a few drops of rosolic acid T. S., and titrate with $\frac{N}{1}$ H_2SO_4 V. S. until the violet-red color is replaced by yellow. 50 cc. of the $\frac{N}{1}$ H_2SO_4 should be required before this change takes place, corresponding to 100% of pure salt.

$$\underset{6)313.54}{\underline{52.256}} \qquad \underset{6)294}{\underline{49}} = \text{to 1000 cc. } \frac{N}{1} \text{ acid V. S.}$$

$$2N_2H_{11}C_2O_5 + 3H_2SO_4 = 3(NH_4)_2SO_4 + 4CO_2 + 2H_2O.$$

Each cc., therefore, represents 0.052256 gm. of ammonium carbonate.

$$50 \text{ cc.} = 50 \times .052256 = 2.6128 \text{ gms.}$$

$$\frac{2.6128 \times 100}{2.613} = 100\%$$

Although rosolic acid, on account of its sensitiveness to ammonia, is recommended in the U. S. P. process, yet it must be remembered that this indicator is affected by CO_2, and therefore great care should be exercised in this estimation. It must also be remembered that if heat is employed to dispel the CO_2 it is apt to occasion a loss of ammonia.

Methyl orange is not affected by CO_2 and might be employed in this case, but it is not as sensitive to ammonia as rosolic acid.

The method usually employed by skilled analysts is to add a measured excess of the standard acid solution, and thus convert the ammonium carbonate into the less volatile ammonium sulphate; then gently boil to get rid of CO_2, and titrate back with a standard alkaline V. S. (using litmus as an indicator) until the excess of acid is neutralized. The quantity of free acid is thus found, which, when deducted from the amount of acid first added, gives the quantity which was required to neutralize the ammonium carbonate.

Thus, 2.613 gm. in solution of ammonium carbonate are treated with 70 cc. of $\frac{N}{1}$ H_2SO_4 V. S., which is more than sufficient to neutralize it; the solution is then gently boiled to drive off CO_2, a few drops of litmus tincture added, and then titrated with $\frac{N}{1}$ KOH V. S. until the litmus no longer shows an acid reaction and the solution is neutral.

Let us assume that 20 cc. of the $\frac{N}{1}$ KOH V. S. were used. By deducting the 20 cc. from the 70 cc. of $\frac{N}{1}$

acid first added we find that 50 cc. of the acid went into combination with the ammonium salt. Thus,

$$50 \times .052256 = 2.6128 \ (*2.613)$$

$$\frac{2.613 \times 100}{2.613} = 100\%$$

Borax, $Na_2B_4O_7 . 10H_2O = \left\{ \begin{matrix} 380.92 \\ *382 \end{matrix} \right.$.—Two gms. of borax are dissolved in a small quantity of water, a few drops of tincture of litmus are added, and the solution titrated with normal oxalic acid V. S., or some other $\frac{N}{1}$ acid V. S.

Boric acid is liberated during the operation, which colors the litmus wine-red. This is not regarded, and the titration is continued until the bright red, due to the action of free oxalic acid, makes its appearance. Apply the following equation:

$$\underset{\underset{191}{2)382}}{Na_2B_4O_7.10H_2O} + \underset{\underset{63}{2)126}}{H_2C_2O_4.2H_2O} \text{ gms.} = 1000 \text{ cc.} \frac{N}{1} \text{ V. S.}$$

$$= Na_2C_2O_4 + H_2B_4O_7 + 12H_2O.$$

Thus each cc. of $\frac{N}{1}$ oxalic acid V. S. represents 0.191 gm. crystallized borax.

MIXED ALKALINE HYDROXIDE AND CARBONATE.

If it is desired to ascertain the proportion in which these exist in a mixture, we proceed as follows:

First determine the total alkalinity by means of

normal hydrochloric acid, using methyl orange as indicator. Then dissolve a like quantity of the mixture in 150 cc. of water and add sufficient barium chloride to precipitate all of the carbonate as barium carbonate, and then add water to make 200 cc. and set aside to settle. When the supernatant liquid is clear take one fourth (50 cc.) of it, and titrate with normal hydrochloric acid, using phenolphthalein as indicator. The number of cc. multiplied by 4 will be the quantity of normal acid required by the caustic alkali. The difference between this and the number of cc. representing the total alkalinity is calculated as carbonate.

Example.—Assuming that we are analyzing a mixture of sodium hydroxide and carbonate.

2 grammes of the substance are dissolved in water, and titrated with normal acid solution. 43.2 cc. of the latter are required. Another 2 grammes is dissolved, treated with barium chloride as directed, and one fourth of the clear solution titrated with normal acid. 5.6 cc. are required; then $5.6 \times 4 = 22.4$ cc., representing the sodium hydroxide.

43.2 cc. = total alkalinity;
$-\ 22.4 \times .040 =$ .896 grammes sodium hydroxide;
$20.8 \times .053 = 1.1024$ " sodium carbonate.

A slight error occurs in this process, because the volume of the precipitate is included in the measured liquid.

Another way is to filter the mixture after barium chloride has been added, titrate the filtrate with normal acid to find the quantity of hydroxide, then dissolve the precipitated barium carbonate in normal

hydrochloric acid in excess, and retitrate with normal alkali, thus ascertaining the amount of carbonate.

When the alkaline carbonate is present in very small quantities the method of Lunge may be employed.

A few drops of phenacetolin solution are added to impart a scarcely perceptible yellow to the liquid. Normal acid solution is then run in until a pale rose tint appears, indicating that all the alkali hydroxide is neutralized; the volume of acid is noted, and the titration continued; the red color is intensified, and when the carbonate is entirely decomposed a golden-yellow color results.

Considerable practice is required with solutions of known composition to accustom the eye to the changes of color.

ESTIMATION OF ALKALINE BICARBONATES WHEN MIXED WITH CARBONATES.

Thompson's Method.—Take 2 grammes of the salt and dissolve in 100 cc. of water. Divide the solution into two equal parts and titrate one portion with normal acid solution, using methyl orange as indicator, and note the quantity required. We will assume 13 cc.

Then treat the second portion with a measured excess (say 25 cc.) of normal sodium hydroxide solution free from CO_2. This converts the bicarbonate into carbonate. Now add an excess of pure neutral barium chloride solution in order to precipitate all the carbonate as barium carbonate, and then titrate with normal acid, using phenolphthalein as indicator, to

determine the excess of sodium hydroxide. 15 cc. are required. Thus

25 — 15 = 10 cc., the equivalent of bicarbonate,

and

13 — 10 = 3 cc., the equivalent of carbonate;
10 × .084 = .840 gm., sodium bicarbonate;
3 × .053 = .159 gm., sodium carbonate.

ESTIMATION OF ALKALIES IN THE PRESENCE OF SULPHITES.

This is accomplished by adding hydrogen peroxide to the solution in order to convert the sulphite into sulphate, and then titrating in the usual way with normal acid.

MIXED POTASSIUM AND SODIUM HYDROXIDES.

These are estimated by treatment with tartaric acid solution, which converts them into bitartrates. The bitartrate of potassium is almost insoluble in solution of sodium bitartrate and hence may be separated by filtering. The sodium bitartrate is estimated in the filtrate by titration with normal sodium hydroxide solution. The potassium is found by difference.

ORGANIC SALTS OF THE ALKALIES.

The tartrates, citrates, and acetates of the alkali metals are converted by ignition into carbonates, the whole of the base remaining in the form of carbonate.

Each molecular weight of a normal tartrate gives when ignited one molecular weight of carbonate:

$$\underline{K_2}C_4H_4O_6 = \underline{K_2}CO_3.$$

Every two molecular weights of an acetate or an acid tartrate give one molecular weight of carbonate:

$$\underline{2K}C_2H_3O_2 = \underline{K_2}CO_3;$$

$$\underline{2K}HC_4H_4O_6 = \underline{K_2}CO_3.$$

Every two molecular weights of a normal citrate give three molecular weights of carbonate:

$$\underline{2K_3}C_6H_5O_7 = \underline{3K_2}CO_3.$$

These reactions are taken advantage of in volumetric analysis, and the tartrates, citrates, and acetates of the alkalies are indirectly estimated by calculating upon the quantity of carbonate formed by burning them, the quantity of carbonate being found by titration in the usual manner.

Potassium Tartrate, $K_2C_4H_4O_6.H_2O = \begin{cases} 243.66 \\ *244 \end{cases}$.—Two gms. of the salt are placed in a platinum or porcelain crucible and heated to redness in contact with the air until completely charred; that is to say, until nothing is left in the crucible but carbonate and free carbon.

The crucible is now cooled, and its contents treated with boiling water, which dissolves the potassium carbonate, the carbon being separated by filtration. In order to obtain every trace of carbonate it is well to wash the crucible with several small portions of hot

water, and add the washings to the rest of the filtrate through the filter.

If the salt is completely carbonized the filtrate will be colorless, but if the carbonization is not complete the solution will be more or less colored, and should be rejected, and a fresh quantity of the salt subjected to ignition.

To the filtrate, which contains potassium carbonate, add a few drops of methyl-orange, and titrate with $\frac{N}{1}$ sulphuric acid V. S. until a light orange-red color appears and the carbonate is neutralized.

The following equations will explain the reactions:

$$* \underbrace{2(K_2C_4H_4O_6.H_2O)}_{488} + 5O_2 = \underbrace{2K_2CO_3}_{276} + 6CO_2 + 6H_2O;$$

then

$$\underset{276}{2K_2CO_3} + \underset{196}{2H_2SO_4} = 2K_2SO_4 + 2H_2O + 2CO_2;$$

therefore

$$\underbrace{2(K_2C_4H_4O_6.H_2O)}_{4)488} = \underbrace{2K_2CO_3}_{4)276} = \underbrace{2H_2SO_4}_{4)196},$$

$$122 \text{ gms.} = 69 \text{ gms.} = 49 \text{ gms.} = 1000 \text{ cc.} \frac{N}{1} \text{ V. S.},$$

and each cc. of $\frac{N}{1}$ H_2SO_4 represents 0.122 gm. of potassium tartrate.

Example.—Two gms. of potassium tartrate treated as described above require 16.3 cc. of $\frac{N}{1}$ H_2SO_4 V. S. It therefore contains $0.122 \times 16.3 = 1.9886$ gms.

$$\frac{1.9886 \times 100}{2} = 99.43\%$$

* Since some carbon is always left behind, the reaction is probably more accurately written thus:

$$2(K_2C_4H_4O_6.H_2O) = 2K_2CO_3 + 5C + CO_2 + 6H_2O.$$

Potassium and Sodium Tartrate (Rochelle Salt), $KNaC_4H_4O_6.4H_2O = \begin{cases} 281.51 \\ *282 \end{cases}$.—This salt is treated in exactly the same way as described for potassium tartrate.

When ignited the double tartrate is converted into a double carbonate of potassium and sodium:

$$*\underbrace{2(KNaC_4H_4O_6.4H_2O)}_{564} + 5O_2 = \underset{244}{2KNaCO_3} + 6CO_2 + 12H_2O;$$

then

$$\underset{244}{2KNaCO_3} + \underset{196}{2H_2SO_4} = 2KNaSO_4 + 2CO_2 + 2H_2O;$$

therefore

$$\underset{4)\overline{141}}{2KNaC_4H_4O_6.4H_2O} = \underset{4)\overline{61}}{2KNaCO_3} = \underset{4)\overline{49}}{2H_2SO_4}, = 1000\text{ cc.}\frac{N}{1}\text{ V. S.}$$

and each cc. of $\frac{N}{1}$ H_2SO_4 represents 0.141 gm. of $KNaC_4H_4O_6.4H_2O$.

The U. S. P. directs that 1.41 gms. of Rochelle salt when completely decomposed by ignition should leave an alkaline residue, which requires not less than 10cc. of $\frac{N}{1}$ H_2SO_4 for complete neutralization, corresponding to 100% of the pure salt.

The factor is 0.141; 10 cc. $= .141 \times 10 = 1.41$.

$$\frac{1.41 \times 100}{1.41} = 100\%$$

* The reaction is probably more accurately written thus:
$2(KNaC_4H_4O_6.4H_2O) = 2KNaCO_3 + 5C + CO_2 + 12H_2O$.

Potassium Bitartrate (Cream of Tartar), $KHC_4H_4O_6 = \begin{cases} 187.67 \\ *188 \end{cases}$.—The estimation of this salt is affected in the same way as the tartrate.

The bitartrate having but one atom of potassium in its molecule, it takes two molecules to form one molecule of carbonate.

$$*2\underset{376}{KHC_4H_4O_6} + 5O_2 = \underset{138}{K_2CO_3} + 7CO_2 + 5H_2O;$$

then

$$\underset{138}{K_2CO_3} + \underset{98}{H_2SO_4} = K_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{2)376}{\underset{188}{2KHC_4H_4O_6}} = \underset{2)138}{\underset{69}{K_2CO_3}} = \underset{2)98}{\underset{49}{H_2SO_4}},$$

= 1000 cc. of $\frac{N}{1}$ V. S.

and each cc. of $\frac{N}{1}$ H_2SO_4 V. S. = 0.188 gm. of $KHC_4H_4O_6$.

Another way of estimating bitartrate is to dissolve a weighed quantity in hot water and titrate with $\frac{N}{1}$ potassium hydrate until neutral, and thus the amount of tartaric acid existing as bitartrate is found. The bitartrate is always acid in reaction. This latter is the U. S. P. method. In detail it is as follows:

1.88 gms. of the bitartrate are dissolved in 100 cc. of hot water, a few drops of phenolphthalein T. S. added, and then titrated with $\frac{N}{1}$ KOH V. S. until a faint pink color indicates that all of the acid has been neutralized.

* The reaction may also be written thus:

$$2KHC_4H_4O_6 = K_2CO_3 + 5C + 2CO_2 + 5H_2O.$$

Not less than 9.9 cc. of the normal alkali should be required, corresponding to 99% of pure salt.

The following equation will show the reaction:

$$KHC_4H_4O_6 + KOH = K_2C_4H_4O_6 + H_2O.$$
$$188 \qquad 56 = 1000 \text{ cc. of } \frac{N}{1} \text{ KOH V. S.}$$

Each cc. of $\frac{N}{1}$ KOH V. S. represents .188 gm. of $KHC_4H_4O_6$.

If 9.9 cc. are required for neutralization, then $9.9 \times .188 = 1.8612$ gms.

$$\frac{1.8612 \times 100}{1.88} = 99\%$$

Lithium Citrate, $Li_3C_6H_5O_7 = \begin{cases} 209.57 \\ *210 \end{cases}$.—This salt is estimated in the same way as the other organic salts.

1 gm. of the salt is thoroughly ignited in a porcelain crucible, and the resulting lithium carbonate mixed with 20 cc. of water and titrated with $\frac{N}{1}$ H_2SO_4 V. S. after having added a few drops of methyl-orange T. S. Each cc. of the $\frac{N}{1}$ V. S. used before neutralization is effected represents .070 gm. of pure lithium citrate. The U. S. P. salt requires not less than 14.2 cc. of the $\frac{N}{1}$ V. S.

The following are the reactions:

$$*\underset{420}{2Li_3C_6H_5O_7} + 9O_2 = \underset{222}{3Li_2CO_3} + 5H_2O + 9CO_2;$$

* The reaction may also be written thus:

$$2Li_3C_6H_5O_7 + 4O = 3Li_2CO_3 + 7C + 2CO_2 + 5H_2O.$$

then

$$\underset{222}{3Li_2CO_3} + \underset{294}{3H_2SO_4} = 3Li_2SO_4 + 3H_2O + 3CO_2;$$

therefore

$$\underset{6)420}{2Li_3C_6H_5O_7} = \underset{6)222}{3Li_2CO_3} = \underset{6)294}{3H_2SO_4}$$

70 gms. 37 gms. 49 gms. = 1000 cc.

of the $\frac{N}{1}$ sulphuric acid V. S., and thus each cc. of $\frac{N}{1}$ H_2SO_4 V. S. = .070 gm. of the pure lithium citrate.

If 14.2 cc. of the normal acid are required, then 1 gm. of the salt contains $.070 \times 14.2 = .994$ gm., or 99.4%. If the more accurate factor .069856 is used, the per cent will be 99.2.

Potassium Citrate, $K_3C_6H_5O_7.H_2O$ $\left\{ \begin{matrix} 323.59. \\ *324 \end{matrix} \right.$—Two gms. of the salt are placed in a platinum or porcelain crucible and thoroughly ignited at a red heat in contact with air.

The potassium citrate is thus converted into potassium carbonate, carbon, and gases. When the crucible is cool, hot water is added to its contents, and the solution of potassium carbonate thus obtained is filtered to separate the carbon. To the solution, which must be colorless, add a few drops of methyl-orange T. S., and titrate with $\frac{N}{1}$ H_2SO_4 V. S. until the change of color indicates complete neutralization. Each cc. of the $\frac{N}{1}$ H_2SO_4 required before neutralization is effected represents 0.108 gm. of the pure salt.

$$*\underbrace{2(K_2C_6H_6O_7.H_2O)}_{648} + 9O_2 = \underset{414}{3K_2CO_3} + 3CO_2 + 7H_2O;$$

then

$$\underset{414}{3K_2CO_3} + \underset{294}{3H_2SO_4} = 3K_2SO_4 + 3CO_2 + 3H_2O;$$

therefore

$$\underset{6)\underline{648}}{2K_2C_6H_6O_7.H_2O} = \underset{6)\underline{414}}{3K_2CO_3} = \underset{6)\underline{294}}{3H_2SO_4}.$$

108 gms. 69 gms. 49 gms. = 1000 cc. $\frac{N}{1}$ acid.

Thus each cc. of $\frac{N}{1}$ acid represents 0.108 gm. of pure potassium citrate.

The U. S. P. directs that 1.080 gms. of potassium citrate be thoroughly ignited at a red heat, and that the alkaline residue should require for complete neutralization not less than 10 cc. of $\frac{N}{1}$ H_2SO_4 V. S. (corresponding to 100% of the pure salt), using methyl-orange as indicator.

The factor, as has been shown, is 0.108 for potassium citrate.

$$.108 \times 10 = 1.08$$

$$\frac{1.08 \times 100}{1.08} = 100\%$$

Potassium Acetate, $KC_2H_3O_2 = \left\{ \begin{matrix} 97.89 \\ *98 \end{matrix} \right.$.—In estimating potassium acetate the salt is ignited and the residue treated in exactly the same manner as in the estimation of the citrates and tartrates before men-

* The reaction may also be written thus :

$$2(K_2C_6H_6O_7.H_2O) + 4O = 3K_2CO_3 + 7C + 2CO_2 + 7H_2O.$$

tioned. According to the U. S. P., "if 1 gm. of potassium acetate be by thorough ignition converted into carbonate, the residue should require for complete neutralization not less than 10 cc. of $\frac{N}{1}$ H_2SO_4 V. S. (corresponding to at least 98 per cent of pure potassium acetate), methyl-orange being used as indicator."

$$*\underset{196}{2KC_2H_3O_2} + 4O_2 = \underset{138}{K_2CO_3} + 3H_2O + 3CO_2;$$

then

$$\underset{138}{K_2CO_3} + \underset{98}{H_2SO_4} = K_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{\underset{98 \text{ gms.}}{2)196}}{2KC_2H_3O_2} = \underset{\underset{69 \text{ gms.}}{2)138}}{K_2CO_3} = \underset{\underset{49 \text{ gms.} = 1000 \text{ cc. } \frac{N}{1} H_2SO_4.}{2)98}}{H_2SO_4}.$$

Each cc. therefore of $\frac{N}{1}$ H_2SO_4 V. S. corresponds to .098 gm. of potassium acetate.

If 10 cc. are required to neutralize the residue from 1 gm. of potassium acetate, the salt contains $10 \times .098 = 0.98$ gm., or $\frac{98}{100}$ of 1 gm., which is 98%.

Sodium Acetate, $NaC_2H_3O_2.3H_2O = \left\{ \begin{matrix} 135.74 \\ *136 \end{matrix} \right.$.—This salt is estimated in the same manner as the potassium acetate U. S. P. 1.36 gm. of the salt is ignited until completely carbonized, the residue is treated with hot water, the solution thus obtained is filtered, and to the filtrate a few drops of methyl-orange T. S. are added, and then the $\frac{N}{1}$ sulphuric acid until neutra-

* The reaction may also be written thus:

$$2KC_2H_3O_2 + 4O = K_2CO_3 + 2C + CO_2 + 3H_2O.$$

lization is effected. 10 cc. of the latter should be required.

$$2(\underset{272}{NaC_2H_3O_2 \cdot 3H_2O}) + 4O_2 = \underset{106}{Na_2CO_3} + 9H_2O + 3CO_2;$$

then

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2;$$

therefore

$$2(\underset{2)272}{NaC_2H_3O_2 \cdot 3H_2O}) = \underset{2)106}{Na_2CO_3} = \underset{2)98}{H_2SO_4}.$$

$$\underset{136 \text{ gms.}}{} \qquad \underset{53 \text{ gms.}}{} \qquad \underset{49 \text{ gms.},}{}$$

$$\text{or } 1000 \text{ cc. } \frac{N}{1} H_2SO_4.$$

Each cc. therefore represents 0.136 gm. of sodium acetate.

If 10 cc. of the $\frac{N}{1}$ acid are required to neutralize, multiply the factor 0.136 gm. by 10 = 1.36 gms.

$$\frac{1.36 \times 100}{1.36} = 100\%$$

Lithium Benzoate, $LiC_7H_5O_2 \left\{ \begin{matrix} 127.72 \\ *128 \end{matrix} \right.$.—This salt when ignited chars, emits inflammable vapors having a benzoin-like odor, and finally leaves a residue of lithium carbonate mixed with free carbon. It may therefore be estimated in the same manner as are the citrates, tartrates, and acetates.

One gm. of the salt is placed in a porcelain crucible and thoroughly ignited. The resulting residue, consisting of lithium carbonate and free carbon, is then mixed with

about 20 cc. of water and a few drops of methyl-orange. The titration is then begun, and each cc. of the $\frac{N}{1}$ H_2SO_4 V. S. used represents about 0.128 gm. of pure lithium benzoate. The U. S. P. requires the salt to be 99.6%.

The reactions are expressed as follows:

$$\underbrace{2LiC_7H_5O_2}_{256} + 15O_2 = \underset{74}{Li_2CO_3} + 5H_2O + 13CO_2;$$

then

$$\underset{74}{Li_2CO_3} + \underset{98}{H_2SO_4} = Li_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{128 \text{ gms.}}{\overset{2)256}{2LiC_7H_5O_2}} = \underset{37 \text{ gms.}}{\overset{2)74}{Li_2CO_3}} = \underset{49 \text{ gms. or 1000 cc. } \frac{N}{1} H_2SO_4.}{\overset{2)98}{H_2SO_4}}.$$

If 7.8 cc. of $\frac{N}{1}$ H_2SO_4 V. S. are used to neutralize the residue from the ignition of the lithium benzoate, then

$$.128 \times 7.8 = .9984 \text{ gm.}; \quad \text{then} \quad \frac{.9984 \times 100}{1} = 99.84\%$$

Sodium Benzoate, $NaC_7H_5O_2 = \left\{ \begin{matrix} 143.71. \\ *144 \end{matrix} \right.$.—Ignite 2 gms. of the salt in a porcelain crucible until completely carbonized. Dissolve the residue in about 20 cc. of hot water, filter the solution, rinse the crucible with a little water, and add it through the filter to the

first filtrate. Then add a few drops of methyl-orange T. S. and titrate with $\frac{N}{1}$ H_2SO_4 until neutralization is effected, as shown by the indicator. It should require not less than 13.9 cc. of the $\frac{N}{1}$ H_2SO_4 V. S., which corresponds to 99.8% of pure salt.

The following are the reactions:

$$\underset{288}{2NaC_7H_5O_2} + 15O_2 = \underset{106}{Na_2CO_3} + 5H_2O + 13CO_2;$$

then

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{\underset{144 \text{ gms.}}{2)288}}{2NaC_7H_5O_2} = \underset{\underset{53 \text{ gms.}}{2)106}}{Na_2CO_3} = \underset{\underset{49 \text{ gms. or 1000 cc. } \frac{N}{1} H_2SO_4 \text{ V. S.}}{2)98}}{H_2SO_4}.$$

Each cc. of $\frac{N}{1}$ H_2SO_4 V. S. therefore represents 0.144 gm. of sodium benzoate, or more accurately 0.14371.

If 13.9 cc. are required, then the 2 gms. contain $0.14371 \times 13.9 = 1.997569$.

$$\frac{1.997569 \times 100}{2} = 99.8\%, \text{ about.}$$

The salicylates of the alkalies are estimated in the same way as are the benzoates, tartrates, etc.

Lithium Salicylate, $LiC_7H_5O_3 = \left\{ \begin{matrix} 143.68 \\ *144 \end{matrix} \right.$.—Lithium salicylate when heated is decomposed, an odor of phenol is emitted, and a residue of lithium carbonate and carbon is left. It may therefore be estimated as are benzoates, tartrates, citrates, etc.

The process is as follows:

Two gms. of the salt are ignited in a porcelain crucible, so as to convert it into carbonate. This carbonate is mixed with about 20 cc. of hot water, a few drops of methyl-orange T. S. added, and then titrated with $\frac{N}{1}$ H_2SO_4 until neutralized. Not less than 13.8 cc. should be required, each cc. representing 0.14368 gm. of the pure salt.

The reactions are:

$$\underset{287.36}{2LiC_7H_5O_3} + 14O_2 = \underset{74}{Li_2CO_3} + 5H_2O + 13CO_2;$$

then

$$\underset{74}{Li_2CO_3} + \underset{98}{H_2SO_4} = Li_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{\underset{143.68 \text{ gms.}}{2)287.36}}{2LiC_7H_5O_3} = \underset{\underset{37 \text{ gms.}}{2)74}}{Li_2CO_3} = \underset{\underset{49 \text{ gms. or 1000 cc. } \frac{N}{1} \text{ acid.}}{2)98}}{H_2SO_4}.$$

Each cc. of $\frac{N}{1}$ H_2SO_4 therefore represents 0.14368 gm. of lithium salicylate.

If 13.8 cc. of $\frac{N}{1}$ H_2SO_4 are required for neutralization, then $.14368 \times 13.8 = 1.982784$.

$$\frac{1.982 \times 100}{2} = 99.13\%.$$

Sodium Salicylate, $NaC_7H_5O_3 = \begin{cases} 159.67 \\ *160 \end{cases}$.—This salt, when heated, is decomposed, inflammable vapors and an odor of phenol being given off, and a residue of sodium carbonate and free carbon being left.

No volumetric process is given in the U. S. P. for the estimation of this salt. The foregoing processes, however, may be applied to it, the alkaline carbonate which is left being titrated with sulphuric acid V. S., each cc. of $\frac{N}{1}$ H_2SO_4 V. S. representing 0.15967 gm., or approximately 0.160 gm., of the pure salicylate.

$$\underset{319.34}{2NaC_7H_5O_3} + 14O_2 = \underset{106}{Na_2CO_3} + 5H_2O + 13CO_2;$$

then

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2;$$

therefore

$$\underset{2)319.34}{2NaC_7H_5O_3} = \underset{2)106}{Na_2CO_3} = \underset{2)98}{H_2SO_4}.$$

159.67 gms. 53 gms. 49 gms. or 1000 cc.

TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., OF THE ORGANIC SALTS OF THE ALKALINE METALS.

Substance.	Formula.	Molecular Weight.	Equivalent Weight in Carbonate.	Normal Factor.*
Lithium benzoate.....	$LiC_7H_5O_2$	128	37	0.128
" citrate.....	$Li_3C_6H_5O_7$	210	111	0 070
" salicylate.....	$LiC_7H_5O_3$	144	37	0.144
Sodium acetate.....	$NaC_2H_3O_2.3H_2O$	136	53	0.136
" benzoate.....	$NaC_7H_5O_2$	144	53	0.144
" salicylate.....	$NaC_7H_5O_3$	160	53	0.160
Potassium acetate.....	$KC_2H_3O_2$	98	69	0.098
" bitartrate.....	$KHC_4H_4O_6$	188	69	0.188
" citrate.....	$K_3C_6H_5O_7.H_2O$	324	207	0.108
" tartrate.....	$K_2C_4H_4O_6.H_2O$	244	138	0.122
" and sodium tartrate.....	$KNaC_4H_4O_6.4H_2O$	282	122	0.141

* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure substance present in the material examined.

ACIDIMETRY.—ESTIMATION OF ACIDS BY NEUTRALIZATION.

In the previous experiments it has been shown how alkalies are estimated by the use of acid solutions of known neutralizing power. In the estimation of acids, which will now be described, the order is reversed, alkaline solutions of known power being used in determining the strength of acids.

Either an alkaline carbonate or an alkaline hydroxide may be used in the form of standard solution for this purpose.

The hydroxide, however, is to be preferred, for the carbonate when used for titrating an acid gives off carbonic-acid gas (CO_2), which interferes to a great extent with the indicators.

In the U. S. P., 1890, volumetric solutions of both potassium and sodium hydroxides are official. The former, however, is preferable, because it attacks glass more slowly and less energetically, and also foams much less than does the sodium hydroxide. The neutralizing power of each is, however, the same.

The caustic alkalies and their solutions are very prone to absorb carbon dioxide from the atmosphere. Therefore the solutions often contain some carbonates, the presence of which will occasion errors when used with most indicators, especially litmus and phenolphthalein. Hence when these indicators or others which are affected by carbon dioxide are used gentle heat should be employed toward the close of each titration to drive off the liberated gas.

The standard solutions of alkaline hydroxides should always be preserved in small vials provided with well-fitting cork or rubber stoppers.

In order to keep solutions of this kind special vessels have been devised (see Fig. 39). The bottle is provided with a well-fitting rubber stopper through which a tube passes, which is filled with a mixture of soda and lime, which absorbs CO_2 and prevents its access to the solution.

An improvement upon this is shown in Fig. 40, since it allows of the burette being filled without removing the stopper, and consequently without any access of CO_2 whatever.

Preparation of Normal Potassium Hydroxide Volumetric Solution, $KOH = \left\{ {}^{*}\frac{55.99}{56} \text{ contains } {}^{*}\frac{55.99}{56} \right\}$ gms. in 1 litre.—Potassium hydroxide is so prone to absorb carbon dioxide that the pure substance is not

readily obtained in commerce. If pure potassa were easily obtained it would only be necessary to dissolve 56 gms. in sufficient water to make a litre. But since it always contains some CO_2 and H_2O, it is necessary

FIG. 39.

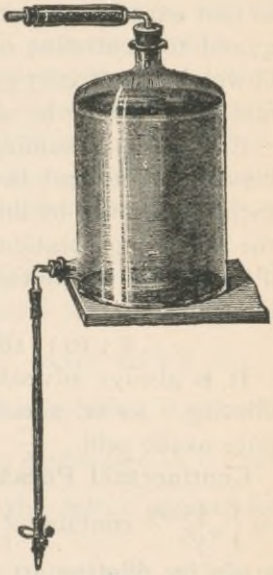

FIG. 40.

to take a slight excess and dilute the solution to the proper volume after having determined its strength.

The U. S. P. process is as follows: Dissolve 75 gms. of potassa in sufficient water to make about 1050 cc. at 15° C. (59° F.), and fill a burette with a portion of this solution.

Dissolve 0.63 gm. of pure oxalic acid in about 10 cc. of water in a beaker or flask, add a few drops of phenolphthalein T. S., and then carefully add from the

burette the potassium-hydroxide solution, agitating frequently and regulating the flow to drops towards the end of the operation until a permanent pale-pink color is obtained. Note the number of cc. of the potassa solution consumed, and then dilute the remainder so that exactly 10 cc. of the diluted liquid will be required to neutralize 0.63 gm. of oxalic acid. Instead of weighing off 0.63 gm. of the acid, 10 cc. of its normal solution may be used.

Example.—Assuming that 8 cc. of the stronger potassa solution had been consumed in the trial, then each 8 cc. must be diluted to 10 cc., or the whole of the remaining solution in the same proportion. Thus if 8 cc. must be diluted to 10 cc., 1000 cc. must be diluted to 1250 cc.

$$8 : 10 :: 1000 : x \quad x = 1250 \text{ cc.}$$

It is always advisable to make another trial after diluting. 10 cc. should then neutralize 0.63 gm. of pure oxalic acid.

Centinormal Potassium Hydroxide V. S., KOH $= \left\{ \begin{matrix} 55.99 \\ *56 \end{matrix} \right.$ contains $\left\{ \begin{matrix} 0.5599 \text{ gm.} \\ 0.56 \text{ gm.} \end{matrix} \right.$ in 1 litre.—This is made by diluting 10 cc. of the normal solution with enough distilled water to make 1000 cc.

Normal Sodium Hydroxide V. S., NaOH $= \left\{ \begin{matrix} 39.96 \\ *40 \end{matrix} \right.$ contains $\left\{ \begin{matrix} 39.96 \text{ gms.} \\ 40 \text{ gms.} \end{matrix} \right.$ in 1 litre.—Dissolve 54 gms. of sodium hydroxide in enough water to make about 1050 cc. at 15° C. (59° F.), and fill a burette with a portion of this solution.

Dissolve 0.63 gm. of pure oxalic acid in about 10 cc. of water in a flask or beaker, add a few drops of phenolphthalein T. S., and then carefully add from a burette

the soda solution, agitating the flask or beaker frequently, as directed under $\frac{N}{1}$ KOH V. S., until a permanent pale-pink color is produced. Note the number of cc. of soda solution consumed, and then dilute the remainder of the solution so that exactly 10 cc. will be required to neutralize 0.63 gm. of pure oxalic acid.

Example. — If 8 cc. of the stronger soda solution had been consumed in the trial, then each 8 cc. must be diluted to 10 cc., or the whole of the remaining solution in the same proportion. Thus if 980 cc. should be still remaining, this must be diluted with water to make 1225 cc.

Now make a new trial with the diluted solution to see whether 10 cc. will be required to neutralize 0.63 gm. of oxalic acid (or 10 cc. of $\frac{N}{1}$ oxalic acid V. S.).

The neutralizing power of this solution is exactly the same as that of $\frac{N}{1}$ potassium hydroxide V. S., and may be employed in place of the latter, volume for volume.

The following acids may be tested with either of these alkaline solutions:

Acidum aceticum.
" " dilutum.
" " glaciale.
" citricum.
" hydrobromicum dilutum.
" hydrochloricum.
" " dilutum.
" hypophosphorosum dilutum.
" lacticum.

Acidum nitricum.
" " dilutum.
" phosphoricum.
" " dilutum.
" sulphuricum.
" " aromaticum.
" " dilutum.
" tartaricum.

Acidum Aceticum, $HC_2H_3O_2 = \left\{ \begin{matrix} 59.86 \\ *60 \end{matrix} \right.$. — The U. S. P. acetic acid contains 36%, by weight, of absolute $HC_2H_3O_2$ and 64% of water.

Mix 3 gms. of the acid with a small quantity of water, add a few drops of phenolphthalein T. S., and titrate with normal potassium hydroxide V. S. until a permanent pale-pink color is obtained, and apply the following equation:

$$\underset{60}{HC_2H_3O_2} + \underset{56}{KOH} = KC_2H_3O_2 + H_2O.$$

Thus 56 gms. or 1000 cc. of $\frac{N}{1}$ KOH V. S. will neutralize 60 gms. of acetic acid; therefore each cc. of $\frac{N}{1}$ KOH V. S. represents .060 gm. of acetic acid.

If 18 cc. are required to neutralize 3 gms. of the acid, it contains $18 \times .060 = 1.08$ gms. of absolute acetic acid.

$$\frac{1.08 \times 100}{3} = 36\%.$$

According to the U. S. P., 6 gms. of the acid should require 36 cc. of $\frac{N}{1}$ KOH V. S. for complete neutralization.

Acidum Aceticum Dilutum.—A solution containing 6%, by weight, of absolute acetic acid.

The estimation is conducted exactly as the above. The diluted acetic acid U. S. P. should contain 6% of absolute acid. 24 gms. should require 24 cc. of $\frac{N}{1}$ KOH V. S.

$$24 \times .060 = 1.440$$
$$\frac{1.440 \times 100}{24} = 6\%$$

Acidum Aceticum Glaciale.—Three gms. of glacial acetic acid are mixed with a small quantity of water, a few drops of phenolphthalein T. S. added, and the solution titrated with $\frac{N}{1}$ potassium hydroxide V. S. until a very pale pink color appears. Each cc. represents .06 gm. of absolute acetic acid.

49.5 cc. are required by 3 gms. of the U. S. P. acid.

$$49.5 \times .06 = 2.970 \text{ gms.}$$
$$\frac{2.970 \times 100}{3} = 99\%$$

Acidum Citricum, $H_3C_6H_5O_7.H_2O = \left\{ \begin{matrix} 209.5 \\ *210 \end{matrix} \right.$.—3.5 gms. of citric acid are dissolved in a sufficient quantity of water, a few drops of phenolphthalein added, and the solution titrated with $\frac{N}{1}$ potassium hydroxide V. S. until a very pale pink color appears. Each cc. of $\frac{N}{1}$ potassium hydroxide consumed before neutralization

is effected represents .070 gm. of the pure acid, and 50 cc. should be required.

The reaction is expressed by the following equation:

$$\underbrace{H_2C_6H_5O_7.H_2O}_{3)\frac{210}{70}} + 3KOH = K_3C_6H_5O_7 + 4H_2O. \qquad 3)\frac{168}{56}$$

Thus 56 gms. of KOH or 1000 cc. of its normal solution represent 70 gms. of pure crystallized acid, and each cc. represents .070 gm. Therefore

$$50 \times .070 = 3.5 \text{ gms.}$$
$$\frac{3.5 \times 100}{3.5} = 100\%$$

Acidum Oxalicum, $H_2C_2O_4+2H_2O$ $\left\{ {}^{125.7}_{*126} \right.$.—This acid may be estimated by oxidation with potassium permanganate V. S. as described under oxidimetry, but it is more conveniently tested by neutralization with an alkaline V. S.

1 gm. of the acid is placed in a beaker, a sufficient quantity of water is added to dissolve it, and then a few drops of phenolphthalein T. S., and the solution titrated with a normal alkali solution.

Each cc. of the normal alkali solution represents 0.063 gm. of crystallized oxalic acid as the equation shows:

$$H_2C_2O_4.2H_2O + 2KOH = K_2C_2O_4 + 4H_2O.$$
$$2)\frac{126}{63} \qquad 2)\frac{112}{56} = 1000 \text{ cc. } \frac{N}{1} \text{ V. S.}$$

Acidum Hydrobromicum Dilutum (Diluted Hydrobromic Acid), HBr= $\left\{ {}^{80.76}_{*81} \right.$.—A liquid containing 10

per cent. of pure hydrobromic acid (HBr) and 90 per cent. of water.

8.1 gms. of the acid are diluted with a small quantity of water, a few drops of phenolphthalein T. S. added, and then $\frac{N}{1}$ potassium hydroxide V. S. added from a burette, until a very faint pink color is produced. Note the quantity of $\frac{N}{1}$ alkali used, and multiply this by the factor .081 gm. to obtain the weight of HBr in the diluted acid taken.

The reaction is expressed by the following equation:

$$\underset{81 \text{ gms.}}{HBr} + \underset{56 \text{ gms.} = 1000 \text{ cc. of } \frac{N}{1} \text{ V. S.}}{KOH} = KBr + H_2O.$$

Each cc. therefore represents .081 gm., or 1 per cent, of HBr.

If this acid is made with tartaric acid and potassium bromide, a white, crystalline precipitate will be produced upon the addition of the $\frac{N}{1}$ alkali, some of which will be neutralized by the dissolved potassium bitartrate and the excess of tartaric acid, and an incorrect indication will be given.

Acidum Hydrochloricum (Muriatic Acid), $HCl = \left\{ {}^{36.37}_{*36.4} \right.$. — A liquid containing 31.9 per cent., by weight, of absolute HCl and 68.1 per cent. of water.

3 gms. of hydrochloric acid are diluted with a little water, a few drops of phenolphthalein added, and then $\frac{N}{1}$ potassium hydroxide V. S. from a burette, until a

faint pink color is produced. Note the quantity of $\frac{N}{1}$ alkali used, and apply the following equation:

$$HCl + KOH = KCl + H_2O.$$
$$36.4 \text{ gms.} \quad 56 \text{ gms.} = 1000 \text{ cc. } \frac{N}{1} \text{ V. S.}$$

Each cc. of $\frac{N}{1}$ alkali required before the acid is neutralized represents .0364 gm. of pure HCl.

3.64 gms. of the U.S.P. acid should require for complete neutralization 31.9 cc. of $\frac{N}{1}$ KOH V. S.

Diluted hydrochloric acid, U. S. P., contains 10 per cent. of absolute HCl. 3.64 gms. of the diluted acid should require for neutralization 10 cc. of $\frac{N}{1}$ KOH V. S.

Let us assume that the 3 gms. of hydrochloric acid required 20 cc. of $\frac{N}{1}$ KOH V. S. Then

$$20 \times .0364 = .7280 \text{ gm.}$$

of pure HCl in 3 gms. of the acid.

$$\frac{.7280 \times 100}{3} = 24.26\%$$

Acidum Hypophosphorosum Dilutum (Diluted Hypophosphorous Acid).—The U. S. P. acid contains 10 per cent. of absolute $HPH_2O_2 = \left\{ \begin{matrix} 65.88 \\ *66 \end{matrix} \right.$.

This acid is estimated in exactly the same way as the acids previously noticed:

$$HPH_2O_2 + KOH = KPH_2O_2 + H_2O.$$
$$66 \text{ gms.} = 56 \text{ gms.} = 1000 \text{ cc.} \frac{N}{1} \text{ alkali.}$$

Thus each cc. of $\frac{N}{1}$ alkali represents .066 gm. of HPH_2O_2.

Take 5 gms. of the acid, dilute it with a small quantity of water, add a few drops of phenolphthalein T. S., and titrate with $\frac{N}{1}$ KOH V. S. until a very faint pink color appears. If 8 cc. of the $\frac{N}{1}$ alkali are used, the 5 gms. contain $8 \times .066 = .528$ gm.

$$5 : .528 :: 100 : x. \qquad x = 10.56\%$$

6.6 gms. of the U. S. P. acid should require for neutralization 10 cc. of $\frac{N}{1}$ KOH V. S.

Acidum Lacticum, $HC_3H_5O_3 = \left\{ \begin{matrix} 89.79. \\ *90 \end{matrix} \right.$—An organic acid containing 75 per cent., by weight, of absolute lactic acid and 25 per cent. of water.

5 gms. of lactic acid are slightly diluted with water, a few drops of phenolphthalein T. S. added, and then the $\frac{N}{1}$ KOH V. S. from a burette, until a pale-pink color is produced. Note the quantity of normal alkali used,

and multiply that number by .090 gm. to get the quantity of absolute acid in the 5 gms. taken.

$$HC_3H_5O_3 + KOH = KC_3H_5O_3 + H_2O,$$
$$90 \text{ gms.} = 56 \text{ gms.} = 1000 \text{ cc. } \frac{N}{1} \text{ KOH V. S.}$$

and 1 cc. of $\frac{N}{1}$ KOH = .090 gm. of $HC_3H_5O_3$.

If 40 cc. of $\frac{N}{1}$ KOH are required for neutralization of the 5 gms. of the lactic acid, then

$$\times 40 \quad .09 = 3.60 \text{ gms.}$$
$$5 : 3.6 :: 100 : x. \quad x = 72\%$$

Acidum Nitricum (Nitric Acid), $HNO_3 = \begin{cases} 62.89. \\ *63 \end{cases}$ —The U. S. P. acid contains 68 per cent., by weight, of absolute nitric acid and 32 per cent. of water.

Take 3 gms. of nitric acid, dilute with a little water, add a few drops of phenolphthalein T. S., and then pass into the mixture from a burette $\frac{N}{1}$ potassium hydroxide V. S. until neutralization is effected, and the liquid acquires a faint pink color.

Apply the following equation:

$$HNO_3 + KOH = KNO_3 + H_2O.$$
$$63 \text{ gms.} \quad 56 \text{ gms.} = 1000 \text{ cc. } \frac{N}{1} \text{ KOH V. S.}$$

Thus each cc. of $\frac{N}{1}$ KOH V. S. required before neutralization is effected represents 0.063 gm. of absolute nitric acid.

If 30 cc. of the $\frac{N}{1}$ alkali are required, then the 3 gms. contain $.063 \times 30 = 1.890$ gms.

$$3 : 1.89 :: 100 : x. \qquad x = 63\%$$

3.145 gms. of the U. S. P. acid require 34 cc. of $\frac{N}{1}$ KOH V. S., which corresponds to 68% of absolute acid.

Acidum Nitricum Dilutum, U. S. P., contains 10% of absolute nitric acid, and is estimated in the same way as the nitric acid.

Acidum Phosphoricum (Phosphoric Acid), $H_3PO_4 = \begin{cases} 97.8 \\ *98 \end{cases}$.—The U. S. P. acid contains 85% of absolute orthophosphoric acid and 15% of water.

Take 1 gm. of phosphoric acid, dilute it with water, add a few drops of phenolphthalein T. S., and titrate with $\frac{N}{1}$ potassium hydroxide V. S. until neutralization is complete and the liquid has acquired a faint pink color.

$$\underset{\underset{49 \text{ gms.}}{2)98}}{H_3PO_4} + 2KOH = \underset{\underset{56 \text{ gms.} = 1000 \text{ cc. } \frac{N}{1} \text{ KOH V. S.}}{2)112}}{K_2HPO_4} + 2H_2O.$$

Thus each cc. of $\frac{N}{1}$ KOH required represents .049 gm. of absolute orthophosphoric acid.

If 1 gm. of the acid requires for neutralization 18 cc. of $\frac{N}{1}$ KOH V. S., it contains

$$.049 \times 18 = .882 \text{ gm.} \quad \text{or} \quad 88.2\%$$

0.98 gm. of the U. S. P. acid should require 17 cc. of $\frac{N}{1}$ KOH V. S., which means 85% of absolute phosphoric acid.

In the estimation of phosphoric acid litmus cannot be used as an indicator, for the disodic or dipotassic hydric phosphate (Na_2HPO_4 or K_2HPO_4) which is formed when the standard alkaline solution is added to free tribasic phosphoric acid is slightly alkaline to litmus, but not to phenolphthalein.

It is recommended, therefore, in order to estimate phosphoric acid alkalimetrically, to prevent the formation of soluble phosphate of the alkali, and to bring the acid into a definite compound with an alkaline earth as follows:

The free acid in a diluted state is placed in a flask and a known volume of normal alkali in excess added in order to convert the whole of the acid into a basic salt. A few drops of rosolic acid are now added, and sufficient neutral $BaCl_2$ solution poured in to combine with the phosphoric acid. The mixture is heated to boiling, and while hot the excess of alkali is titrated with $\frac{N}{1}$ acid.

The suspended basic phosphate, together with the liquid, possesses a rose-red color until the last drop or two of acid, after continuous heating and agitation, gives a permanent white or slightly yellowish milky appearance, when the process is ended.

The volume of normal alkali, less the volume of normal acid, represents the amount of alkali required to convert the phosphoric acid into a normal trisodic or tripotassic phosphate.

$$H_3PO_4 + 3KOH = K_3PO_4 + 3H_2O.$$

$\underset{32.66 \text{ gms.}}{\overset{3)98}{}}$ $\underset{56 \text{ gms.}}{\overset{3)168}{}}$ = 1000 cc. of $\frac{N}{1}$ KOH V. S.

Thus 1 cc. of $\frac{N}{1}$ alkali = .03266 gm. of H_3PO_4.

Diluted phosphoric acid is estimated in the same manner.

Acidum Sulphuricum, $H_2SO_4 = \left\{ \begin{matrix} 97.82 \\ *98 \end{matrix} \right.$.—U. S. P. sulphuric acid contains 92.5 per cent., by weight, of absoluted sulphuric acid and 7.5 per cent. of water.

Aromatic Sulphuric Acid U. S. P. contains 18.5% of absolute sulphuric acid, by weight.

Diluted Sulphuric Acid U. S. P. contains 10% by weight of absolute sulphuric acid. Operate upon 1 gm. of the strong acid or upon 5 gms. of either dilute or aromatic sulphuric acid.

One gm. of sulphuric acid is diluted with about 10 cc. of water. Add a few drops of phenolphthalein T. S. and titrate with $\frac{N}{1}$ potassa V. S. until the acid is neutralized and the solution has acquired a faint pink color. Each cc. of $\frac{N}{1}$ alkali solution represents 0.049 gm. of absolute sulphuric acid.

The reaction is shown by the following equation:

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O.$$

$\underset{49 \text{ gms.}}{\overset{2)98}{}}$ $\underset{56 \text{ gms.}}{\overset{2)112}{}}$ = 1000 cc. of $\frac{N}{1}$ KOH V. S.

If 18 cc. of $\frac{N}{1}$ KOH V. S. are required for the complete neutralization of the sulphuric acid, then it contains $18 \times .049$ gm. = 0.882 gm.

$1 : 0.882 :: 100 : x \quad x = 88.2\%$ absolute sulphuric acid.

Diluted Sulphuric Acid is estimated in the same way. Operate upon 5 gms. instead of upon 1 gm.

Aromatic Sulphuric Acid contains ethyl sulphuric acid. Therefore in estimating the sulphuric acid in this preparation it must be boiled with water for a few minutes so as to decompose the ethyl sulphuric acid. The mixture is then allowed to cool, and titrated in the usual manner with $\frac{N}{1}$ KOH V. S., using phenolphthalein as indicator.

The U. S. P. requires that 4.89 gms. when mixed with 15 cc. of water and boiled for several minutes should, after cooling, be neutralized by not less than 18.5 cc. of $\frac{N}{1}$ KOH.

Acidum Tartaricum (Tartaric Acid), $H_2C_4H_4O_6 = \left\{ \begin{matrix} 149.64 \\ *150 \end{matrix} \right.$.—Dissolve 3.75 gms. of tartaric acid in sufficient water to make a solution, add a few drops of phenolphthalein T. S., and then pass into the solution from a burette $\frac{N}{1}$ potassium hydroxide V. S. until a faint pink tint is acquired by the solution, and apply the equation

$$\underset{2)150}{H_2C_4H_4O_6} + 2KOH = \underset{2)112}{K_2C_4H_4O_6} + 2H_2O.$$

$$\underset{75\text{ gms.}}{} \qquad \underset{56\text{ gms.} = 1000\text{ cc. } \frac{N}{1}\text{ KOH V. S.}}{}$$

Thus each cc. required for the neutralization of the acid represents 0.075 gm. If 50 cc. are required, then $50 \times .075 = 3.75$ gms. or 100%.

TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., FOR THE ACIDS.

Acid.	Formula.	Molecular Weight.	Normal Factors.*
Acetic	$HC_2H_3O_2$	60	.060
Citric	$H_3C_6H_5O_7.H_2O$	210	.070
Hydrobromic	HBr	81	.081
Hydrochloric	HCl	36.4	.0364
Hypophosphorous	HPH_2O_2	66	.066
Lactic	$HC_3H_5O_3$	90	.090
Nitric	HNO_3	63	.063
Phosphoric	H_3PO_4	98	.049
Sulphuric	H_2SO_4	98	.049
Tartaric	$H_2C_4H_4O_6$	150	.075

Phosphoric, after conversion into a neutral phosphate and retitrating with $\frac{N}{1}$ acid = ... .03266

Phosphoric acid, as ammonia-magnesian phosphate with decinormal acid = ... .0049

* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure acid in the sample analyzed.

ESTIMATION OF ACIDS IN COMBINATION IN NEUTRAL SALTS.

This may be done in the case of a large number of salts, by adding to the solution of the salt a measured excess of alkali or alkali carbonate in the form of normal solution, and then ascertaining the excess by retitration with normal acid. Thus the amount of alkali which went into combination with the acid is obtained. Most bases are precipitated by the hydroxide; some, however, require the addition of carbonate to effect their precipitation.

The carbonate is required for alkaline-earth salts,

magnesium salts, alum, zinc salts, bismuth salts, nickel, cobalt, and lead salts.

Example.—2 gms. of barium chloride are dissolved in water and sufficient normal sodium carbonate added to make the liquid decidedly alkaline (say 20 cc.), and the whole diluted to 300 cc. and set aside to settle. 100 cc. of the clear supernatant liquid are then removed with a pipette and titrated for excess of alkali with normal nitric acid or normal hydrochloric acid, of which say 1.2 cc. are required, making it 3.6 cc. for the whole quantity; therefore $20 - 3.6 = 16.4$ cc. is the measure of the alkali which combined with the acid of the original salt. This multiplied by 0.03537, the factor for chlorine, gives 0.58007 gm. of chlorine.

ESTIMATION OF THE SALTS OF THE ALKALINE EARTHS.

Standard solution of hydrochloric or of nitric acid is preferred by many operators for the titration of caustic or carbonated alkaline earths.

These acids have the advantage over most other acids in forming soluble salts.

The hydroxides may be estimated by any of the indicators, but as they readily absorb CO_2 out of the air, they are generally contaminated with more or less carbonate, and the residual method should be used, i.e., a known excess of standard acid should be added, the mixture boiled to expel any trace of CO_2, and retitrated with standard alkali.

The carbonates are of course estimated in the same way.

If methyl-orange is used, heat need not be employed, unless it is impossible to dissolve the substance in the cold. A good excess of acid is, however, generally sufficient.

Soluble salts of calcium, barium, and strontium, such as chlorides, nitrates, etc., may be readily estimated as follows :

A weighed quantity of the salt is dissolved in water, cautiously neutralized if it is acid or alkaline, phenolphthalein is added, the mixture heated to boiling, and standard solution of sodium carbonate delivered in from time to time, with boiling until the red color is permanent.

This process depends upon the fact that sodium carbonate forms with soluble salts of these bases insoluble and neutral carbonates.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$
$$Ba(NO_3)_2 + Na_2CO_3 = BaCO_3 + 2NaNO_3.$$

Magnesium salts cannot be estimated in this way, as magnesium carbonate affects the indicator.

The alkaline earth salts may also be estimated by dissolving them in water, precipitating the base as carbonate, with an excess of ammonium carbonate and some free ammonia.

The mixture is heated for a few minutes, and the carbonate separated by filtration, thoroughly washed with hot water till all soluble matters are removed, and then titrated with normal acid V. S. as carbonate.

Normal Sodium Carbonate V. S.—$Na_2CO_3 = \left\{ \begin{matrix} 105.85 \\ *106 \end{matrix} \right.$ contains $\left. \begin{matrix} 52.925 \\ *53. \end{matrix} \right\}$ gms. in 1 litre.—This solution is made by dissolving 53 gms. of pure sodium car-

bonate (anhydrous) previously ignited and cooled, in distilled water, and diluting to 1 litre at 15° C. (59° F.).

If pure salt is not at hand the solution may be made as follows:

About 85 gms. of pure sodium bicarbonate, free from thiosulphate, chloride, etc., are heated to dull redness (not to fusion) for about fifteen minutes to expel one half of the CO_2; it is then cooled under a desiccator. When cool, weigh off 53 gms. and dissolve it in distilled water to 1 litre at 15° C. (59° F.). This solution should neutralize $\frac{N}{1}$ acid V. S. volume for volume.

Liquor Calcis (Lime-water), $Ca(OH)_2 = \begin{cases} 73.83.— \\ *74 \end{cases}$ The U. S. P. directs lime-water to be estimated with *deci*normal oxalic acid V. S., using phenolphthalein as indicator.

Take 50 cc. of lime-water, add a few drops of phenolphthalein, and then carefully from a burette $\frac{N}{10}$ oxalic acid V. S. until the red color is just discharged. 20 cc. of the $\frac{N}{10}$ acid V. S. should be required for the neutralization. This corresponds to 0.14 (0.148) per cent. of calcium hydroxide.

$$\underset{20)74}{Ca(OH)_2} + \underset{20)126}{H_2C_2O_4 \cdot 2H_2O} = CaC_2O_4 + 4H_2O.$$

3.7 gms. 6.3 gms. or 1000 cc. $\frac{N}{10}$ V. S.

Each cc. of $\frac{N}{10}$ oxalic acid V. S. represents .0037 gm. of $Ca(OH)_2$.

Then $.0037 \times 20 = 0.074$ gm.

$$\frac{.074 \times 100}{50} = 0.148\%$$

Syrupus Calcis, U. S. P. (Liquor Calcis Saccharatus, Br. P.).—This is estimated in exactly the same way as the lime-water, except that the solution is weighed for analysis, not measured, as its specific gravity is much higher than that of water.

Operate upon about 25 grammes.

Calcium Carbonate, $CaCO_3 = \left\{ {}^{99.76}_{*100} \right.$.—No method is given for the estimation of calcium carbonate in the Pharmacopœia, but the following process may be used:

One gm. of calcium carbonate is mixed with 5 cc. of water. A measured excess of normal sulphuric acid V. S. is now added, and the solution boiled to drive off the CO_2. Then add a few drops of phenolphthalein T. S., and titrate with $\frac{N}{1}$ alkali V. S. until a faint pink color is obtained.

Note the quantity of $\frac{N}{1}$ alkali used, and deduct this from the quantity of $\frac{N}{1}$ acid first added, and the remainder will represent the amount of acid which combined with the calcium.

Each cc. of $\frac{N}{1}$ acid V. S. represents .05 gm. of $CaCO_3$.

$$\underset{\substack{2)100 \\ 50 \text{ gms.}}}{CaCO_3} + \underset{\substack{2)98 \\ 49 \text{ gms. or } 1000 \text{ cc. } \frac{N}{1} \text{ acid V. S.}}}{H_2SO_4} = CaSO_4 + H_2O + CO_2.$$

Assuming that 30 cc. of $\frac{N}{1}$ H_2SO_4 V. S. were added to the 1 gm. of $CaCO_3$, and that 11 cc. of $\frac{N}{1}$ KOH V. S. were required to bring the mixture back to neutrality, then 19 cc. of $\frac{N}{1}$ H_2SO_4 were actually required to saturate the $CaCO_3$.

Therefore $.05 \times 19 = .95$ gm., or 95%.

Calcium Bromide, $CaBr_2 = \left\{ \begin{matrix} 199.43 \\ *200 \end{matrix} \right.$.—This salt when dissolved in water may be estimated directly with normal solution of sodium carbonate.

One gm. of the salt is dissolved in a small quantity of water. The solution is neutralized, if it is acid or alkaline, heated to boiling, a few drops of phenolphthalein T. S. added, and the solution titrated with $\frac{N}{1}$ sodium carbonate V. S. delivered cautiously, with boiling, until the red color is permanent.

$$\underset{\underset{100 \text{ gms.}}{2)200}}{CaBr_2} + \underset{\underset{53 \text{ gms. or } 1000 \text{ cc. } \frac{N}{1} Na_2CO_3 \text{ V. S.}}{2)106}}{Na_2CO_3} = CaCO_3 + 2NaBr.$$

Each cc. of $\frac{N}{1}$ Na_2CO_3 V. S. represents 0.1 gm. of calcium bromide.

If 9 cc. are used, the salt contains $0.1 \times 9 = .9$ gm., or 90%, of pure $CaBr_2$.

Another way is to add an excess of ammonium-carbonate solution with some free ammonia to the solution of calcium bromide, in order to precipitate all the base in the form of carbonate. The carbonate is then

separated by filtration, thoroughly washed with hot water to remove all soluble matters, and then titrated as directed for carbonate.

$$\underset{2)200}{CaBr_2} = \underset{2)100}{CaCO_3} = \underset{2)98}{H_2SO_4}.$$

100 gms. 50 gms. 49 gms. or 1000 cc. $\frac{N}{1}$ V. S.

Each cc. of $\frac{N}{1}$ acid thus represents 0.1 gm. of $CaBr_2$.

See U. S. P. method, page 103.

Calcium Chloride, $CaCl_2 = \begin{cases} 110.65 \\ *110.8 \end{cases}$. — This salt may be estimated in exactly the same way as described for the bromide.

$$\underset{2)110.8}{CaCl_2} + \underset{2)106}{Na_2CO_3} = CaCO_3 + 2NaCl.$$

55.4 gms. 53 gms. or 1000 cc. $\frac{N}{1}$ V. S.

1 cc. $\frac{N}{1}$ Na_2CO_3 = .0554 gm. of $CaCl_2$.

$$\underset{2)110.8}{CaCl_2} = \underset{2)100}{CaCO_3} = \underset{2)98}{H_2SO_4}.$$

55.4 50 49 gms. or 1000 cc. $\frac{N}{1}$ V. S.

1 cc. $\frac{N}{1}$ H_2SO_4 = .0554 gm. of $CaCl_2$.

Barium Chloride, $BaCl_2$, and **Barium Nitrate,** $Ba(NO_3)_2$.—These two salts are estimated in the same way as the soluble salts of calcium noted in the previous chapter.

The factor for $BaCl_2$ is 0.10385 gm.,

the factor for $Ba(NO_3)_2$ is 0.13045 gm.,

using normal volumetric solutions.

Strontium Lactate, $Sr(C_3H_5O_3)_2+3H_2O = \begin{cases} 318.76. \\ *319.3 \end{cases}$ —1.33 gms. of the salt, rendered anhydrous before being weighed, by careful drying at 110° C. (230° F.), is ignited, until most of the carbon has disappeared, and then mixed with 10 cc. of water. A few drops of methyl-orange T. S. are now added, and the mixture titrated with $\frac{N}{1}$ H_2SO_4 V. S. until a faint red color is produced.

9.9 cc. of the $\frac{N}{1}$ acid should be required, corresponding to 98.6% of the pure salt.

The first step in this process is to drive off the water of crystallization.

$$\underset{318.78}{(Sr(C_3H_5O_3)_2 + 3H_2O)} + \text{heat} = \underset{264.88}{Sr(C_3H_5O_3)_2} + 3H_2O;$$

then

$$\underset{264.88}{Sr(C_3H_5O_3)_2} + 6O_2 = \underset{147.15}{SrCO_3} + 5CO_2 + 5H_2O.$$

Thus

$$\underset{2)264.88}{Sr(C_3H_5O_3)_2} = \underset{2)147.15}{SrCO_3} = \underset{2)98}{H_2SO_4}.$$

$$\underset{132.44}{} \qquad \underset{73.57}{} \qquad \underset{49 \text{ gms. or } 1000 \text{ cc. } \frac{N}{1} \text{ acid V. S.}}{}$$

Thus each cc. of $\frac{N}{1}$ H_2SO_4 represents 0.13244 gm. of pure anhydrous strontium lactate.

If 9.9 cc. are required, then

$$0.13244 \times 9.9 = 1.311156 \text{ gms.}$$

$$\frac{1.311156 \times 100}{1.33} = 98.6\%$$

In this process, if the ignition is carried too far, the strontium carbonate is decomposed into strontium oxide.

Magnesium salts may be estimated by precipitating as ammonia-magnesian phosphate, and titrating this precipitate as directed for phosphoric acid.

CHAPTER XI.

ANALYSIS BY PRECIPITATION.

THE general principle of this method is that the determination of the quantity of a given substance is effected by the formation of a precipitate, upon the addition of the standard solution to the substance under examination.

The end of the reaction is determined in three ways:

1. By adding the standard solution until no further precipitate occurs, as in the estimation of chlorides, etc., by silver nitrate.

2. By the use of an indicator. This may either be contained in the liquid under analysis; or used externally, by frequently bringing a portion of it in contact with a drop of the liquid during the titration.

The titration is continued until the slightest excess of the standard solution is shown by the production of a characteristic reaction with the indicator.

3. By adding the standard solution until a precipitate is produced, as in the estimation of cyanogen by standard silver solution.

The first of these endings can only be applied with accuracy to silver and chlorine estimations, as the silver chloride which is formed is almost perfectly insoluble and has a tendency to curdle closely by shaking, so as to leave a clear supernatant liquid.

Most of the other precipitates, such as barium sulphate, calcium oxalate, etc., although heavy and insoluble, do not readily and perfectly subside, because of their finely divided or powdery nature. They must therefore be excluded from this class.

In these cases, therefore, it is necessary to find an indicator which brings them into class 2.

The third class comprises only two processes, viz., the determination of cyanogen by silver, and that of chlorine by mercuric nitrate.

ESTIMATION OF HALOID SALTS.

The estimation of these salts is based upon the powerful affinity existing between the halogens and silver, and the ready precipitation of the resulting chloride, bromide, or iodide.

Standard solution of silver nitrate is used for this purpose, and for the sake of exactness and convenience is made of decinormal strength, and in many cases it is advisable to use centinormal solutions.

The Decinormal $\left(\frac{N}{10}\right)$ Silver Nitrate V. S. is official. $AgNO_3 = \left\{ \begin{matrix} 169.55 & 16.955 \\ *169.7 & 16.97 \end{matrix} \right\}$ gms. are contained in 1 litre.—Dissolve 16.97 gms. of pure silver nitrate in sufficient water to make, at or near 15° C. (59° F.), exactly 1000 cc. 1 litre of this solution thus contains $\frac{1}{10}$ of the molecular weight in grammes of silver nitrate. It is therefore a decinormal solution.

If pure crystals of silver nitrate are not readily obtainable, and pure sodium chloride is at hand, a solution of the silver nitrate may be made of approximate

strength, a little stronger than necessary, and then standardized by means of the sodium chloride, as follows: 0.117 gm. of sodium chloride is dissolved in water, and a burette is filled with the solution of silver nitrate to be standardized. The silver solution is now slowly added from the burette to the sodium-chloride solution contained in a beaker until no more precipitate of silver chloride is produced.

If neutral potassium chromate is used as an indicator, the end of the reaction is shown by the appearance of yellowish-red silver chromate. This indication is extremely delicate. The silver nitrate does not act upon the chromate until all of the chloride is converted into silver chloride.

In the above reaction 20 cc. of silver nitrate should be required. But since the silver-nitrate solution is too strong, less of it will complete the reaction, and the solution must be diluted so that exactly 20 cc. will be required to precipitate the chlorine in 0.117 gm. of NaCl.

Thus if 17 cc. are used, each 17 cc. must be diluted to 20 cc., or each 170 cc. to 200 cc., or the entire remaining solution in the same proportion.

After dilution a fresh trial should always be made.

Nitrate of silver solution should be kept in dark amber-colored, glass-stoppered bottles, carefully protected from dust.

Titration by decinormal silver nitrate V. S. may be managed in various ways, adapted to the special preparation to be tested.

1. In most cases it is directed by the U. S. P. to be used in the presence of a small quantity of potassium chromate T. S.

2. In some cases it is added until the first appearance of a permanent precipitate, as in potassium cyanide and hydrocyanic acid.

3. It may be used in all cases without an indicator by observing the exact point when no further precipitate occurs. But since this consumes too much time in waiting for the precipitate to subside, so as to render the supernatant liquid sufficiently clear to recognize whether a further precipitate is produced by the addition of the silver solution, it is impracticable. It may, however, be practised in the case of ferrous iodide, where the addition of potassium chromate T. S. would be improper, since it reacts with the iron.

4. It may be added in definite amount, known to be in excess of the quantity required, and the excess measured back by titration with decinormal potassium sulphocyanate V. S., or even with decinormal sodium chloride V. S. (residual titration).

In case an excess of the $\frac{N}{10}$ silver nitrate V. S. is added accidentally, it is only necessary to add a definite volume of a $\frac{N}{10}$ solution of the salt under examination, and finish the titration with $\frac{N}{10}$ silver nitrate, deducting, of course, the same number of cc. of silver solution as has been added of the salt solution.

Ammonium Bromide, $NH_4Br = \left\{ \begin{matrix} 97.77 \\ *98 \end{matrix} \right.$.—3 grms. of the salt are dried at 100° C. (212° F.) and dissolved in water to the measure of 100 cc. 10 cc. of this solution are placed in a beaker, a few drops of potassium chromate T. S. added, and then the decinormal silver

nitrate V. S. carefully added from a burette, until a permanent red coloration is produced. The red coloration is due to the formation of red chromate of silver, which takes place after all of the bromine has combined with the silver. Apply the equation:

$$\underset{10)97.77}{NH_4Br} + \underset{10)169.7}{AgNO_3} = AgBr + NH_4NO_3.$$

9.777 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. of the $\frac{N}{10}$ V. S. represents .009777 gm. of NH_4Br.

3 gms. of the U. S. P. salt should require 30.9 cc. of $\frac{N}{10}$ $AgNO_3$ V. S.

But as a rule this salt contains an impurity (ammonium chloride) which will be precipitated by the silver nitrate as well as the bromide. The presence of this impurity must therefore be taken into account in calculating the percentage of bromide.

$$\underset{10)53.38}{NH_4Cl} + \underset{10)169.7}{AgNO_3} = AgCl + NH_4NO_3.$$

5.338 16.97 gms. = 1000 cc. of $\frac{N}{10}$ V. S.

The amount of the salt examined equivalent to 1000 cc. of $\frac{N}{10}$ silver solution is first calculated by simple proportion:

$$30.9 \text{ cc.} : .3 \text{ gm.} :: 1000 \text{ cc.} : x. \qquad x = 9.708.$$

Then

$$9.777 - 9.708 = y. \qquad y = .069.$$

.069 = the excess of $\frac{N}{10}$ $AgNO_3$ V. S. used up by the ammonium chloride, reckoned in terms of bromide (NH_4Br); and since 5.338 gms. of NH_4Cl = 9.777 gms. of NH_4Br, the excess which NH_4Cl can consume is represented by 9.777 − 5.338 = 4.439. Therefore, as

$$4.439 : 5.338 :: .069 : z. \qquad z = 0.08297.$$

0.08297 = the amount of ammonium chloride present in x grammes of the sample taken.

Lastly, calculate the percentage by simple proportion:

$$9.708 : .0829 :: 100 : P. \quad P = 0.85\% \text{ of } NH_4Cl.$$

Lithium Bromide, $LiBr = \left\{ \begin{matrix} 86.77 \\ *87 \end{matrix} \right.$.—Dissolve 0.3 gm. of dry lithium bromide in 10 cc. of water, add 2 drops of potassium chromate T. S., and then titrate with decinormal silver nitrate V. S. until a permanent red color of silver chromate makes its appearance. 0.3 gm. of the U. S. P. salt requires 35.3 cc. of $\frac{N}{10}$ V. S.

$$\underset{10)86.77}{LiBr} + \underset{10)169\ 7}{AgNO_3} = AgBr + LiNO_3.$$

8.677 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. of $\frac{N}{10}$ $AgNO_3$ V. S. = 0.008677 gm. of pure lithium bromide.

Potassium Bromide, $KBr = \left\{ \begin{matrix} 118.79 \\ *119 \end{matrix} \right.$.—Operate upon 0.1 gm. of the salt dissolved in about 10 cc. of

water. Add a few drops of potassium chromate T. S., and titrate with $\frac{N}{10}$ $AgNO_3$ V. S. until a permanent red color of silver chromate is produced. According to the U. S. P., 0.5 gm. of the well-dried salt should require 42.85 cc. of $\frac{N}{10}$ $AgNO_3$ V. S.

$$KBr + AgNO_3 = AgBr + KNO_3.$$

$$\underset{11.879 \text{ gms.}}{10)118.79} \qquad \underset{16.97 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} AgNO_3 \text{ V. S.}}{10)169.7}$$

Thus each cc. represents .011879 gm. of KBr. Potassium chloride is a common impurity; to calculate it, proceed as for NH_4Cl, 74.4 of KCl being equal to 118.79 of KBr.

Sodium Bromide, $NaBr = \left\{ \begin{matrix} 102.76 \\ *103 \end{matrix} \right.$.—This salt is tested in exactly the same manner as the potassium bromide. A convenient quantity to operate upon is 0.1 gm.

The U. S. P. directs that 0.3 gm. of the well-dried salt be dissolved in 10 cc. of water, two drops of potassium chromate T. S. added, and the mixture titrated with decinormal silver nitrate V. S. until a permanent red color of silver chromate appears.

Note the number of cc. required to produce this effect, and multiply this number by the factor 0.010276 gm. This will give the quantity of NaBr present in the sample taken.

According to the U. S. P., not more than 29.8 cc. of the standard silver solution, corresponding to at least 97.29% of the pure salt, should be required.

The chloride which is present as an impurity may

be calculated in the same manner as ammonium chloride, 5.837 gms. of the chloride being equal to 10.276 gms. of sodium bromide.

Calcium Bromide, $CaBr_2 \left\{ \begin{matrix} 199.43 \\ *200 \end{matrix} \right.$.—This salt may be tested as described on page 108.

The U. S. P. method is as follows: 0.25 gm. of the well-dried salt is dissolved in 10 cc. of water; 2 drops of potassium chromate T. S. are then added, and the solution titrated with decinormal silver nitrate V. S. until a permanent red color is produced. 25 cc. of the standard silver-nitrate solution should be required to produce this result, corresponding to 99.7% of the pure salt, a greater amount of the standard solution indicating the presence of calcium chloride, a smaller amount indicating other impurities.

$$CaBr_2 + 2AgNO_3 = 2AgBr + Ca(NO_3)_2.$$

2)199.43 2)339.4
10)99.715 10)169.7
9.9715 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents .0099715 gm. of $CaBr_2$.

Therefore 25 cc. represent $.0099715 \times 25 = 0.2492875$ gm.

$$\frac{.2492875 \times 100}{0.25} = 99.7\%$$

Strontium Bromide, $SrBr_2 + 6H_2O = \left\{ \begin{matrix} 354.58 \\ *355.3 \end{matrix} \right.$.—This salt is tested volumetrically, according to the U. S. P., in the following manner:

0.3 gm. of strontium bromide, rendered anhydrous by

thorough drying before being weighed, is dissolved in 10 cc. of water, 3 drops of potassium *di*chromate T. S. are added, and then the decinormal silver nitrate V. S. is poured in from a burette until all of the bromide has combined with the silver nitrate and a permanent red coloration is produced.

Not more than 24.6 cc. of decinormal silver nitrate V. S. should be required, corresponding to at least 98% of the pure salt.

$$SrBr_2 + 2AgNO_3 = 2AgBr + Sr(NO_3)_2.$$

2)246.82 2)339.4
10)123.41 10)169.7
12.341 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.012341 gm. of strontium bromide.

Zinc Bromide, $ZnBr_2 = \begin{cases} 224.62 \\ *225 \end{cases}$.—This salt is estimated as follows: 0.3 gm. of the dry salt is dissolved in 10 cc. of water, 2 drops of potassium chromate T. S. are added, and then decinormal silver nitrate V. S. is poured in from a burette until all of the bromide has combined with silver nitrate, and a permanent red color is produced. Note the number of cc. of the standard silver solution used, and multiply this number by the factor shown by the following equation, to obtain the amount of pure zinc bromide in the quantity taken:

$$ZnBr_2 + 2AgNO_3 = 2AgBr + Zn(NO_3)_2.$$

20)224.62 20)339.4
11.231 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. represents .011231 gm. of pure $ZnBr_2$. The U. S. P. salt should require 26.7 cc. of decinormal silver nitrate V. S. to produce the desired reaction, corresponding to not less than 99.95% of the pure salt.

Thus $0.011231 \times 26.7 = 0.2998677$ gm.

$$\frac{0.2998677 \times 100}{0.3} = 99.95\%.$$

Potassium Iodide, $KI = \begin{cases} 165.56 \\ *165.5 \end{cases}$.—This is estimated, according to the U. S. P., in a manner similar to the haloid salts just considered.

0.5 gm. of the well-dried salt is dissolved in 10 cc. of water, 2 drops of neutral potassium chromate T. S. are added, and then the $\frac{N}{10}$ $AgNO_3$ V. S. slowly added from a burette until a permanent red color of silver chromate is produced. Not more than 30.25 cc. nor less than 30 cc. of decinormal silver nitrate V. S. should be required. This quantity corresponds to 99.5% of the pure salt.

$$KI + AgNO_3 = AgI + KNO_3.$$

$\underset{16.556 \text{ gms.}}{10)165.56}$ $\underset{16.97 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} AgNO_3 \text{ V. S.}}{10)169.7}$

Each cc. of $\frac{N}{10}$ $AgNO_3$ V. S. thus corresponds to 0.016556 gm. of potassium iodide.

Thus $0.016556 \times 30 = 0.49668$ gm.

$$\frac{0.49668 \times 100}{0.5} = 99.3\%$$

Potassium iodide may also be estimated volumetrically by $\frac{N}{20}$ mercuric chloride V. S., the termination of the operation being indicated by the formation of a red precipitate.

$$4KI + HgCl_2 = 2KCl + HgI_2.2KI \text{ (soluble)}. \quad (1)$$

$$HgI_2.2KI + HgCl_2 = 2KCl + 2HgI_2. \quad (2)$$

This process originated with M. Personne, and is founded on the fact that if a solution of mercuric chloride be added to one of potassium iodide, in the proportion of one equivalent of mercuric chloride to four of potassium iodide, red mercuric iodide is formed, which dissolves at once to a colorless solution. The slightest excess of mercuric chloride will cause a brilliant red precipitate to make its appearance, HgI_2.

$$4KI + HgCl_2 = 2KCl + HgI_2.2KI \text{ (soluble)}.$$

20)662.24 20)270.54

33.112 gms. 13.527 gms. or 1000 cc. of standard solution.

Thus each cc. of standard solution of the above strength represents 0.033112 gm. of potassium iodide, which means that 1 cc. is the largest quantity of this standard solution which can be added to 0.033112 gm. of potassium iodide without producing a permanent precipitate.

The above solution of mercuric chloride is not strictly a $\frac{N}{20}$ V. S. Potassium iodide is a univalent salt; and since four molecules of it are precipitated by one molecule of mercuric chloride, the latter is chemically equivalent to four atoms of hydrogen; and $\frac{1}{4}$ of its

molecular weight in grammes, dissolved in water to one litre, is a normal solution, and $\frac{1}{20}$ of this is a $\frac{N}{20}$ V. S.

The author of this process states that neither chlorides, bromides, nor carbonates interfere with the reaction.

Sodium Iodide, NaI $= \begin{cases} 149.53 \\ *149.5 \end{cases}$.—Dissolve 0.5 gm. of the well-dried salt in 10 cc. of water, add 2 drops of potassium chromate T. S., and then pass into the solution from a burette $\frac{N}{10}$ $AgNO_3$ V. S. until a permanent red coloration is produced.

Note the number of cc. used, and multiply this by the factor.

$$\underset{10)149.53}{NaI} + \underset{10)169.7}{AgNO_3} = AgI + NaNO_3.$$

14.953 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Each cc. of $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.014953 gm. of NaI.

Assuming that 33.4 cc. of $\frac{N}{10}$ $AgNO_3$ V. S. were required, each representing 0.014953 gm. of NaI, then the quantity tested contained

$$33.4 \times 0.014953 \text{ gm. or } 0.4994302 \text{ gm.}$$

$$\frac{0.4994302 \times 100}{0.5} = 99.8\%$$

The U. S. P. requirement is that the salt contain 98%, at least, of pure NaI.

Strontium Iodide, $SrI_2 + 6H_2O = \begin{cases} 448.12 \\ *448.3 \end{cases}$.—0.3 gm. of strontium iodide, rendered anhydrous before being weighed, is dissolved in 10 cc. of water, 3 drops of potassium dichromate T. S. are then added, and the $\frac{N}{10}$ $AgNO_3$ V. S. run in from a burette until a permanent red coloration is produced.

Apply the following equation:

$$SrI_2 + 6H_2O + 2AgNO_3 = 2AgI + Sr(NO_3)_2 + 6H_2O.$$

2)448.12 2)339.4
10)224.06 10)169.7
22.406 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

This equation shows that each cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.022406 gm. of SrI_2.

Zinc Iodide, $ZnI_2 = \begin{cases} 318.16 \\ *318 \end{cases}$.—Dissolve 0.5 gm. of dry zinc iodide in 10 cc. of water, add 2 drops of potassium chromate T. S., and then run into the mixture from a burette $\frac{N}{10}$ $AgNO_3$ V. S. until a permanent red color is produced, indicating that all of the iodide has been precipitated in the form of silver iodide. Each cc. of the $\frac{N}{10}$ silver solution used represents 0.015908 gm. of zinc iodide.

$$ZnI_2 + 2AgNO_3 = 2AgI + Zn(NO_3)_2.$$

2)318.16 2)339.4
10)159.08 10)169.7
15.908 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

The U. S. P. directs that not less than 31 cc. nor more than 31.4 cc. of $\frac{N}{10}$ $AgNO_3$ V. S. be required to produce the desired result, 31 cc. corresponding to 98.62% and 31.4 cc. to 99.9% of pure zinc iodide.

$$0.015908 \times 31.4 = 0.4995112 \text{ gm. of } ZnI_2.$$

Then

$$\frac{0.4995112 \times 100}{0.5} = 99.9\%$$

Ammonium Chloride, $NH_4Cl = \left\{ \begin{matrix} 53.38 \\ *53.4 \end{matrix} \right.$.—It is estimated in the same manner as the other soluble haloid salts. A weighed quantity of the salt is dissolved in a small quantity of water and the solution titrated with $\frac{N}{10}$ silver-nitrate solution until no more precipitation takes place, or, if potassium chromate T. S. has been added as indicator, until a red color makes its appearance.

$$NH_4Cl + AgNO_3 = AgCl + NH_4NO_3.$$

$$\underset{5.338 \text{ gms.}}{10)53.38} \qquad \underset{16.97 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} \text{ V. S.}}{10)169.7}$$

Thus each cc. of $\frac{N}{10}$ V. S. used represents 0.005338 gm. of NH_4Cl.

Potassium Chloride, $KCl = \left\{ \begin{matrix} 74.40 \\ *74.40 \end{matrix} \right.$.—This is estimated in the same manner as the above, applying the following equation :

$$KCl + AgNO_3 = AgCl + KNO_3.$$

$$\underset{7.44 \text{ gms.}}{10)74.4} \qquad \underset{16.97 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} \text{ } AgNO_3 \text{ V. S.}}{10)169.7}$$

Thus each cc. of $\frac{N}{10}$ V. S. represents 0.00744 gm. of KCl.

Sodium Chloride, NaCl $= \left\{ \begin{matrix} 58.37 \\ *58.4 \end{matrix} \right.$.—A weighed quantity of the well-dried salt, say 0.2 gm., is dissolved in about 10 cc. of water and the solution mixed with a few drops of potassium chromate T. S. Then $\frac{N}{10}$ $AgNO_3$ V. S. is run in from a burette until all the chloride is precipitated and a permanent red color of silver chromate is produced.

The U. S. P. directs that 0.195 gm. of the salt should require not less than 33.4 cc. of $\frac{N}{10}$ $AgNO_3$ V. S. to produce this reaction.

The following equation shows the reaction which takes place between the sodium chloride and the silver nitrate:

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

$$\underset{5.837 \text{ gms.}}{10)58.37} \qquad \underset{16.97 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} AgNO_3 \text{ V. S.}}{10)169.7}$$

Each cc. of the standard solution thus represents 0.005837 gm. of NaCl.

$$.005837 \times 33.4 = 0.194958 \text{ gm. of NaCl.}$$

$$\frac{0.194958 \times 100}{0.195} = 99.9\%$$

Zinc Chloride, $ZnCl_2 = \left\{ \begin{matrix} 135.84 \\ *135.8 \end{matrix} \right.$.—This salt is tested in exactly the same way as the other haloid salts.

Dissolve 0.3 gm. of the dry salt in about 10 cc. of water, add a few drops (2 drops) of potassium chromate T. S., and then run into the mixture from a burette, $\frac{N}{10}$ $AgNO_3$ V. S. until a permanent red color is produced.

It should require 44.1 cc. of the standard silver solution to produce this result.

The reaction is shown by the following equation:

$$\underset{\substack{2)135.84\\10)\,67.92\\6.792\text{ gms.}}}{ZnCl_2} + \underset{\substack{2)339.4\\10)169.7\\16.97\text{ gms. or 1000 cc. }\frac{N}{10}\text{ V. S.}}}{2AgNO_3} = 2AgCl + Zn(NO_3)_2.$$

Thus it is seen that each cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.006792 gm. of $ZnCl_2$.

$$0.006792 \times 44.1 = 0.2995272 \text{ gm.}$$

$$\frac{0.2995272 \times 100}{0.3} = 99.84\%$$

The U. S. P. requires 99.84%.

Syrupus Acidi Hydriodici, a syrupy liquid containing about 1% of HI U. S. P. $HI = \begin{cases} 127.53 \\ *127.5 \end{cases}$.—Operate upon 15 grammes. The reaction which occurs is as follows:

$$\underset{\substack{10)127.5\\12.75\text{ gms.}}}{HI} + \underset{\substack{10)169.7\\16.97\text{ gms. or 1000 cc. }\frac{N}{10}\text{ }AgNO_3\text{ V. S.}}}{AgNO_3} = AgI + HNO_3.$$

The end of the reaction is shown by the cessation of the formation of a precipitate.

Since nitric acid is liberated, potassium chromate is not admissible as indicator.

The U. S. P. directs that the syrup be neutralized by ammonia water before titration. This prevents the formation of nitric acid, and admits of the use of potassium chromate as indicator.

(31.875) *32 gms. of the syrup, neutralized, and mixed with 2 drops of the indicator, should require 25 cc. of decinormal silver-nitrate solution to produce a permanent red tint.

Each cc. represents 0.01275 gm. of HI.

$$0.01275 \times 25 = 0.31875 \text{ gm.}$$

$$\frac{0.31875 \times 100}{31.875} = 1\%$$

Syrupus Ferri Iodidi, a syrup containing about 10% by weight of ferrous iodide (FeI_2) U. S. P. $FeI_2 = \begin{cases} 308.94 \\ *309 \end{cases}$.—Take 2 gms. of the syrup, mix it with a small quantity of water, and run in the $\frac{N}{10}$ silver solution. The close of the reaction is shown by the cessation of the formation of a precipitate. Potassium chromate is not admissible as an indicator in this case.

$$FeI_2 + 2AgNO_3 = 2AgI + Fe(NO_3)_2.$$

$$\begin{array}{cc} 2)308.94 & 2)339.4 \\ 10)154.47 & 10)169.7 \\ 15.447 \text{ gms.} & 16.97 \text{ gms. or 1000 cc. } \frac{N}{10} \text{ V. S.} \end{array}$$

Thus each cc. represents 0.015447 gm. of ferrous iodide.

The U. S. P. method originated with Volhard. It has the advantage over the direct method for haloids

with chromate indicator, in that it may be used in the presence of nitric acid. It thus enables the haloids to be estimated in the presence of a phosphate or other salt which precipitates silver in a neutral, but not in an acid solution.

It depends upon entirely precipitating the chloride, in the presence of nitric acid, by a known excess of standard solution of silver nitrate, and then estimating the excess of silver left uncombined, by the aid of a standard solution of potassium sulphocyanate, using ferric alum as an indicator.

The sulphocyanate has a greater affinity for silver than it has for iron, and therefore so long as any silver is in solution, the sulphocyanate will combine with it and form a precipitate of silver sulphocyanate.

As soon as the silver is all taken up, the sulphocyanate will combine with the ferric alum and strike a brownish-red color.

The sulphocyanate solution is to be made of such strength that it corresponds with the silver solution, volume for volume.

The difference between the volume of silver solution originally added, and the volume of sulphocyanate solution used, will give the volume of silver solution equivalent to the haloid salt present.

Decinormal Potassium Sulphocyanate V. S. (Volhard's Solution), $KSCN = \left\{ \begin{matrix} 96.99 & 9.699 \\ *97 & *9.7 \end{matrix} \right\}$ gms. in 1 litre.—Dissolve 10 gms. of pure crystallized potassium sulphocyanate (thiocyanate) in 1000 cc. of water.

This solution, which is too concentrated, must be adjusted so as to correspond in strength exactly with decinormal silver nitrate V. S. For this purpose in-

troduce into a flask 10 cc. of $\frac{N}{10}$ $AgNO_3$ V. S., 0.5 cc. of ammonio-ferric sulphate T. S., and 5 cc. of diluted nitric acid.

Run into this mixture from a burette the sulphocyanate solution.

At first a white precipitate of silver sulphocyanate is produced, giving the fluid a milky appearance, and then, as each drop of sulphocyanate falls in, it is surrounded by a deep brownish-red cloud of ferric sulphocyanate, which quickly disappears on shaking, as long as any of the silver nitrate remains unchanged.

When the point of saturation is reached and the silver has all been precipitated, a single drop of the sulphocyanate solution produces a faint brownish-red color, which does not disappear on shaking.

Note the number of cc. of the sulphocyanate 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-red tint. (The same tint of brown or red to which the volumetric solution is adjusted must be attained when the solution is used in volumetric testing.)

Assuming that 9.5 cc. of the sulphocyanate solution were required to produce the reaction, then each 9.5 cc. must be diluted to make 10 cc., or the whole of the remaining solution in the same proportion.

Always make a new trial after the dilution to see if the solutions correspond.

The U. S. P. method for estimating *syrup of ferrous iodide* is as follows:

1.5447 gms. (*1.55 gms.) of the syrup and 10 cc. of

water are introduced into a flask, 11 cc. of decinormal silver nitrate V. S. are added, then 5 cc. of diluted nitric acid, and 5 cc. of ferric ammonium sulphate T. S. The decinormal potassium sulphocyanate V. S. is now run into the mixture from a burette until a reddish-brown tint is produced, which does not disappear upon shaking. Not more than 1 cc. should be required.

This corresponds to 10% of ferrous iodide. The reactions which take place are shown by the following equations:

$$FeI_2 + 2AgNO_3 = 2AgI + Fe(NO_3)_2; \quad . \quad (1)$$

15.447 gms. 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

$$AgNO_3 + KSCN = AgSCN + KNO_3; \quad . \quad (2)$$

16.97 gms. 9.699 gms. or 1000 cc. $\frac{N}{10}$ KSCN V. S.

$$Fe_2(NH_4)_2(SO_4)_4 + 6KSCN = Fe_2(SCN)_6 + (NH_4)_2SO_4 + 3K_2SO_4. \quad (3)$$

The $Fe_2(SCN)_6$ gives the brownish-red color to the solution.

The object of the nitric acid is to acidulate the solution, facilitate the precipitation of the silver, and to oxidize the ferrous nitrate.

In the above case 11 cc. of silver nitrate are originally added. If 1 cc. of potassium sulphocyanate be required, it shows that 1 cc. of the silver-nitrate solution was in excess, and that 10 cc. went into combination with the ferrous iodide. The equation shows us that

each cc. of silver nitrate V. S. represents 0.015447 gm. of ferrous iodide; then 10 cc. represent

$$0.015447 \times 10 = 0.15447 \text{ gm.},$$

and $$\frac{.15447 \times 100}{1.5447} = 10\%$$

of FeI_2 in the U. S. P. syrup.

Saccharated Ferrous Iodide.—The process for estimating this compound is exactly the same as that for syrup of ferrous iodide.

1.5447 gms. (*1.55 gms.) of the saccharated ferrous iodide are dissolved in about 20 cc. of water in a small flask, and to this solution is added first 22 cc. of $\frac{N}{10}$ $AgNO_3$ V. S., then 5 cc. of diluted nitric acid, and 5 cc. of ferric ammonium sulphate T. S. The $\frac{N}{10}$ KSCN V. S. is then run in, from a burette, until the reddish-brown color of ferric sulphocyanate is produced. Not more than 2 cc. of the $\frac{N}{10}$ KSCN V. S. should be required.

This corresponds to 20% of pure ferrous iodide.

22 cc. of $\frac{N}{10}$ silver nitrate

— 2 cc. of $\frac{N}{10}$ potassium sulphocyanate

= 20 cc. of $\frac{N}{10}$ silver nitrate,

which reacted with the ferrous iodide, then

$$0.015447 \times 20 = 0.30894 \text{ gm.},$$

$$\frac{0.30894 \times 100}{1.5447} = 20\%$$

Syrup of Ferrous Bromide, U. S. P. 1880, $FeBr_2 = \left\{ \begin{matrix} 215.4 \\ *216 \end{matrix} \right.$.—This syrup may be tested in the same manner as the syrup of ferrous iodide, either by the direct method, using the cessation of precipitation as the end reaction, or by the residual method with potassium sulpho- cyanate.

The factor is 0.01077.

Hydrocyanic Acid, $HCN = \left\{ \begin{matrix} 26.98 \\ *27 \end{matrix} \right.$.—Dilute hydrocyani cacid may be estimated by weighing out about 5 gms., and adding to this sufficient soda or potassa solution to convert the acid into sodium or potassium cyanide (NaCN or KCN), and leave the solution strongly alkaline.

To this solution is added the decinormal silver-nitrate solution until a permanent turbidity occurs.

This turbidity is due to the precipitation of silver cyanide, and affords a delicate proof of the completion of the reaction.

The difficulty experienced in this process is in the conversion of the acid into the cyanide. The sodium cyanide has a strong alkaline reaction, turning litmus blue when only a small proportion of the acid has been neutralized.

If the titration is conducted before the acid is completely neutralized, that which is free will not be acted

upon. Indeed, cyanide of sodium may be estimated in the presence of hydrocyanic acid in this way.

According to Senier, the following procedure will answer well:

To the dilute hydrocyanic acid add soda solution to a strong alkaline reaction, determined by litmus tincture. Then titrate with $\frac{N}{10}$ silver nitrate V. S., drop by drop, from the burette. If the liquid becomes acid, add a little more soda solution to bring it back to alkalinity, and continue the titration until the turbidity indicates the end of the reaction. The liquid must be kept alkaline throughout the process. It is not well to add too much soda solution at the beginning, as this would use up too much of the silver solution, and make the reading a trifle too high.

The following equations, etc., explain the reactions:

$$2HCN + 2NaOH = 2NaCN + 2H_2O;$$

$$\underset{5.396 \text{ gms.}}{10)53.96} \qquad \underset{9.796 \text{ gms.}}{10)97.96}$$

$$2NaCN + AgNO_3 = AgCN,NaCN + NaNO_3.$$

$$\underset{9.796 \text{ gms.}}{10)97.6} \qquad \underset{16.97 \text{ gms. or 1000 cc. } \frac{N}{10} \text{ V. S.}}{10)169.7}$$

It is seen that 5.396 gms. of real HCN are equivalent to 9.796 gms. of sodium cyanide, and represent 16.97 gms. of silver nitrate, or 1000 cc. of the $\frac{N}{10}$ V. S. That is, 1000 cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. may be added to a solution containing 9.796 gms. of sodium cyanide, and

no precipitate be produced; but if one or two drops more of the standard solution be added, a precipitate is at once formed.

Each cc. of $\frac{N}{10}$ $AgNO_3$ V. S., which fails to produce a precipitate with a solution of sodium cyanide, represents 0.009796 gm. of NaCN, which is equivalent to .005396 gm. of HCN.

With 2 molecular weights of sodium or potassium cyanide, one molecule of silver nitrate forms a double salt, having the composition NaCN,AgCN, and which is soluble.

When more silver-nitrate solution is added, this soluble double salt is decomposed, and a precipitate of silver cyanide occurs, thus:

$$AgCN,NaCN + AgNO_3 = 2AgCN + NaNO_3.$$

The U. S. P. method is as follows:

A weighed quantity of the acid is mixed with sufficient of an aqueous suspension of magnesia to make an opaque and decidedly alkaline mixture.

To this a few drops of potassium chromate T. S. are added, and the $\frac{N}{10}$ silver solution delivered from a burette until the red color of silver chromate appears.

1.35 gms. of the diluted acid is mixed with enough water and magnesia to make an opaque mixture of about 10 cc. Add to this 2 or 3 drops of potassium chromate T. S., and then from a burette deliver the decinormal silver nitrate V. S. until a red tint is produced which does not again disappear by shaking.

Each cc. of the standard silver solution used, represents 0.002698 gm. of absolute HCN.

$$HCN + AgNO_3 = AgCN + HNO_3.$$

10)26.98 — 10)169.7

2.698 gms. — 16.97 gms. or 1000 cc. $\frac{N}{10}$ silver nitrate V. S.

Potassium Cyanide, KCN = $\begin{cases} 65.01 \\ *65 \end{cases}$.—This salt may be estimated in the following manner:

1 gm. of the salt is dissolved in sufficient water, and into the solution, is delivered in drops the standard silver solution until a precipitate appears which is not redissolved on agitation.

If 0.65 gm. of KCN are taken, not less than 45 cc. of $\frac{N}{10}$ $AgNO_3$ V. S. should be required.

$$2KCN + AgNO_3 = AgCN,KCN + KNO_3.$$

10)130.02 — 10)169.7

13.002 gms. — 16.97 gms. or 1000 cc. $\frac{N}{10}$ $AgNO_3$ V. S.

Thus each cc. of the standard silver solution represents 0.013 gm. of KCN.

$$0.013 \times 45 = 0.585 \text{ gm.}$$

$$\frac{.585 \times 100}{.65} = 90\%$$

Cyanides may be estimated also by iodine, according to Fordos and Gelis.

This process depends upon the fact that potassium cyanide decolorizes iodine, potassium iodide and cyanogen iodide being formed.

When iodine solution is added to a solution of po-

tassium cyanide, the iodine is decolorized as long as there is any undecomposed cyanide present.

The following equation expresses the reaction

$$\underset{\substack{2)65.01\\10)32.505\\3.2505\text{ gms.}}}{KCN} + \underset{\substack{2)153.06\\10)126.53\\12.653\text{ gms. or 1000 cc. }\frac{N}{10}\text{ iodine V. S.}}}{I_2} = KI + CNI,$$

Thus each cc. of the volumetric solution represents 0.00325 gm. of KCN.

The end of the reaction is known by the yellow color of the iodine solution becoming permanent.

Silver Nitrate, (Argenti Nitras) $AgNO_3 = \left\{ \begin{matrix} 169.55 \\ *169.7 \end{matrix} \right.$. —Nitrate of silver and other salts of this metal may be volumetrically estimated by standard solution of sodium chloride.

The silver salt is dissolved in sufficient water in a beaker, and a decinormal volumetric solution of sodium chloride run in until a precipitate is no longer produced.

The estimation may also be performed by retitration as follows:

To the silver solution contained in a beaker add a measured excess of $\frac{N}{10}$ sodium chloride V. S., and then, after adding a few drops of potassium chromate T. S., titrate the mixture with $\frac{N}{10}$ silver nitrate V. S. until a permanent red color appears. Deduct the number of cc. of silver nitrate V. S. from the quantity of sodium chloride V. S. and the quantity of the latter is obtained which actually combined with the silver solution under examination.

The sulphocyanate method of Volhard may also be employed in the estimation of silver.

$\frac{N}{10}$ **Sodium Chloride V. S.**, NaCl $= \left\{ \begin{matrix} 58.37. \\ *58.4. \end{matrix} \right.$ $\left. \begin{matrix} 5.837 \\ *5.84 \end{matrix} \right\}$ gms. in 1 litre.—Dissolve 5.837 gms. of pure sodium chloride in enough water to make exactly 1000 cc. at the ordinary temperature of the atmosphere.

Check this solution with decinormal silver nitrate V. S. The two solutions should correspond, volume for volume.

Pure Sodium Chloride may be prepared by passing into a saturated aqueous solution of the purest commercial chloride of sodium a current of dry hydrochloric-acid gas. The crystalline precipitate is then separated and dried at a temperature sufficiently high to expel all traces of free acid.

The U. S. P. method for silver nitrate is as follows: *0.34 gm. (0.3391 gm.) of silver nitrate is dissolved in 10 cc. of distilled water, and the solution carefully titrated with $\frac{N}{10}$ NaCl V. S. until precipitation ceases. 20 cc. of the standard solution should be required.

$$\underset{10)\underline{169.55}}{AgNO_3} + \underset{10)\underline{58.37}}{NaCl} = AgCl + NaNO_3.$$

16.955 gms. 5.837 gms. or 1000 cc. $\frac{N}{10}$ NaCl V. S.

Each cc. of the standard solution represents 0.016955 gm. of pure $AgNO_3$.

$$0.016955 \times 20 = 0.3391 \text{ gm.}$$

$$\frac{0.3391 \times 100}{.3391} = 100\%$$

Argenti Nitras Dilutus (Mitigated Caustic).—This may be estimated in the same manner as the above.

The U. S. P. method is as follows:

1 gm. is dissolved in 10 cc. of distilled water, to this is added 20 cc. of $\frac{N}{10}$ NaCl V. S. and a few drops of potassium chromate T. S., and the excess of $\frac{N}{10}$ NaCl V. S. found by titration with $\frac{N}{10}$ $AgNO_3$ V. S. until a permanent red color is produced. Not more than 0.5 cc. of the latter should be required. This indicates that 19.5 cc. of $\frac{N}{10}$ NaCl V. S. were actually required to completely precipitate the silver nitrate tested.

Therefore

$$0.016955 \times 19.5 = .3306225 \text{ gm.}$$

$$\frac{.33+ \times 100}{1} = 33+\%$$

Argenti Nitras Fusus (Moulded Silver Nitrate. Lunar Caustic).—This is treated in exactly the same manner as the above. 0.34 gm. of the lunar caustic is dissolved in water, and 20 cc. of standard sodium chloride added; not more than 1 cc. of this should be in excess, as shown by retitration with silver nitrate V. S., using chromate indicator.

This corresponds to about 95% of pure silver nitrate.

Silver Oxide, $Ag_2O = 231.28$.—May be converted into nitrate by solution in nitric acid, and then testing as above for silver nitrate. There will probably be some free nitric acid present if this is done,

and therefore the sulphocyanate method is best employed.

The Sulphocyanate Method.—A weighed quantity of the silver salt is dissolved in water, some diluted nitric acid and ammonium ferric sulphate solution are added, and the mixture then titrated with $\frac{N}{10}$ potassium sulphocyanate V. S. until a permanent reddish-brown color of feric sulphocyanate is produced.

The following equation explains the reactions:

$$AgNO_3 + KSCN = AgSCN + KNO_3.$$

10)169.55 10)96.99

16.955 gms. 9.699 gms. or 1000 cc. standard V. S.

Thus each cc. of the standard V. S. represents 0.016955 gm. of pure silver nitrate, or 0.010766 gm. of metallic silver.

Liquor Plumbi Subacetatis (Goulard's Extract).—This is an aqueous solution containing about 25% of lead subacetate, the formula of which is approximately $Pb_2O(C_2H_3O_2)_2 = 546.48$. This is estimated by precipitation with sulphuric acid.

(13.6622 gms.) *13.67 gms. of the solution are diluted with 50 cc. of water, a few drops of methyl-orange added, and the mixture titrated with normal sulphuric acid until the lead is completely precipitated and the mixture has assumed a red color. The red color indicates an acid reaction. The reaction is illustrated by the following equation:

$$Pb_2O(C_2H_3O_2)_2 + 2H_2SO_4 = 2PbSO_4 + 2HC_2H_3O_2 + H_2O.$$

4)546.48 4)196

136.62 gms. 49 gms. or 1000 cc. $\frac{N}{1}$ H_2SO_4 V. S.

Thus each cc. of $\frac{N}{1}$ H_2SO_4 V. S. represents 0.13662 gm. of the subacetate.

If 25 cc. of the standard solution are required, then the solution under analysis contains $0.13662 \times 25 = 3.4155$ gms.

$$\frac{3.4155 \times 100}{13.662} = 25\%$$

The Diluted Solution of Lead Subacetate (Lead Water) may be estimated in the same manner.

TABLE OF SUBSTANCES ESTIMATED BY PRECIPITATION, GIVING FORMULA, MOLECULAR WEIGHT, STANDARD SOLUTION USED, AND FACTOR.

Name.	Formula.	Molecular weight.	Standard Solution Used.	Factor.
Acid hydrobromic	HBr	80.76	$\frac{N}{10}$ $AgNO_3$	0.008076
" hydrocyanic	HCN	26.98	$\frac{N}{10}$ $AgNO_3$	0.002698
" hydriodic	HI	127.53	"	0.01275
Ammonium bromide	NH_4Br	97.77	"	0.009777
" chloride	NH_4Cl	53.38	"	0.005338
" iodide	NH_4I	144.54	"	0.014454
Calcium bromide	$CaBr_2$	199.43	"	0.0099715
" chloride	$CaCl_2$	110.65	"	0.005532
Ferrous bromide	$FeBr_2$	215.40	"	0.01077
" iodide	FeI_2	308.94	$\frac{N}{10}$ $AgNO_3$ and $\frac{N}{10}$ $KSCN$	0.015447
Lead acetate	$Pb(C_2H_3O_2)_2.3H_2O$	378.0	$\frac{N}{1}$ H_2SO_4	0.189
" subacetate	$Pb_2O(C_2H_3O_2)_2$	546.48	"	0.13662
Lithium bromide	$LiBr$	86.77	$\frac{N}{10}$ $AgNO_3$	0.008677
Potassium bromide	KBr	118.79	"	0.011879
" chloride	KCl	74.40	"	0.00744
" cyanide	KCN	65.01	"	0.01300
" iodide	KI	165.56	"	0.016556
" sulphocyanide	$KSCN$	96.99	"	0.009699
Silver (metallic)	Ag_2	215.32	$\frac{N}{10}$ $NaCl$ or $\frac{N}{10}$ $KSCN$	0.010766
" nitrate	$AgNO_3$	169.55	"	0.016955
" oxide	Ag_2O	231.28	"	0.011564
Sodium bromide	$NaBr$	102.76	$\frac{N}{10}$ $AgNO_3$	0.010276
" chloride	$NaCl$	58.37	"	0.005837
" iodide	NaI	149.53	"	0.014953
Strontium bromide	$SrBr_2.6H_2O$	354.58	"	0.012341
" iodide	$SrI_2.6H_2O$	448.12	"	0.022406
Zinc bromide	$ZnBr_2$	224.62	"	0.011231
" chloride	$ZnCl_2$	135.84	"	0.006792
" iodide	ZnI_2	318.16	"	0.015908

CHAPTER XII.

OXIDIMETRY—ANALYSIS BY OXIDATION.

AN extensive series of analyses are made by this method, with extremely accurate results—in fact, the results are generally more accurate than any which can be obtained by weighing.

The principle involved in this method is extremely simple.

Substances which are capable of absorbing oxygen or are susceptible of an equivalent action are subjected to the action of an oxidizing agent of known power, and the quantity of the latter required for complete oxidation ascertained.

The substances which are used as oxidizing agents in volumetric analysis are potassium dichromate, potassium permanganate, iodine, etc.

The reducing agents, or deoxidizers, are sodium thiosulphate, oxalic acid, arsenous oxide, stannous chloride, metallic zinc, and magnesium.

Thus ferrous oxide (FeO), an oxidizable substance, is ever ready and willing to take up oxygen, while potassium dichromate and permanganate are always ready to give up some of their oxygen. When potassium permanganate gives up its oxygen in this way it loses its color, and in volumetric analysis advantage is taken of this fact. When the permanganate, which is added in drops from a burette, is no longer decolor-

ized, the iron salt is completely oxidized. The reaction is as follows:

$$10FeO + 2KMnO_4 = 5Fe_2O_3 + 2MnO + K_2O.$$

Ferrous oxide. Ferric oxide.

The oxidation of ferrous oxide by potassium dichromate is shown by the following equation:

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + K_2O.$$

An oxidation is always accompanied by a reduction, the oxidizing agent being itself reduced in the operation. As seen in the above equations, the manganic compound is reduced to a manganous compound, and the chromic to a chromous compound.

ESTIMATION OF FERROUS SALTS.

Ferrous salts are estimated by oxidizing them either with potassium dichromate or potassium permanganate.

In some respects the dichromate possesses advantages over permanganate.

1. It may be obtained in a pure state.

2. Its solution does not deteriorate upon standing as does that of permanganate.

3. It is not decomposed by contact with rubber as the permanganate is, and may therefore be used in Mohr's burette. Its great disadvantage, however, is that when used in the estimation of ferrous salts the end reaction can only be found by using an external indicator. The indicator which must be used is freshly

prepared potassium ferricyanide T. S., a drop of which is brought in contact with a drop of the solution being tested, on a white slab, at intervals during the titration, the end of the reaction being the cessation of the production of a blue color, when the two liquids are brought together. Thus the estimation by potassium dichromate is cumbersome, and very exact results are not easily obtained.

If potassium-permanganate solution is used for the estimation of these salts the end of the reaction is easily found without the use of an indicator.

The permanganate is decomposed the instant it is brought in contact with a ferrous salt in an acid solution; therefore as long as any ferrous salt remains in solution the permanganate is decolorized, and when it ceases to lose its color the reaction is complete.

Preparation of Standard Solution Decinormal Potassium Dichromate V. S., $K_2Cr_2O_7 = \left\{ \begin{matrix} 293.78 \\ *294 \end{matrix} \right.$. $\left\{ \begin{matrix} 4.896 \\ *4.9 \end{matrix} \right.$ gms. in 1 litre.—4.896 gms. (*4.9 gms.) of pure potassium dichromate are dissolved in sufficient water to make, at the ordinary temperature of the atmosphere, exactly 1000 cc.

Pure Potassium Dichromate for use in volumetric analysis should respond to all the tests for purity given in the text of the U. S. P. (under *Potassii Dichromate*), as well as to the following: A solution of 0.5 gm. of the salt in 10 cc. of water, rendered acid by 0.5 cc. of nitric acid, should produce no visible change when treated with barium chloride T. S. (absence of *sulphate*), nor with silver nitrate T. S. (absence of *chloride*).

If a mixture of 10 cc. of an aqueous solution of the

salt (1–20) with 1 cc. of ammonia water be treated with ammonium oxalate T. S., no precipitate should be produced (absence of *calcium*).

Standard solution of potassium dichromate is sometimes used as a neutralizing solution for estimating alkalies, phenolphthalein being used as indicator.

When used for this purpose the normal solution contains 146.89 gms. in 1 litre (one half the molecular weight in grammes). It is then the exact equivalent of any normal acid V. S.

$$2KOH + K_2Cr_2O_7 = 2K_2CrO_4 + H_2O.$$

$$\underset{56 \text{ gms.}}{2)112} \qquad \underset{146.89 \text{ gms., or 1000 cc. normal V. S.}}{2)293.78}$$

Decinormal potassium dichromate V. S. may also be used in conjunction with potassium iodide and sulphuric acid for standardizing sodium thiosulphate V. S. Iodine is liberated from potassium iodide in this reaction. The reaction is expressed by the equation

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2.$$

When used as an oxidizing agent to convert ferrous into ferric salts, or to liberate iodine from potassium iodide, the $\frac{N}{10}$ solution of potassium dichromate must contain 4.689 gms. in 1 litre. If the decinormal solution containing 14.689 gms. in 1 litre is used, it has the effect of a $\frac{3N}{10}$ solution.

The decinormal solution which is used as an oxidizing agent is chemically equivalent to decinormal potassium permanganate. When used for the purpose of liberating iodine from potassium iodide, it is the equivalent of an equal volume of decinormal sodium thiosulphate.

For titrating ferrous salts the decinormal solution of dichromate is used in the following manner:

Make an aqueous solution of the ferrous salt, introduce it into a flask, and acidulate it with sulphuric or hydrochloric acid. Now add gradually from a burette the decinormal potassium dichromate V. S. until a drop taken out upon a white slab no longer shows a blue color with a drop of freshly prepared potassium ferricyanide T. S. Note the number of cc. of the standard solution used, multiply this number by the factor, and thus obtain the quantity of pure salt in the sample taken.

Ferrous salts strike a blue color with potassium ferricyanide T. S; but as the quantity of ferrous salts gradually diminishes during the titration, the blue becomes somewhat turbid, acquiring first a green, then a gray, and lastly a brown shade. The process is finished when the greenish-blue tint has entirely disappeared.

The reaction of potassium dichromate with ferrous salts always takes place in the presence of free sulphuric or hydrochloric acid at ordinary temperatures. Nitric acid should not be used.

If it is desired to estimate ferric salts by this standard solution it is necessary to first reduce them.

This may be done by metallic zinc, magnesium, sulphurous acid, the alkali sulphites, or by stannous chloride.

Standard potassium dichromate may be checked in the same way as standard permanganate, with pure metallic iron, as described below.

Decinormal Potassium Permanganate V. S., $2KMnO_4 = \left\{ {}^{315.34}_{*316} \right.$. It contains $\left. {}^{3.1534}_{*3.16} \right\}$ gms. in 1 litre.—This solution may be prepared by dissolving the pure crystals in fresh distilled water. If the salt can be

obtained perfectly pure and dry, a decinormal solution will be obtained if 3.1534 gms. are dissolved in distilled water, sufficient to make 1000 cc. at the ordinary atmospheric temperature; but nevertheless it is always well to verify it as described below. The solution will retain its strength for several weeks if well kept, but it should always be checked by titration before it is used.

The standardization of permanganate solution may be effected as follows:

With Metallic Iron—Thin annealed binding-wire, free from rust, is one of the purest forms of iron.

0.1 gm. of such iron is placed in a flask which is provided with a cork through which a piece of glass tubing passes, to the top of which a piece of rubber tubing is attached, which has a vertical slit about one inch long in its side, and which is closed at its upper end by a piece of glass rod (see Fig. 41). Diluted sulphuric acid is added and gentle heat applied. The iron dissolves and the steam and liberated hydrogen escape through the slit under slight pressure. The air is thus prevented from entering and the ferrous solution protected from oxidation.

FIG. 41.

When the iron is completely dissolved a small quantity of cold, recently boiled, distilled water should be added, and the titration with potassium permanganate at once begun and continued until a faint permanent

red color is produced. If the solution is decinormal, exactly 17.85 cc. will be required to produce this result.

The iron is converted by the sulphuric acid into ferrous sulphate, $Fe_2 + 2H_2SO_4 = 2FeSO_4 + 2H_2$. This ferrous sulphate is easily oxidized by the air, and therefore it is directed that access of air should be prevented, and the distilled water, with which the solution is diluted, previously boiled in order to drive off any dissolved free oxygen.

$$\underset{100)558.8}{10FeSO_4} + \underset{100)315.34}{2KMnO_4} + 8H_2SO_4$$

5.588 gms. 3.1534 gms. or 1000 cc. $\frac{N}{10}$ V. S.

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

This equation, etc., shows that each cc. of $\frac{N}{10}$ $2KMnO_4$ V. S. represents .005588 gm. of metallic iron.

With Oxalic Acid.—0.063 gm. of the pure crystallized acid is weighed (or 10 cc. of decinormal oxalic acid V. S. carefully measured) and placed in a flask, with some dilute sulphuric acid and considerable water, the mixture warmed to about 60° C. (140° F.), and the permanganate added from a burette.

The action is in this case less decisive and rapid than in the titration with iron, and more care should be used. The color disappears slowly at first, but afterwards more rapidly.

Note the number of cc. of the permanganate solution used, and then dilute the remainder so that equal volumes of decinormal oxalic acid and decinormal permanganate solution will exactly correspond.

Example.—Assuming that 9 cc. of the permanganate solution first prepared had been required to produce a permanent pink tint when titrated into 10 cc. of $\frac{N}{10}$ oxalic-acid solution, then the permanganate must be diluted in the proportion of 9 of permanganate and 1 of distilled water, or 900 and 100.

The U. S. P. gives the following method for the preparation of this solution:

A stronger and a weaker solution is made and mixed in certain proportions to form a solution of the proper strength. It is said that when thus prepared the solution will keep its titre for months if properly preserved.

The Stronger Solution.—3.5 gms. of pure crystallized permanganate are dissolved in 1000 cc. of water by the aid of heat, and the solution then set aside in a closed flask for two days, so that any suspended matters may deposit.

The Weaker Solution.—Dissolve 6.6 gms. of the salt in 2200 cc. of water in the same manner as above, and set this solution aside for two days.

These two solutions are then separately titrated in the following manner:

Introduce 10 cc. of decinormal oxalic-acid solution into a flask, add 1 cc. of pure concentrated sulphuric acid, and before the mixture cools add the permanganate solution slowly from a burette, shaking the flask after each addition, and towards the end of the operation reducing the flow to drops. When the last drop is no longer decolorized, but imparts a pinkish tint to the liquid, the reaction is completed. Note the number of cc. consumed. Finally, mix the two solutions in such proportions that equal volumes of the

mixture and of $\frac{N}{10}$ oxalic acid V. S. will exactly correspond.

To obtain the accurate proportions for mixing the two solutions, deduct 10 from the number of cc. of the weaker solution consumed in the above titration; with this difference multiply the number of cc. of the stronger solution consumed: the product shows the number of cc. of the *stronger solution* needed for the mixture.

Then deduct the number of cc. of the stronger solution consumed in the titration from 10, and with the difference multiply the number of cc. of the weaker solution consumed: the product shows the number of cc. of the *weaker solution* needed for the mixture.

Or, designating the number of cc. of the stronger solution by S, and the number of cc. of the weaker solution by W, and using the following formula, the proportions in which the solutions must be mixed are obtained:

$$\underset{\text{Stronger Solution.}}{(W - 10)S} + \underset{\text{Weaker Solution.}}{(10 - S)W.}$$

Example.—Assuming that 9 cc. of the stronger and 10.5 cc. of weaker had been consumed in decomposing 10 cc. of $\frac{N}{10}$ oxalic acid V. S.; then, substituting these values in the above formula, we obtain

$$(10.5 - 10)9 + (10 - 9)10.5,$$
$$\text{or } 4.5 + 10.5,$$

making 15 cc. of final solution.

The bulk of the two solutions is now mixed in the same proportion: 450 cc. of the stronger and 1050 cc. of the weaker, or 900 cc. of the stronger and 2100 cc. of the weaker.

After the solutions are thus mixed a new trial should be made, when 10 cc. of the solution should exactly decompose 10 cc. of $\frac{N}{10}$ oxalic acid V. S.

The reaction between potassium permanganate and oxalic acid is illustrated by the following equation:

$$2KMnO_4 + 5(H_2C_2O_4.2H_2O) + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

ESTIMATION OF FERROUS SALTS WITH POTASSIUM DICHROMATE.

One molecule of potassium dichromate yields, under favorable circumstances, three atoms of oxygen for oxidizing purposes. This is shown by the following equation:

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + K_2O.$$

Here it is seen that the three liberated atoms of oxygen combine at once with the ferrous oxide, converting it into ferric oxide:

$$6FeO + O_3 = Fe_6O_9 \quad \text{or} \quad 3Fe_2O_3.$$

In the oxidation of a ferrous salt, the reaction takes place only in the presence of an acid.

The dichromate then gives up its oxygen. Four of

its oxygen atoms combine at once with the replaceable hydrogen of the accompanying acid, the other three being liberated. The three oxygen atoms thus set free are available either for direct oxidation or for combination with the hydrogen of more acid. In the latter case a corresponding quantity of acidulous radicals is set free.

The following equation indicates this reaction:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3.$$

In this case four of the liberated atoms of oxygen combine with eight of the atoms of hydrogen of sulphuric acid and liberate four SO_4 radicals, which at once combine with the K_2 and Cr_2 of the dichromate. The other three atoms are set free. If seven sulphuric-acid molecules are used instead of four molecules, the three free atoms of oxygen will liberate $3(SO_4)$:

$$K_2Cr_2O_7 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + (SO_4)_3.$$

If this liberation of $3(SO_4)$ takes place in the presence of a ferrous salt, the $3(SO_4)$ will combine with six molecules of the ferrous salt, converting it into a ferric salt:

$$6FeSO_4 + 3SO_4 = Fe_6(SO_4)_9 = 3Fe_2(SO_4)_3;$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + (3Fe_2(SO_4)_3).$$

If in the above case hydrochloric acid is used instead of sulphuric, fourteen molecules of the former must be taken to supply the necessary hydrogen.

The seven liberated atoms of oxygen must have fourteen atoms of hydrogen to combine with.

Three of these atoms of oxygen liberate six univalent, or three bivalent, acidulous radicals.

Therefore, since one molecule of $K_2Cr_2O_7$ will give up for oxidizing purposes three atoms of oxygen, which are equivalent chemically to six atoms of hydrogen, one sixth of the molecular weight in grammes of the dichromate, dissolved in sufficient water to make one litre, constitutes a normal solution, and one tenth of this quantity of $K_2Cr_2O_7$ in a litre, a decinormal solution.

Thus the estimation of ferrous salts is effected by oxidizing them to ferric with an oxidizing agent of known power, the strength of the ferrous salt being determined by the quantity of the oxidizing agent required to convert it to ferric.

Ferri Carbonas Saccharatus (Saccharated Ferrous Carbonate), $FeCO_3 = \left\{ \begin{matrix} 115.73 \\ *116 \end{matrix} \right.$.—*1.16 (1.1573) gms. of saccharated ferrous carbonate are dissolved in 10 cc. of diluted sulphuric acid and the solution diluted with water to about 100 cc. The decinormal potassium dichromate is carefully added, until a drop of the solution taken out and brought in contact with a drop of freshly prepared solution of potassium ferricyanide ceases to give a blue color.

The number of cc. of the dichromate solution is read off and the following equations applied:

$$6FeCO_3 + 6H_2SO_4 = 6FeSO_4 + 6H_2O + 6CO_2;$$

$$\begin{matrix} 115.73 \\ 6 \\ \hline 694.38 \end{matrix} \qquad \begin{matrix} 151.7 \\ 6 \\ \hline 910.2 \end{matrix}$$

then

$$6FeCO_3 \text{ or } 6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 =$$

6)694.38 6)910.2 6)293.78

10)115.73 10)151.7 10) 48.96

11.573 gms. 15.17 gms. 4.896 gms., or 1000 cc. $\frac{N}{10}$ $K_2Cr_2O_7$ V.S.

$$K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3.$$

Thus each cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ represents 0.011573 gm. of pure ferrous carbonate or 0.005588 gm. of metallic iron.

The U. S. P. saccharated ferrous carbonate requires about 15 cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. for complete neutralization, corresponding to about 15%.

$$.011573 \times 15 = 0.173585 \text{ gm.}$$

$$\frac{0.173585 \times 100}{1.1573} = 15\%$$

If strong sulphuric acid is added to saccharated ferrous carbonate it will char the sugar, and a black mass of burnt sugar is obtained. This may be prevented by adding water first and then, slowly, the sulphuric acid.

Instead of sulphuric acid, hydrochloric acid may be used. This will not char the sugar; but the ferrous chloride which is then formed is too readily oxidized by the air.

It has also been suggested that as hydrochloric acid so rapidly converts ordinary sugar into invert sugar as to render it easily attacked by the dichromate, it should be cautiously used, if at all. Phosphoric acid

has none of these disadvantages, and may be employed with good results.

In making estimations of ferrous salts with potassium dichromate, care should be taken to avoid atmospheric oxidation. It is good practice to calculate approximately how much of the standard solution will probably be required to complete the oxidation, and then add almost enough of the standard solution at once, instead of adding it slowly.

A white porcelain slab is then got ready, and placed alongside of the flask in which the titration is to be performed. Upon this slab is placed a number of drops of the freshly prepared solution of potassium ferricyanide, and at intervals during the titration a drop is taken from the flask on a glass rod and brought in contact with one of the drops on the slab. The glass rod should always be dipped in clean water after having been brought in contact with a drop of the indicator. See Fig. 42.

When a drop of the solution ceases to give a blue color on contact with the indicator, the reaction is complete.

Ferrous Sulphate, $FeSO_4 + 7H_2O = \begin{cases} 277.42. \\ *278. \end{cases}$—Dissolve about one gramme of crystallized ferrous sulphate in a little water, add a good excess of sulphuric or hydrochloric acid, titrate with the decinormal potassium dichromate V. S. as directed under Ferrous Carbonate, and apply the following equation:

$$\underset{\substack{6)1668 \\ 10)\ 278 \\ 27.8 \text{ gms.}}}{6(FeSO_4.7H_2O)} + \underset{\substack{6)293.78 \\ 10)\ 48.96 \\ 4.896 \text{ gms., or 1000 cc. } \frac{N}{10} K_2Cr_2O_7 \text{ V.S.}}}{K_2Cr_2O_7} + 7H_2SO_4 =$$

$$3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 49H_2O.$$

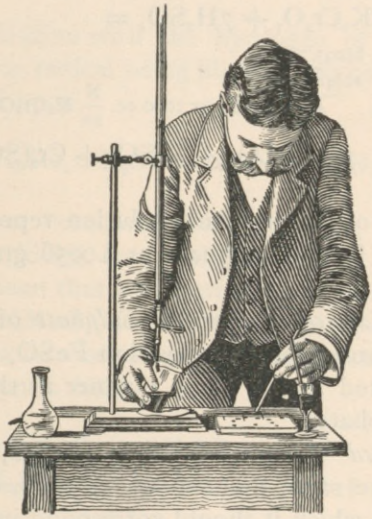

FIG. 42.

Thus each cc. of the $\frac{N}{10}$ $K_2Cr_2O_7$ V. S. represents 0.0278 gm. of crystallized ferrous sulphate or 0.0152 anhydrous. If 1 gm. of the salt is taken and dissolved as above, it should require about 37 cc. of the standard solution, equivalent to about 100%.

Anhydrous Ferrous Sulphate.—

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 =$$

6)912 6)293.78
10)152 10)48.96
15.2 gms. 4.896 gms., or 1000 cc. $\frac{N}{10}$ $K_2Cr_2O_7$ V. S.

$$3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Each cc. of the standard solution represents 0.0152 gm. of real ferrous sulphate or *.0056 gm. of metallic iron.

Dried (*Exsiccated*) *Ferrous Sulphate* of the U. S. P. has the approximate composition $FeSO_4 + 3H_2O$.

It is tested in the same manner as the anhydrous ferrous sulphate.

Granulated Ferrous Sulphate, $FeSO_4 + 7H_2O$, is tested in the same manner as crystallized ferrous sulphate, with which it should correspond in strength.

ESTIMATION OF FERROUS SALTS WITH POTASSIUM-PERMANGANATE SOLUTION.

The action of potassium permanganate in oxidation is very similar to that of the dichromate.

The molecule $2KMnO_4$ has 8 atoms of oxygen, which it gives up in the process of oxidation. These 8 atoms of oxygen unite with the replaceable hydrogen

of an accompanying acid, liberating an equivalent amount of acidulous radical.

Three of these atoms of oxygen liberate sufficient acidulous radical to combine with the potassium and manganese of the permanganate, while the other five atoms are available either for direct oxidation or

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

For combination with the hydrogen of more acid, more acidulous radical being liberated to combine with the salt acted upon,

$$2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5(SO_4).$$

$5(SO_4)$ when combined with $10FeSO_4$ forms $Fe_{10}(SO_4)_{15}$ or $5Fe_2(SO_4)_3$, ferric sulphate.

It is thus seen that one molecule of potassium permanganate $2KMnO_4$ has the power of converting 10 molecules of a ferrous salt into the ferric state.

The equation in full is

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

We have seen that $2KMnO_4$ has 5 atoms of oxygen available for oxidizing purposes, and that each of these will combine with 2 atoms of hydrogen. $2KMnO_4$ is consequently chemically equivalent to 10 atoms of replaceable hydrogen, and a normal solution of this salt when used as an oxidizing agent is one that contains in 1 litre one tenth of the molecular weight of $2KMnO_4$, and a decinormal solution one which contains one hundredth of the molecular weight.

When potassium permanganate is brought in contact with a ferrous salt or other oxidizable substance, it is decomposed and decolorized. Hence when titrating with a standard solution of this salt it is decolorized so long as an oxidizable substance is present; as soon, however, as the oxidation is completed the standard solution retains its color when added to the substance, and the first appearance of a faint red color is the end reaction, and the oxidation is known to be completed.

In titrating with potassium permanganate it must be remembered that free acid should always be present in the solution titrated, in order to keep the resulting manganous oxide in solution. Diluted sulphuric acid is generally used for this purpose. Hydrochloric acid may also be employed, but in that case the titration must be conducted at a low temperature, otherwise chlorine will be evolved and the analysis spoiled.

Ferrum Reductum is estimated for metallic iron, according to the U. S. P., in the following manner:

0.56 (0.559) gm. of reduced iron is introduced into a glass-stoppered bottle, 50 cc. of *mercuric chloride* T. S. are added, and the bottle heated on a water-bath for one hour, agitating frequently, but keeping the bottle well stoppered.

$$2HgCl_2 + Fe_2 = 2FeCl_2 + 2Hg.$$

Then allow it to cool, dilute the contents with water to 100 cc., and filter. Take 10 cc. of the filtrate, add to it 10 cc. of diluted sulphuric acid, introduce the mixture into a glass-stoppered bottle (having a capacity of about 100 cc.), and titrate the mixture with decinormal potassium permanganate V. S. until a permanent red color is produced.

Each cc. of the standard solution represents *0.0056 gm. of metallic iron, or 10%.

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

To confirm the assay, add a few drops of alcohol to decolorize (or decompose) the excess of permanganate, then add 1 gm. of potassium iodide, and digest for half an hour at a temperature of 40° C. (104° F.).

$$\underset{\substack{2)112\\10)\ 56\\5.6}}{Fe_2(SO_4)_3} + 2KI = 2FeSO_4 + \underset{\substack{2)254\\10)127\\12.7}}{I_2} + K_2SO_4.$$

The cooled solution is mixed with a few drops of starch test solution, which gives it a dark-blue color, because of the formation of iodide of starch. Then add carefully, from a burette, decinormal sodium thiosulphate V. S. until the blue color is discharged.

$$\underset{\substack{2)254\\10)127\\12.7\text{ gms.}}}{I_2} + 2(\underset{\substack{2)495.28\\10)247.64\\24.76\text{ gms. or 1000 cc. }\frac{N}{10}\ Na_2S_2O_3\text{ V. S.}}}{Na_2S_2O_3.5H_2O}) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Thus each cc. of the standard thiosulphate represents 0.0127 gm. of iodine, or 0.0056 gm. of metallic iron.

In both of these estimations the quantity of standard solution used should be the same.

The U. S. P. requirement is 8 cc.

$$0.0056 \times 8 = 0.0448 \text{ gm.}$$

$$\frac{0.0448 \times 100}{0.056} = 80\%$$

Ferrous Sulphate (Crystallized), $FeSO_4 + 7H_2O$ = $\left\{ \begin{matrix} 277.42 \\ *278 \end{matrix} \right.$.—*1.39 (1.3871) gms. of ferrous sulphate are dissolved in about 25 cc. of water, and the solution acidulated with sulphuric acid. Decinormal potassium permanganate V. S. is then delivered in from a burette until a permanent pink color is obtained, indicating the complete oxidation of the ferrous salt.

$$\underset{100)2774.2}{10(FeSO_4 + 7H_2O)} + \underset{100)315.34}{2KMnO_4} + 8H_2SO_4 =$$

27.742 gms. 3.1534 gms. or 1000 cc. $\frac{N}{10}$ standard solution.

$$5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Thus each cc. of the standard solution represents 0.027742 gm. of crystallized ferrous sulphate.

Not less than 50 cc. should be used before the potassium permanganate ceases to be decolorized.

$$0.027742 \times 50 = 1.387100 \text{ gms.}$$

$$\frac{1.387100 \times 100}{1.3871} = 100\%$$

Granulated Ferrous Sulphate, $FeSO_4 + 7H_2O$, is estimated in the same way as the foregoing, and should correspond with it in strength.

Exsiccated (*Dried*) *Ferrous Sulphate*.—This salt is tested in the same manner as the other two sulphates. It contains a larger percentage of ferrous sulphate than the other two, having less water of crystallization. Its composition is approximately $FeSO_4 + 3H_2O$.

In estimating ferrous sulphate in this salt the water of crystallization is not taken into account. Then by

deducting the percentage of ferrous sulphate from 100 the percentage of water of crystallization is obtained.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4$$

100)1520 — 15.20 gms. 100)315.34 — 3.1534 gms. or 1000 cc. $\frac{N}{10}$ standard solution.

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Each cc. of the standard solution represents 0.0152 gm. of anhydrous (real) ferrous sulphate. If one gm. of the dried salt, treated as above described, requires 48 cc. of $\frac{N}{10}$ permanganate solution, it contains

$$0.0152 \times 48 = 0.7296 \text{ gm.},$$

or 72.96% of real ferrous sulphate, and 100.00 — 72.96 = 27.04% of water of crystallization.

Any salt may be analyzed in this way for water of crystallization. If the salt is *pure*, the difference between the percentage of real salt and 100 always represents the percentage of water of crystallization.

ESTIMATION OF HYPOPHOSPHOROUS ACID, HYPOPHOSPHITES, AND OTHER OXIDIZABLE SUBSTANCES.

Acidum Hypophosphorosum Dilutum.—An aqueous solution containing about 10 per cent, by weight, of absolute hypophosphorous acid.

$$(H_3PO_2) \quad HPH_2O_2 = \begin{cases} 65.88 \\ *66 \end{cases}.$$

This acid may be tested by neutralization with $\frac{N}{1}$ potassium hydrate V. S., as described on page 96.

The U. S. P. also directs the estimation by residual titration, given below.

0.5 gm. of diluted hypophosphorous acid is mixed with 7 cc. of sulphuric acid, and 35 cc. of decinormal potassium permanganate V. S., and the mixture boiled for fifteen minutes.

The potassium permanganate, in the presence of sulphuric acid, oxidizes the hypophosphorous acid to phosphoric, as the equation shows:

$$5HPH_2O_2 + 6H_2SO_4 + 2(2KMnO_4)$$

2)329 40 — 100)164.7 — 1.647 gms.

2)630.68 — 100)315.34 — 3.1534 gms. or 1000 cc. $\frac{N}{10}$ V. S.

$$= 5H_3PO_4 + 6H_2O + 2K_2SO_4 + 4MnSO_4.$$

Each cc. of the decinormal V. S. represents 0.001647 gm. of absolute hypophosphorous acid. The quantity of permanganate solution directed to be added is slightly in excess. The excess is then ascertained by retitration with decinormal oxalic acid V. S. Each cc. of oxalic acid required corresponds to one cc. of decinormal permanganate V. S., which has been added in excess of the quantity actually required for the oxidation.

The excess of permanganate colors the solution red, and the oxalic acid V. S. is then added until the red color just disappears, which indicates that the excess of permanganate is decomposed.

$$2KMnO_4 + 5(H_2C_2O_4.2H_2O) + 3H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2.$$

If 4.7 cc. of decinormal oxalic acid V. S. are required, it indicates that 35 cc. − 4.7 cc. = 30.3 cc. of deci-

normal permanganate were actually used up in oxidizing the hypophosphorous acid.

Therefore

$$0.001647 \text{ gm.} \times 30.3 = 0.0499 \text{ gm.},$$

$$\text{or} \quad \frac{0.0499 \times 100}{.5} = 9.98\% \text{ of } HPH_2O_2.$$

In the above process the boiling facilitates the oxidation, but if the acid is boiled before it is completely oxidized it will decompose. Hence the necessity for adding an excess of the permanganate and retitrating.

Calcium Hypophosphite, $Ca(PH_2O_2)_2 = \begin{cases} 169.67 \\ *170 \end{cases}$.

—0.1 gm. of the salt is dissolved in 10 cc. of water, then 10 cc. of sulphuric acid and 50 cc. of decinormal potassium permanganate V. S. are added, and the mixture boiled for fifteen minutes.

The excess of permanganate is then found by retitrating with decinormal oxalic-acid solution.

The reactions which take place are expressed by the following equations:

$$5Ca(PH_2O_2)_2 + 5H_2SO_4 = 5CaSO_4 + 10HPH_2O_2; \quad (1)$$

$$10HPH_2O_2 + 12H_2SO_4 + 4(2KMnO_4) = 10H_3PO_4 + 12H_2O + 4K_2SO_4 + 8MnSO_4. \quad (2)$$

These two reactions may be written together thus:

$$5Ca(PH_2O_2)_2 + 17H_2SO_4 + 4(2KMnO_4)$$

4)848.35 — 100)212.08 — 2.1208 gms.

4)1261.36 — 100)315.34 — 3.1534 gms. or 1000 cc. standard V. S.

$$= 5CaSO_4 + 4K_2SO_4 + 8MnSO_4 + 10H_3PO_4 + 12H_2O.$$

Thus each cc. of the standard permanganate represents 0.0021208 gm. of pure $Ca(PH_2O_2)_2$. 50 cc. of decinormal potassium permanganate are about 3 cc. more than is necessary to oxidize 0.1 gm. of pure calcium hypophosphite. Therefore not more than 3 cc. of the standard oxalic-acid solution should be required to decolorize the solution to which 50 cc. of permanganate has been added.

Then

$$0.0021208 \text{ gm.} \times 47 = .09968 \text{ gm.}$$

$$\frac{0.9968 \times 100}{0.1} = 99.68\% \text{ pure salt.}$$

Ferric Hypophosphite, $Fe_2(PH_2O_2)_6 = \begin{cases} 501.04 \\ *501 \end{cases}$. —This salt is estimated in the same manner as the foregoing.

0.1 gm. is dissolved in 10 cc. of water, then 10 cc. of sulphuric acid and 50 cc. of decinormal potassium permanganate V. S. are added, and the mixture boiled for 15 minutes.

The quantity of permanganate solution here added is slightly in excess of the quantity actually required to oxidize the hypophosphite. The excess is determined by retitrating with decinormal oxalic acid V. S., which corresponds volume for volume with the permanganate.

Not more than 3 cc. of the standard oxalic acid solution should be required to decolorize the excess of permanganate, which means that 47 c.c. of the per-

manganate should actually be required to oxidize the 0.1 gm. of hypophosphite taken.

The reaction is illustrated by the following equation:

$$5Fe_2(PH_2O_2)_6 + 51H_2SO_4 + 12(2KMnO_4)$$

12)2505.20
100) 208.77
2.0877 gm.

12)3784.08
100) 315.34
3.1534 gms. or 1000 cc. $\frac{N}{10}$ V.S.

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 24MnSO_4 + 30H_3PO_4 + 36H_2O.$$

This shows that each cc. of $\frac{N}{10}$ potassium permanganate V. S. represents 0.0020877 gm. of ferric hypophosphite. If 47 cc. are required to oxidize 0.1 gm. of the salt, the latter contains $0.0020877 \times 47 = 0.0981+$ gm., or 98.1+ % of pure salt.

Potassium Hypophosphite, $KPH_2O_2 = \left\{ \begin{matrix} 103.91 \\ *104 \end{matrix} \right.$.

—0.1 gm. of dry potassium hypophosphite is dissolved in about 10 cc. of water, then 7.5 cc. of sulphuric acid and 40 cc. of decinormal potassium permanganate V. S. are added, and the mixture is boiled for 15 minutes.

Decinormal oxalic acid is then carefully delivered into the mixture until the red color, due to the excess of permanganate, is discharged. The number of cc. of the standard oxalic acid required for this purpose, subtracted from the 40 cc. of permanganate originally added, gives the quantity of permanganate which was actually required for the oxidation of the hypophosphite. If the salt conforms in purity to the U. S. P. requirement, not more than 2 cc. of the oxalic acid V. S. will be required.

The following equation illustrates the reaction which takes place in this operation:

$$5KPH_2O_2 + 6H_2SO_4 + 2(2KMnO_4)$$

2)519.55 — 100)259.77 — 2.5977 gm.

2)630.68 — 100)315.34 — 3.1534 gms.

or 1000 cc. $\frac{N}{10}$ permaganate V. S.

$$= 5KH_2PO_4 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

Each cc. of decinormal permanganate V. S. required for the oxidation of the hypophosphite, represents 0.0025977 gm. of the pure salt. If 38 cc. are required, then 0.0025977 × 38 = .0987126 gm., or 98.7+ %.

Sodium Hypophosphite, $NaPH_2O_2 + H_2O = \left\{ \begin{matrix} 105.84 \\ *106 \end{matrix} \right.$.—0.1 gm. of the dry salt is dissolved in 10 cc. of water and mixed with 7.5 cc. sulphuric acid and 40 cc. of decinormal potassium permanganate V. S. The mixture is then boiled for 15 minutes, and titrated with decinormal oxalic-acid solution to determine the excess of permanganate.

Not more than 3 cc. of the oxalic acid V. S. should be required to discharge the red color, which means that 0.1 gm. of the salt should require 37 cc. of $\frac{N}{10}$ permaganate solution for its oxidation.

The following equation shows the reaction:

$$5(NaPH_2O_2.H_2O) + 6H_2SO_4 + 2(2KMnO_4) =$$

2)529.2 — 100)264.6 — 2.646 gm.

2)630.68 — 100)315.34 — 3.1534 gm., or 1000 cc. $\frac{N}{10}$ V.S.

$$5NaH_2PO_4 + 2Na_2SO_4 + 4MnSO_4 + 11H_2O.$$

Thus each cc. of the decinormal permanganate represents 0.002646 gm. of $NaPH_2O_2$.

Therefore $0.002646 \times 37 = 0.097902$ gm. or 97.9%.

Aqua Hydrogenii Dioxidi U. S. P. (Solution of Hydrogen Peroxide).—It is described in the U. S. P. as an aqueous solution of hydrogen dioxide, $H_2O_2 = \left\{ \begin{matrix} 33.92 \\ *34 \end{matrix} \right.$, slightly acid and containing about 3%, by weight, of pure dioxide, corresponding to 10 volumes of available oxygen.

This substance is official for the first time in the U. S. P. 1890, in which methods for its preparation, preservation, and assay are given. Solution of hydrogen peroxide is an important commercial product, being used in the arts as well as in medicine.

It is sold as containing 5, 10, 15, or 20 volumes of oxygen, in solution. This should mean that a given volume of the solution yields from itself 5, 10, 15, or 20 times its own volume of oxygen.

Thus, 1 cc. of a 5-volume solution yields 5 cc. of oxygen; a 10-volume solution is one of which 1 cc. will yield 10 cc. of oxygen; etc.

Many solutions of hydrogen dioxide are sent into the market under false pretences, being labelled as containing 10, 15, or 20 volumes of oxygen.

It is true a given volume of these solutions will yield the specified volume of oxygen when decomposed with potassium permanganate, but half of this oxygen comes from the permanganate itself. Therefore the peroxide of hydrogen solution contains only half as much available oxygen as is given off in this decomposition.

Freshly bought samples of the five largest manufac-

turers, according to the analyses of Dr. Edward R. Squibb (*Ephemeris*, vol. IV. No. 2), gave 9.2, 8.7, 8.4, 10.9. 9.7, 8.6, 8.5, 7.3, and 7.4 volumes. All of these were labelled as being of 15 volumes strength. The author has had a similar experience.

In its purest and most concentrated form peroxide of hydrogen is a syrupy colorless liquid, having an odor resembling that of chlorine or ozone.

One cc. of this concentrated hydrogen peroxide when decomposed at 0° C. evolves 330.3 times its own volume of oxygen, at a pressure of 760 mm. at 45° N. latitude.

At a temperature of 100° C. (212° F.) H_2O_2 decomposes rapidly into water and oxygen. This change also takes place at ordinary temperatures, but more slowly. In diluted solutions it is more stable, and may be concentrated by boiling without suffering much decomposition.

Dr. Squibb made a series of experiments in order to prove this, as well as the fact that solutions of hydrogen peroxide when kept in open vessels at the ordinary temperature become stronger, instead of weaker as was generally supposed. The water evaporates more rapidly than the peroxide decomposes. Part of the results of these experiments as published in the *Ephemeris*, vol. IV. No. 2, is as follows:

A freshly made solution that yielded 10.3 volumes of available oxygen was taken as the basis of the experiment. The evaporation was done on a water-bath, at temperatures varying from 55° to 62° C. (131° to 143.6° F.); one cc. of the concentrated solution being taken out for testing after each evaporation.

200 cc. evaporated in 2 hours to 100 cc. tested 20.6 volumes: no apparent loss.

100 cc. of the 10.3-volume solution were added, and evaporated in 2 hours to 100 cc., tested 29.6 volumes: 1.3 volumes loss.

100 cc. of the 10.3-volume solution were added, and evaporated in 2 hours to 100 cc., tested 36.5 volumes: 4.7 volumes loss.

100 cc. of the 10.3-volume solution were added, and evaporated in 2.5 hours to 23 cc., tested 146.8 volumes.

Another series of evaporations were made at higher temperatures, which also showed an increase in strength, but the loss was a little larger.

The Assay of Hydrogen Peroxide, H_2O_2 $= \left\{ \begin{matrix} 33.92 \\ *34 \end{matrix} \right.$.—The U. S. P. method is as follows: 10 cc. of the solution are diluted with water to make 100 cc. Transfer 17 cc. of this liquid (containing 1.7 cc. of the solution of H_2O_2) to a beaker, add 5 cc. of diluted sulphuric acid, and then from a burette $\frac{N}{10}$ potassium permanganate V. S. until the liquid just retains a faint-pink tint after being stirred.

The reaction is expressed by the following equation:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4$$

100)169.6 — 1.696 gms. *100)170. — 1.70

100)315.34 — 3.1534 gms. or 1000 cc. $\frac{N}{10}$ permanganate V. S.

$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Thus each cc. of the $\frac{N}{10}$ potassium permanganate represents .001696 (*.0017) gm. of absolute hydrogen dioxide.

The U. S. P. requires that 1.7 cc. of the solution of peroxide should decolorize 30 cc. of $\frac{N}{10}$ permanganate solution.

This corresponds to 3 per cent. by weight, of H_2O_2.

$$.0017 \times 30 = .051 \text{ gm.}$$

$$\frac{.051 \times 100}{1.7} = 3\%$$

Estimation of Volume Strength.—Let us look at the above equation in a different light.

We there see that when potassium permanganate and hydrogen peroxide react, 10 atoms of oxygen are liberated.

The permanganate itself when decomposed liberates five atoms of oxygen. Therefore of the above ten atoms only five come from the peroxide of hydrogen.

$$5H_2O_2 = 5H_2O + 5O;$$

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

In order to find the factor for volume of available oxygen, see the following equation, etc.:

$$\underset{\substack{100)315.34 \\ 3.1534 \text{ gms. or } 1000 \text{ cc. of } \frac{N}{10} \text{ V. S.}}}{5H_2O_2 + 2KMnO_4 + 3H_2SO_4} = K_2SO_4 + 2MnSO_4 + \underset{\substack{100)79.8 \\ .798 \text{ gm.}}}{8H_2O} + \underset{\substack{100)\ 80 \\ *.80 \text{ gm.}}}{5O} + 5O.$$

Thus it is seen that each cc. of $\frac{N}{10}$ potassium permanganate represents .000798 (*.0008) gm. of oxygen.

But we wish to find the volume of oxygen, not the weight represented by 1 cc. of the $\frac{N}{10}$ permanganate. 1000 cc. of oxygen at 0° C. and 760 mm. pressure weigh 1.424488 grammes, *(1.43 gms.).

Therefore, if 1.43 gms. measure 1000 cc., .0008 gm. will measure x.

$$x = 0.5594 \text{ cc.}$$

$$\frac{1000 \times .0008}{1.43} = 0.5594 \text{ cc.}$$

The factor, then, for volume of oxygen, liberated when peroxide of hydrogen is titrated with $\frac{N}{10}$ potassium permanganate is 0.5594, and the number of cc. of the $\frac{N}{10}$ potassium permanganate consumed in the titration gives the volume of oxygen liberated by the quantity of hydrogen peroxide taken.

Thus if 30 cc. of the $\frac{N}{10}$ V. S. were required,

$$0.5594 \times 30 = 16.782 \text{ cc. of oxygen,}$$

$$1.7)16.782$$

9.87 volume strength.

or the number of cc. of oxygen liberated by 1 cc. of the peroxide solution tested.

It is convenient to operate upon 1 cc. hydrogen-peroxide solution. Then each cc. of potassium per-

manganate V. S. used will represent 0.5594 cc. of available oxygen, or 0.0008 gm. of oxygen, and it is only necessary to multiply the cc. by these numbers to obtain the volume or weight of available oxygen.

Hydrogen-peroxide solution may also be volumetrically assayed by Kingzett's method, which is described in the chapter on Iodimetry.

The gasometric estimation is also described further on.

Barium Dioxide (Barium Peroxide), $BaO_2 = \begin{cases} 168.82 \\ *168.9 \end{cases}$.—This substance is assayed by treating it with an acid, and then estimating the liberated hydrogen dioxide, as follows:

Weigh off 2.11 gms. of the coarse powder, put it in a porcelain capsule, add about 10 cc. of ice-cold water, then 7.5 cc. of phosphoric acid, U. S. P., and sufficient ice-cold water to make 25 cc. Stir and break up the particles with the end of the stirrer until a clear or nearly clear solution is obtained, and all that is soluble is dissolved.

5 cc. of this solution (which corresponds to 0.422 gm. of barium dioxide) is measured off for assay.

Drop into this from a burette, with constant stirring, decinormal potassium permanganate V. S. until a final drop gives the solution a permanent pink tint.

Not less than 40 cc. of the decinormal permanganate V. S. should be required to produce this result.

In this process, the first step is the formation of hydrogen peroxide by treating the barium peroxide with phosphoric acid, as illustrated by the following equation:

$$BaO_2 + H_3PO_4 = BaHPO_4 + H_2O_2.$$

The hydrogen peroxide is then estimated with decinormal permanganate V. S.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4$$

100)169.6 — 1.696 gms.; 100)315.34 — 3.1534 gms. or 1000 cc. $\frac{N}{10}$ permanganate V. S.

100)1.70 — *1.70

$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Thus each cc. of $\frac{N}{10}$ potassium permanganate V. S. represents 0.001696 gm. (*0.0017 gm.) of H_2O_2; and since 169.6 gms. of H_2O_2 are equivalent to 844.1 gms. of BaO_2, $\left(\underset{844.1 \text{ gms.}}{5BaO_2} = \underset{169.6 \text{ gms.}}{5H_2O_2}\right)$, 1 cc. of the $\frac{N}{10}$ permanganate solution corresponds to 0.008441 gm. of BaO_2.

Not less than 40 cc. of the decinormal solution should be required.

Thus $.008441 \times 40 = 0.3376$ gm.

$$\frac{.3376 \times 100}{.422} = 80\% \text{ of pure } BaO_2.$$

Oxalic Acid, $H_2C_2O_4 + 2H_2O = \left\{ \begin{matrix} 125.7. \\ *126 \end{matrix} \right.$ — Oxalic acid may be estimated either by neutralization with an alkaline V. S., or by oxidation with potassium permanganate V. S.

The permanganate is generally used when the acid is in combination as oxalate.

The reaction is illustrated as follows:

$$5(H_2C_2O_4 + 2H_2O) + 3H_2SO_4 + 2KMnO_4$$

100)628.5
6.285 gms.

100)315.34
3.1534 gms. or 1000 cc. $\frac{N}{10}$ permanganate V. S.

$$= K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2.$$

Thus each cc. of the $\frac{N}{10}$ permanganate represents 0.006285 gm. of pure oxalic acid (crystallized).

Note.—It must be remembered, in titrating with permanganate, that an excess of sulphuric acid is always necessary, in order to keep the resulting manganous compound in solution, by forming a soluble manganous sulphate.

If hydrochloric acid is used the solution must be very dilute, and the temperature not raised too high, otherwise chlorine will be liberated, which will spoil the analysis.

It should be borne in mind that the solution of potassium permanganate should not be filtered through paper, as it is decomposed by organic matter. It may, however, be filtered through gun-cotton or glass-wool. It should never be used in a Mohr's burette.

TABLE OF SUBSTANCES WHICH MAY BE ESTIMATED BY OXIDATION, BY POTASSIUM DICHROMATE OR POTASSIUM PERMANGANATE, SHOWING FORMULA, MOLECULAR WEIGHT, FACTOR, ETC.

Name of Substance.	Formula.	Molecular Wt.	$\frac{N}{10}$ V. S. Used.	Factor (exact).
Ac. hypophosphorous	HPH_2O_2	65.88	$2KMnO_4$*	.001647
Ac. oxalic (crystallized)	$H_2C_2O_4+2H_2O$	125.7	$2KMnO_4$	.006285
Barium dioxide	BaO_2	168.82	$2KMnO_4$	.008441
Calcium hypophosphite	$Ca(PH_2O_2)_2$	169.67	$2KMnO_4$*	.0021209
Ferric hypophosphite	$Fe_2(PH_2O_2)_6$	501.04	$2KMnO_4$*	.0020877
Ferrous carbonate	$FeCO_3$	115.64	$K_2Cr_2O_7$ / $2KMnO_4$	.011573
Ferrous oxide	FeO	71.84	$K_2Cr_2O_7$ / $2KMnO_4$	.007195
Ferrous sulphate (anhydrous)	$FeSO_4$	151.58	$K_2Cr_2O_7$ / $2KMnO_4$	.015170
Ferrous sulphate (dried)	$2FeSO_4+3H_2O$	357.28	$K_2Cr_2O_7$ / $2KMnO_4$	.017864
Ferrous sulphate (crystallized)	$FeSO_4+7H_2O$	277.42	$K_2Cr_2O_7$ / $2KMnO_4$	.027742
Ferrum (metallic)	Fe_2	111.76	$K_2Cr_2O_7$ / $2KMnO_4$	.005588
Hydrogen dioxide	H_2O_2	33.92	$2KMnO_4$	.001696
Oxygen, wt. of available, in H_2O_2	O_2	31 92	$2KMnO_4$	.000798
" volume " " "	O_2		$2KMnO_4$	.5594
Potassium hypophosphite	KPH_2O_2	103 91	$2KMnO_4$*	.002598
Sodium hypophosphite	$NaPH_2O_2+H_2O$	105.84	$2KMnO_4$*	.002646

* Determined by residual titration with decinormal oxalic acid V. S.

The factors given in this table are calculated upon the revised atomic weights, which are indorsed by the U. S. P.

CHAPTER XIII.

ANALYSIS BY INDIRECT OXIDATION.

THIS method of analysis is based upon the oxidizing power of iodine.

Iodine acts upon the elements of water, forming hydriodic acid with the hydrogen, and liberating oxygen in a nascent state.

Nascent oxygen is a very active agent, and readily combines with and oxidizes many substances, such as arsenous oxide, sulphurous acid, sulphites, thiosulphates, etc.

$$As_2O_3 + 2H_2O + 2I_2 = 4HI + As_2O_5;$$
$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4.$$

Therefore iodine is said to be an indirect oxidizer, and may be used for the estimation of a great variety of substances, with extreme accuracy.

The end of the reaction in an analysis by this method is ascertained by the use of starch test solution, which produces, with the slightest trace of free iodine, a distinct blue color.

In making an analysis with standard iodine solution, the substance under examination is brought into dilute solution, the starch solution added, and then the iodine, in the form of a decinormal solution, is delivered in from a burette, stirring or shaking constantly, until a final

drop colors the solution blue—a sign that a slight excess of iodine has been added.

Decinormal Iodine V. S., I $= \left\{ \frac{126.53}{*126.5} \cdot \frac{12.653}{*12.65} \right\}$ in 1 litre.—12.653 gms. of pure iodine are dissolved in 300 cc. of distilled water containing 18 gms. of pure potassium iodide. Then enough water is added to make the solution measure, at 15° C. (59° F.), exactly 1000 cc. The solution should be kept in small glass-stoppered vials, in a dark place.

The potassium iodide used in this solution acts merely as a solvent for the iodine.

If pure iodine be not at hand, it may be prepared from the commercial article as follows:

Powder the iodine and heat it in a porcelain dish placed over a water-bath, stirring constantly with a glass rod for 20 minutes. Any adhering moisture, together with any cyanogen iodide, and most of the iodine bromide and iodine chloride, is thus vaporized.

Then triturate the iodine with about 5 per cent. of its weight of pure, dry potassium iodide. The iodine bromide and chloride are thereby decomposed, potassium bromide and chloride being formed, and iodine liberated from the potassium iodide.

The mixture is then returned to the porcelain dish, covered with a clean glass funnel, and heated on a sand-bath. A pure resublimed iodine is then obtained.

If pure iodine is used in making this solution, there is no necessity for checking (standardizing) it.

But if desired, the solution may be checked against pure arsenous acid or pure sodium thiosulphate.

ESTIMATION OF ARSENOUS ACID.

Arsenous Anhydride, Arsenic Trioxide, $As_2O_3 = \left\{ \begin{matrix} 197.68 \\ *198 \end{matrix} \right.$.—When arsenous acid is brought in contact with iodine in the presence of water and an alkali, it is oxidized into arsenic acid, and the iodine is decolorized. The reaction is:

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI;$$
$$NaHCO_3 + HI = NaI + H_2O + CO_2.$$

The alkali should be in sufficient quantity to combine with the hydriodic acid formed, and must be in the form of potassium or sodium bicarbonate.

The hydroxides or carbonates should not be used, as they interfere with the indicator. Starch solution is used as the indicator, a blue color being formed as soon as the arsenous acid is entirely oxidized into arsenic acid.

0.1 gm. of arsenous acid is accurately weighed and dissolved, together with about 1 gm. of sodium bicarbonate, in 20 cc. of water heated to boiling. Allow the liquid to cool, add a few drops of starch T. S., and allow the decinormal iodine V. S. to flow in, shaking or stirring the mixture constantly, until a permanent blue color is produced. The following equation illustrates the reaction:

$$\underset{\substack{4)197.68 \\ 10)\,49.42 \\ 4.942 \text{ gms.}}}{As_2O_3} + 5H_2O + \underset{\substack{4)506 \\ 10)126.5 \\ 12.65 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} \text{ Iodine V. S.}}}{2I_2} = 4HI + 2H_3AsO_4.$$

Thus it is seen that each cc. of the $\frac{N}{10}$ standard solution represents 0.004942 gm. of pure As_2O_3.

If 20 cc. are consumed, then

$$0.004942 \times 20 = 0.09884 \text{ gm.}$$

$$\frac{.09884 \times 100}{.1} = 98.84\%$$

The U. S. P. requirement is 98.8% of As_2O_3. The starch T. S. is not used in the U. S. P. process, and the end of the reaction is known by the iodine being no longer decolorized. But with starch the indication is exceedingly delicate, and it should always be used.

Liquor Acidi Arsenosi, U. S. P.—Measure accurately 10 cc. of the solution, add to it 1 gm. of sodium bicarbonate, and boil for a few minutes. Then allow the liquid to cool, and dilute it to 50 cc. with water. A little starch T. S. is then added and the decinormal iodine V. S. run in from a burette, until a final drop produces the blue color of starch iodide.

Each cc. of $\frac{N}{10}$ I. V. S. represents 0.004942 gm. of As_2O_3. (See Estimation of Arsenous Acid.)

The U. S. P. requirement is that 24.7 cc. of the *liquor acidi arsenosi*, when treated as above, will consume 49.4 to 50 cc. of decinormal iodine V. S. Use 2 gms. of the bicarbonate.

$$0.004942 \times 50 = 0.2471 \text{ gm.}$$

$$\frac{0.2471 \times 100}{24.7} = 1\%$$

Liquor Potassii Arsenitis, U. S. P. (Fowler's Solution).—The process is exactly the same as the foregoing. 24.7 cc., diluted and treated with 2 gms. of sodium bicarbonate, should require 49.4 to 50 cc. of the $\frac{N}{10}$ I. V. S., corresponding to 1% of As_2O_3.

Sulphurous Acid (Acidum Sulphurosum, U. S. P.)—This is an aqueous solution of sulphur dioxide, $SO_2 = \left\{ \begin{matrix} 63.9 \\ *64 \end{matrix} \right.$, containing 6.4 per cent., by weight, of the gas.

Sulphurous acid when brought in contact with iodine is oxidized into sulphuric, the iodine being decolorized because of its union with the hydrogen of the accompanying water, forming hydriodic acid.

Two gms. of sulphurous acid are taken and diluted with distilled water (recently boiled and cooled) to about 25 cc. The decinormal iodine V. S. is then delivered into the solution (to which a little starch T. S. had been previously added) until a permanent blue color is produced. At least 40 cc. of the standard iodine solution should be consumed before this color appears.

The following equations, etc., show the reaction that takes place:

$$\underset{\substack{2)81.86 \\ 10)40.93 \\ 4.093 \text{ gms.}}}{H_2SO_3} + H_2O + \underset{\substack{2)253 \\ 10)126.5 \\ 12.65 \text{ gms. or 1000 cc. } \frac{N}{10} \text{ V. S.}}}{I_2} = 2HI + H_2SO_4.$$

Thus each cc. of the $\frac{N}{10}$ V. S. represents .004093 gm. of pure H_2SO_3.

Sulphurous acid being, however, looked upon as a

solution of SO_2 in water, the quantity of this gas is generally estimated in analysis.

$$\underset{\substack{2)63.9\\10)31.95\\3\ 195\ \text{gms.}}}{H_2O,SO_2} + H_2O + \underset{\substack{2)253\\10)126.5\\12.65\ \text{gms.}}}{I_2} = 2HI + H_2SO_4.$$

Thus each cc. of $\frac{N}{10}$ V. S. consumed before the blue color appears represents 0.003195 gm. of SO_2.

If 40 cc. are consumed in the above analysis, the 2 gms. contain

$$0.003195 \times 40 = 0.1278;$$

then

$$\frac{0.1278 \times 100}{2} = 6.39\% \text{ of } SO_2.$$

The sulphurous acid should be diluted with distilled water to below 0.04 per cent before titrating it; for if it is not sufficiently diluted there is a risk of the sulphuric acid formed, being again reduced to sulphurous, with liberation of iodine, thus causing irregular results.

This may, however, be obviated by adding at once a measured excess of $\frac{N}{10}$ iodine V. S. and titrating back with $\frac{N}{10}$ sodium thiosulphate V. S.

The direction to boil the distilled water is given for the purpose of freeing it from air, which would have a tendency to partially oxidize the sulphurous acid.

Sodium Sulphite, $Na_2SO_3 + 7H_2O = \left\{ \begin{matrix} 251.58 \\ *252 \end{matrix} \right.$.—

One gm. of the salt is dissolved in 25 cc. of distilled

water recently boiled to expel air, a little starch T. S. is added, and then the decinormal iodine V. S. delivered in from a burette, until the blue color of starch iodide appears, which does not disappear upon shaking or stirring.

The reaction is expressed as follows:

$$\underbrace{Na_2SO_3 + 7H_2O}_{\substack{2)251.58 \\ 10)125.79 \\ 12.579 \text{ gms.}}} + \underbrace{I_2}_{\substack{2)253 \\ 10)126.5 \\ 12.65 \text{ gms. or 1000 cc. } \frac{N}{10} \text{ iodine V. S.}}} = 2NaI + H_2SO_4 + 6H_2O.$$

Thus each cc. of the standard solution represents .012579 gm. of crystallized sodium sulphite.

If 1 gm. of the salt is taken, to find the percentage multiply the factor by the number of cc. of standard solution consumed, and the result by 100.

The U. S. P. requirement is 96 per cent. 0.63 gm. of salt should require for complete oxidation 48 cc. of the standard solution. Therefore

$$.012579 \times 48 = .603792 \text{ gm.}$$

$$\frac{0.603792 \times 100}{0.63} = 95.8\%$$

Potassium Sulphite, $K_2SO_3 + 2H_2O = *194.$— Operate upon 0.5 gm. in the same manner as for sodium sulphite.

$$\underbrace{K_2SO_3 + 2H_2O}_{\substack{2)194 \\ 10)\ 97 \\ 9.7 \text{ gms.}}} + \underbrace{I_2}_{\substack{2)253 \\ 10)126.5 \\ 12.65 \text{ gms. or 1000 cc. of standard V. S.}}} = 2KI + H_2SO_4 + H_2O.$$

Each cc. of the decinormal iodine V. S. used represents 0.0097 gm. of crystallized potassium sulphite. If 46 cc. are used, the salt is over 89% strength.

Sodium Bisulphite, $NaHSO_3 = \left\{ \begin{matrix} 103.86 \\ *104 \end{matrix} \right.$.—Dissolve 0.26 gm. of the salt in 20 cc. of distilled water which has been previously boiled to expel air, add a little starch T. S., and pass in the decinormal iodine V. S. from a burette, until a permanent blue color appears. At least 45 cc. should be required.

Apply the following equation:

$$\underset{\substack{2)103.86 \\ 10)\ 51.93 \\ 5.193 \text{ gms.}}}{NaHSO_3} + \underset{\substack{2)253 \\ 10)126.5 \\ 12.65 \text{ gms. or 1000 cc. } \frac{N}{10} \text{ V. S.}}}{I_2} + H_2O = NaI + HI + H_2SO_4.$$

Thus each cc. of decinormal iodine V. S. represents 0.005193 gm. of sodium bisulphite.

$$0.005193 \times 45 = 0.23368 \text{ gm.}$$

$$\frac{0.23368 \times 100}{0.26} = 89.5\%$$

Sodium Thiosulphate (Sodium Hyposulphite), $Na_2S_2O_3 + 5H_2O = \left\{ \begin{matrix} 247.64 \\ *248 \end{matrix} \right.$.—This salt, when brought in contact with iodine, is converted into tetrathionate of sodium, and the iodine is decolorized.

It is estimated as follows: 0.25 gm. of the salt is dissolved in 10 cc. of water, a few drops of starch T. S. are added, and then the $\frac{N}{10}$ iodine V. S. is delivered in from a burette, until the appearance of blue starch iodide indicates an excess of iodine.

At least 9.9 cc. of the standard solution should be added before a final drop produces a permanent blue color.

The reaction is expressed as follows :

$$2(Na_2S_2O_3,5H_2O) + I_2$$

2)495.28 — 2)253

10)247.64 — 10)126.5

24.764 gms. — 12.65 gms. or 1000 cc. $\frac{N}{10}$ I. V. S.

$$= 2NaI + Na_2S_4O_6 + 10H_2O.$$

Thus each cc. represents .024764 gm. of crystallized thiosulphate.

9.9 cc. contain 0.024764 gm. $\times$ 9.9 = .2451636 gm.

$$\frac{0.2451636 \times 100}{0.25} = 98.1\%$$

Iodine may also be used for estimating antimonous compounds. The reaction is similar to that with arsenous compounds ; thus

$$Sb_2O_3 + 2H_2O + 2I_2 = Sb_2O_5 + 4HI.$$

Antimony and Potassium Tartrate (Tartar Emetic), $2(K(SbO)C_4H_4O_6) + H_2O = \left\{ \begin{matrix} 662.42 \\ *664 \end{matrix} \right.$. — This is the only antimonial salt, a process for the volumetric estimation of which is given in the U. S. P.

The U. S. P. directs that 0.331 gm. of the crystallized salt or 0.322 gm. of the salt dried at 110° C. (230° F.) be taken for analysis. The salt is dissolved in 10 cc. of water, and about 20 cc. of a cold saturated solution of sodium bicarbonate and a little starch T. S. added. The decinormal iodine V. S. is then delivered in from a burette, until the blue color of the starch

iodide makes its appearance, indicating that the salt has been completely oxidized and that the iodine solution has been added in slight excess. Not less than 20 cc. of decinormal iodine V. S. should be consumed before the blue color appears.

The reaction is illustrated by the following equation:

$$\underbrace{2(K(SbO)C_4H_4O_6)+H_2O}_{\substack{4)662.42\\10)165.605\\16.5605\text{ gms.}}} + \underbrace{2I_2}_{\substack{4)506.\\10)126.5\\12.65\text{ gms. or 1000 cc. }\frac{N}{10}\text{ I.V.S.}}} + 3H_2O$$

$$= 4HI + 2KHC_4H_4O_6 + 2HSbO_3.$$

Thus each cc. of $\frac{N}{10}$ iodine V. S. represents 0.0165605 gm. of pure *crystallized* tartar emetic.

$2(K(SbO)C_4H_4O_6)$ (anhydrous).

$4)644.46$

$10)161.115$

16.1115 gms. = 12.65 gms. of iodine or 1000 cc. $\frac{N}{10}$ V. S.

Thus each cc. of $\frac{N}{10}$ iodine V. S. represents 0.0161115 gm. of *anhydrous* tartar emetic. Thus

$$20\text{ cc.} = 0.0165605\text{ gm.} \times 20 = .33121\text{ gm.};$$

$$\frac{0.33121 \times 100}{0.331} = 100\%\text{ crystallized salt;}$$

and

$$0.0161115 \times 20 = 0.32223\text{ gm.}$$

$$\frac{0.32223 \times 100}{0.322} = 100\%\text{ anhydrous salt.}$$

The operation should be quickly conducted or a precipitate of antimonous hydrate will be formed, upon which the iodine has little effect. The antimony must be in solution to be properly attacked.

TABLE OF SUBSTANCES ESTIMATED BY IODINE.

Name of Substance.	Formula.	Molecular Weight.	Factor.
Antimony and potassium tartrate	$2(K(SbO)C_4H_4O_6)+H_2O$	662.42	Cryst. .016560 Anhydr. .016111
Arsenic trioxide	As_2O_3	197.68	.004942
Potassium sulphite	$K_2SO_3+2H_2O$	193.84	.009692
Sodium bisulphite	$NaHSO_3$	103.86	.005193
Sodium sulphite	$Na_2SO_3+7H_2O$	251.58	.012579
Sodium thiosulphate (hyposulphite)	$Na_2S_2O_3+5H_2O$	247.64	.024764
Sulphur dioxide	SO_2	63.90	.003195
Sulphurous acid	H_2SO_3	81.86	.004093

CHAPTER XIV.

ESTIMATION OF SUBSTANCES READILY REDUCED.

ANY substance which readily yields oxygen in a definite quantity, or is susceptible of an equivalent action, which involves its reduction to a lower quantivalence, may be quantitatively tested, by ascertaining how much of a reducing agent of known power is required by a given quantity of the substance for its complete reduction.

The principal reducing agents which may be employed in volumetric analysis are *sodium thiosulphate*, sulphurous acid, arsenous acid, oxalic acid, metallic zinc, and magnesium.

The sodium thiosulphate is the only one which is employed officially in the U. S. P. in the form of a volumetric solution. It is used in the estimation of free iodine, and indirectly of other free halogens, or compounds in which the halogen is easily liberated, as in the hypochlorites, etc.

This method of analysis is called *Iodometry*.

It depends upon the fact that iodine is an indirect oxidizer, as shown by its action upon water, the hydrogen of which it abstracts, forming hydriodic acid, thus liberating the oxygen in a nascent state.

When sodium thiosulphate acts upon iodine, sodium tetrathionate and sodium iodide are formed, and the solution is decolorized.

This reaction takes place in definite proportions: one molecular weight of the thiosulphate, absorbs one atomic weight of iodine.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Chlorine cannot be directly titrated with the thiosulphate, but by adding to the solution containing free chlorine an excess of potassium iodide, the iodine is liberated in exact proportion to the quantity of chlorine present, atom for atom.

$$Cl_2 + 2KI = 2KCl + I_2.$$

Then by estimating the iodine, the quantity of chlorine is ascertained. All bodies which contain available chlorine, or which when treated with hydrochloric acid evolve chlorine, may be estimated by this method.

Also, bodies which contain *available oxygen*, and which when boiled with hydrochloric acid evolve chlorine, such as *manganates*, *chromates*, *peroxides*, etc., may be estimated in this way.

Solutions of *ferric salts*, when acidulated and boiled with an excess of potassium iodide, liberate iodine in exact proportion to the quantity of ferric iron present.

Thus sodium thiosulphate may be used in the estimation of a great variety of substances with extreme accuracy.

Preparation of Decinormal Sodium Thiosluphate (Hyposulphite), $Na_2S_2O_3 + 5H_2O = \left\{ \begin{matrix} 247.64 \\ *248 \end{matrix} \right.$ contains $\left. \begin{matrix} 24.746 \\ *24.8 \end{matrix} \right\}$ gms. in 1 litre.—Sodium thiosulphate is a salt of thiosulphuric acid in which two atoms of hydrogen have been replaced by sodium; it therefore seems that a

normal solution of this salt should contain one half the molecular weight in grammes in one litre.

But this salt is used chiefly for the estimation of iodine, and, as stated before, one full molecular weight reacts with and decolorizes one atomic weight of iodine; and since one atom of iodine is chemically equivalent to one atom of hydrogen, a full molecular weight of sodium thiosulphate, must be contained in a litre of its normal solution.

Sodium thiosulphate is easily obtained in a pure state, and therefore the proper weight of the salt, reduced to powder and dried between sheets of blotting-paper, may be dissolved directly in water, and made up to one litre.

The U. S. P. directs that a stronger solution than necessary be made, its titer found by iodine, and then the solution diluted to the proper measure.

30 gms. of selected crystals of the salt are dissolved in enough water to make, at or near 15° C. (59° F.) 1100 cc.

Transfer 10 cc. of this solution into a flask or beaker, add a few drops of starch T. S., and then gradually deliver into it from a burette decinormal iodine solu-solution, in small portions at a time, shaking the flask after each addition, and regulating the flow to drops toward the end of the operation. As soon as a blue color is produced which does not disappear upon shaking, but is not deeper than pale blue, the reaction is completed. Note the number of cc. of iodine solution used, and then dilute the thiosulphate solution so that equal volumes of it and the decinormal iodine V. S. will exactly correspond to each other, under the above-mentioned conditions.

Example.—The 10 cc. of sodium thiosulphate, we will assume, require 10.7 cc. of decinormal iodine V. S.

The sodium-thiosulphate solution must then be diluted in the proportion of 10 cc. to 10.7 cc., or 1000 cc. to 1070 cc.

After the solution is thus diluted a new trial should be made, in the manner above described, in which 50 cc. of the thiosulphate solution should require exactly 50 cc. of the decinormal iodine V. S. to produce a faint-blue color.

The solution should be kept in small dark amber-colored, glass-stoppered bottles, carefully protected from dust and air.

One cc. of this solution is the equivalent of:

Iodine.....	0.012653 gramme.
Bromine.....	0.007976 "
Chlorine.....	0.003537 "
Iron in ferric salts.....	0.005588 "

Iodine, $I = \left\{ \begin{matrix} 126.53 \\ *126.5 \end{matrix} \right.$.—Dissolve 0.32 gm. of iodine in 20 cc. of water, in a beaker or flask, with the aid of 1 gm. of potassium iodide; the solution is mixed with a few drops of starch T. S., and then the decinormal sodium thiosulphate V. S. gradually delivered in from a burette, in small portions at a time, shaking the flask after each addition, and regulating the flow to drops toward the end of the reaction, until a final drop just discharges the blue color.

Note the number of cc. of decinormal sodium thiosulphate V. S. consumed, and multiply this number by the factor for iodine.

$$2(Na_2S_2O_3 + 5H_2O) + I_2 = Na_2S_4O_6 + 2NaI + 10H_2O.$$

$2)496$, $10)248$, 24.8 gms. or 1000 cc. $\frac{N}{10}$ V. S.

$2)253$, $10)126.5$, 12.65 gms.

Thus the factor for iodine, that is, the quantity equivalent to 1 cc. of $\frac{N}{10}$ thiosulphate V. S., is 0.01265 gm.

0.32 gm. of iodine, which answers to the tests of the U. S. P., requires at least 25 cc. of the $\frac{N}{10}$ V. S.

$$0.01265 \times 25 = 0.31625 \text{ gm.}$$

$$\frac{.31625 \times 100}{.32} = 98.8\% \text{ pure iodine.}$$

Liquor Iodi Compositus (Lugol's Solution).—This is an aqueous solution of iodine and potassium iodide.

It is estimated for iodine in the same way as the foregoing. The potassium iodide acts merely as a solvent for free iodine, and does not enter into the reaction.

10 or 12 gms. of the solution is a convenient quantity to operate upon. Starch T. S. is the indicator.

The U. S. P. states that 12.66 gms. of the solution should require for complete decoloration from 49.3 to 50 cc. of decinormal sodium thiosulphate V. S.

As shown by the above equation, each cc. of the $\frac{N}{10}$ V. S. represents 0.01265 gm. of pure iodine. Therefore 50 cc. represent $0.01265 \times 50 = .6325$ gm.

$$\frac{.6325 \times 100}{12.66} = 5\% \text{ pure iodine, about.}$$

Tinctura Iodi (Tincture of Iodine).—This is an alcoholic solution of free iodine, and must be diluted with a solution of potassium iodide, before titration, in order to provide sufficient liquid to keep the resulting salts in solution.

Aqua Chlori (Chlorine Water).—This is an aqueous solution of chlorine, $Cl = \left\{ \begin{matrix} 35{\cdot}37 \\ *35{\cdot}4 \end{matrix} \right.$, containing at least 0.4% of the gas.

The estimation of chlorine is effected in an indirect way, namely, by determining the quantity of iodine which it liberates from potassium iodide.

A definite quantity of chlorine will liberate a definite quantity of iodine from an iodide; these quantities are in exact proportion to their atomic weights, as the equation shows:

$$2KI + Cl_2 = 2KCl + I_2$$

2)70.74	2)253
10)35.37	10)126.5
3.537 gms.	12.65 gms.

Thus it is seen that by estimating the liberated iodine the quantity of chlorine may be determined with accuracy.

Ten gms. is a convenient quantity to operate upon. To this about half a gramme of potassium iodide is added. A little starch T. S. is then introduced, and the titration is begun, with decinormal sodium thiosulphate V. S.

When the blue color of starch iodide has entirely disappeared the reaction is finished.

The reaction between iodine and sodium thiosulphate is illustrated by the following equation:

$$I_2 + 2(Na_2S_2O_3 + 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

2)253 2)496
10)126.5 10)248
12.65 gms. 24.8 gms. or 1000 cc. $\frac{N}{10}$ V. S.

Thus we see that 1000 cc. of $\frac{N}{10}$ $Na_2S_2O_3.5H_2O$ represent 12.65 gms. of iodine, which are equivalent to 3.537 gms. of chlorine.

Each cc. therefore is equivalent to .003537 gm. of chlorine. This number is the factor which, when multiplied by the number of cc. of $\frac{N}{10}$ thiosulphate V. S. used, gives the weight in grammes of chlorine, contained in the quantity of chlorine water acted upon.

The U. S. P. requirement is that 17.7 gms. of chlorine water, when mixed with 1 gm. of potassium iodide dissolved in 10 cc. of water, and titrated with $\frac{N}{10}$ sodium thiosulphate V. S. should consume not less than 20 cc. of the latter in decolorizing the solution.

$$.003537 \times 20 = .07074 \text{ gm.}$$

$$\frac{.07074 \times 100}{17.7} = 0.4\% \text{ of chlorine.}$$

Chlorinated Lime (Calx Chlorata, Chloride of Lime, Bleaching-powder).—This substance was formerly supposed to be a compound of lime and chlorine, $CaOCl_2$, and hence the name chloride of lime. It is now generally considered to be a mixture of calcium chloride and

calcium hypochlorite, $CaCl_2 + Ca(ClO)_2$, or $2(CaOCl_2)$. The hypochlorite is the active constituent. This is a very unstable salt, and is readily decomposed even by carbonic acid. When treated with hydrochloric acid it gives off chlorine.

The value of chlorinated lime as a bleaching or disinfecting agent depends upon its available chlorine, that is, the chlorine which the hypochlorite yields when treated with an acid.

In estimating the available chlorine, the latter is liberated with hydrochloric acid. This liberated gas, then, acting upon potassium iodide, sets free an equivalent amount of iodine. The quantity of iodine is then determined, and thus the amount of available chlorine found. .1 to .2 gm. is a convenient quantity to operate upon.

The U. S. P. directs to weigh off *0.35 (0.354) gm. of chlorinated lime. This is to be thoroughly triturated with 50 cc. of water and carefully transferred, together with the washings into a flask. 0.8 gm. or more of potassium iodide and 5 cc. of diluted hydrochloric acid are then added, and into the resulting reddish-brown liquid, the $\frac{N}{10}$ sodium thiosulphate V. S. is delivered from a burette. Towards the end of the titration, when the brownish color of the liquid is very faint, a few drops of starch T. S. are added and the titration continued until the bluish or greenish color produced by the starch has entirely disappeared. Not less than 35 cc. of the volumetric solution should be required to produce this result.

The reactions which take place in this process are illustrated by the following equations:

$$\underbrace{CaCl_2,Ca(ClO)_2}\ + 4HCl = 2CaCl_2 + 2H_2O + 2Cl_2$$

$$2Cl_2 + 4KI = 4KCl + 2I_2.$$

4)141.48 — 4)506
10) 35.37 — 10)126.5
3.537 gms. — 12.65 gms.

$$2I_2 + 4(Na_2S_2O_3 + 5H_2O) = 4NaI + 2Na_2S_4O_6 + 20H_2O.$$

40)506 — 40)496
12.65 gms. — 24.8 gms. or 1000 cc. $\frac{N}{10}$ thiosulphate V. S.

We thus see that 1 cc. of the decinormal volumetric solution represents 0.01265 gm. of iodine, which is equivalent to 0.003537 gm. of available chlorine. Then

$$0.003537 \times 35 = 0.12379 \text{ gm.}$$

$$\frac{0.12379 \times 100}{.35} = 35\% \text{ of available chlorine.}$$

This is a very rapid method for estimating chlorine; but when calcium chlorate is present in the bleaching-powder (and it often is, through imperfect manufacture) the chlorine from it, is recorded, as well as that from the hypochlorite, the chlorate being decomposed into chlorine, etc., by hydrochloric acid. The chlorate, however, is of no value in bleaching; its chlorine is not available. Hence, unless the powder is known to be free from chlorate, the analysis should be made by means of arsenous-acid solution.

The Arsenous-acid Process. — 0.35 gm. of the bleaching-powder is rubbed to a smooth paste with 50 cc. of water, as described above. A measured excess of decinormal arsenous acid V. S. is then added; this

is followed by a little starch T. S., and then decinormal iodine V. S. added until the blue color appears. Deduct the number of cc. of the standard iodine solution used from those of standard arsenous-acid solution, and the quantity of the latter which went into combination is found.

Each cc. of $\frac{N}{10}$ As_2O_3 V. S. represents .003537 gm. of available chlorine.

$$2CaOCl_2 + As_2O_3 = As_2O_5 + 2CaCl_2$$

$$4)141.48 \qquad 4)198$$

$$10)\ 35.37 \qquad 10)\ 49.5$$

3.537 gms. 4.95 gms. or 1000 cc. $\frac{N}{10}$ V. S.

Decinormal Arsenous-acid Solution is made by dissolving 4.95 gms. of the purest sublimed arsenous anhydride (As_2O_3) in about 250 cc. of distilled water with the aid of about 20 gms. of pure potassium bicarbonate. The acid should be in fine powder, and the mixture warmed, to effect complete solution.

The solution is checked with decinormal iodine V. S., using starch as indicator.

Decinormal arsenous-acid solution and decinormal iodine solution should correspond, volume for volume.

The strength of bleaching powder is expressed in per cent of available chlorine, or in degrees (Gay-Lussac). The latter represents the number of litres of chlorine, at 0° C. and 760 mm. pressure, available from one kilogramme of the bleaching powder. The relation between these two methods is shown in the table following:

Degrees. Gay-Lussac.	Per Cent Chlorine.	Degrees. Gay-Lussac.	Per Cent Chlorine.	Degrees. Gay-Lussac.	Per Cent Chlorine.
65	20.65	80	25.42	95	30.19
66	20.97	81	25.74	96	30.51
67	21.29	82	26.06	97	30.82
68	21.61	83	26.37	98	31.14
69	21.93	84	26.69	99	31.46
70	22.24	85	27.01	100	31.78
71	22.56	86	27.33	101	31.09
72	22.88	87	27.65	102	31.41
73	23.20	88	27.96	103	32.73
74	23.51	89	28.28	104	33.05
75	23.83	90	28.60	105	33.36
76	24.15	91	28.92	106	33.68
77	24.47	92	29.33	107	34.00
78	24.79	93	29.55	108	34.32
79	25.10	94	29.87	109	34.64

The various bleaching preparations of the market which depend upon their available chlorine are all salts of hypochlorous acid (HClO) or solutions of such salts.

Eau de Javelle, *Javelle's Water*, is a solution of potassium hypochlorite and potassium chloride. A solution of magnesium hypochlorite is known in commerce as *Ramsay's* or *Grouvelle's Bleaching Fluid.* The solution known as *Wilson's Bleaching Fluid* contains aluminium hypochlorite.

Liquor Sodæ Chloratæ (Solution of Chlorinated Soda; Labarraque's Solution).—This is an aqueous solution of several chlorine compounds of sodium, principally sodium chloride and hypochlorite, containing at least 2.6% of available chlorine.

In this solution, as in chlorinated lime, it is the available chlorine which is estimated. The chlorine is first liberated with hydrochloric or sulphuric acid; this then liberates iodine from potassium iodide, and the

free iodine is then determined by standard solution of thiosulphate.

*6.7 (6.74) gms. of chlorinated soda solution are mixed with 50 cc. of water, 2 gms. of potassium iodide, and 10 cc. of hydrochloric acid, together with a few drops of starch T. S. Then pass into the mixture from a burette sufficient decinormal sodium thiosulphate V. S. to just discharge the blue or greenish tint of the liquid.

The reaction is illustrated by the following equation. Hydrochloric acid liberates chlorine from the salts in the solution:

$$\underset{70.74}{NaCl,NaClO} + 2HCl = 2NaCl + H_2O + \underset{70.74}{Cl_2}.$$

The chlorine then liberates iodine from potassium iodide:

$$\underset{20)70.74}{\underset{3.537}{Cl_2}} + 2KI = 2KCl + \underset{20)253}{\underset{12.65}{I_2}}.$$

The iodine is then determined by sodium thiosulphate V. S.:

$$\underset{2)253}{\underset{10)126.5}{\underset{12.65\text{ gms.}}{I_2}}} + 2(\underset{2)496}{\underset{10)248}{\underset{24.8\text{ gms. or 1000 cc. } \frac{N}{10}\text{ V. S.}}{Na_2S_2O_3}}} + 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Thus each cc. of standard solution represents .01265 gm. of iodine, which is equivalent to .063537 gm. of available chlorine.

In practice the potassium iodide should always be added before the hydrochloric acid is, so that the

chlorine has potassium iodide to act upon, as soon as it is itself liberated, and thus any loss of chlorine is obviated.

In the pharmacopœial test above given not less than 50 cc. of the $\frac{N}{10}$ V. S. should be required.

$$0.003537 \times 50 = 0.17785 \text{ gm.}$$

$$\frac{0.17785 \times 100}{6.7} = 2.65\% \text{ available Cl.}$$

Instead of weighing off the U. S. P. quantity, any other convenient weight may be taken.

ESTIMATION OF FERRIC SALTS.

When a ferric salt in an acidulated solution is digested with an excess of potassium iodide the salt is reduced to the ferrous state, and iodine is set free.

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

One atom of iodine is liberated for each atom of iron in the ferric state. The liberated iodine is then determined by sodium thiosulphate, in the usual way. 12.65 gms. of iodine = 5.6 gms. of metallic iron.

This is the method of the U. S. P.; it is given in detail here.

*0.56 (0.5588) gm. of the salt is dissolved in 10 or 15 cc. of water and 2 cc. of hydrochloric acid in a glass-stoppered bottle having a capacity of about 100 cc. 1 gm. of potassium iodide is then added, and the mixture digested for half an hour at a temperature of 40° C. (104° F.). During the digestion the stopper should be

left in the bottle, and the heat not allowed to rise too high, otherwise the liberated iodine will be volatilized. When cool a few drops of starch T. S. are added. It is now ready for titrating with $\frac{N}{10}$ sodium thiosulphate. Each cc. corresponds to 1 per cent. of metallic iron.

When the quantity of metallic iron and the chemical formula for the ferric salt under estimation are known, the quantity of pure salt is easily found by calculation.

In all the estimations of ferric iron it is convenient to take 0.56 gm. of the salt. Each cc. of the volumetric solution used will then represent 1% of metallic iron. assuming the atomic weight of iron to be 56.

Ferric salts may be tested in many other ways; for instance:

A ferric salt in solution may be filtered through a column of zinc dust, which reduces it to the ferrous state. This is then estimated with potassium permanganate V. S. in the usual method, or the ferric solution is treated with a few small pieces of zinc or magnesium coarsely powdered, until complete reduction is effected. When a red color is no longer produced by sulphocyanate of potassium the ferric salt is completely reduced, and may be estimated with potassium permanganate V. S.

Stannous chloride, ammonium bisulphite, and other substances may also be used as reducing agents.

Ferric Chloride, $Fe_2Cl_6 + 12H_2O = \begin{cases} 539.5 \\ *540.4 \end{cases}$.— *0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of about 100 cc.) in 10 cc. of water and 2 cc. of hydrochloric acid, and

after the addition of 1 gm. of potassium iodide, is kept for half an hour at a temperature of 40° C. (104° F.), then cooled, mixed with a few drops of starch T. S., and titrated with decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid is discharged. Each cc. represents *0.0056 gm. or 1% of metallic iron, or 0.026975 gm. of pure ferric chloride.

The following equations illustrate the reactions:

$$\underbrace{Fe_2Cl_6 + 12H_2O}_{20)539.5 \text{ — } 26.975 \text{ gms.}} + 2KI = 2FeCl_2 + 2KCl + \underset{20)253 \text{ — } 12.65 \text{ gms.}}{I_2} + 12H_2O.$$

Then

$$\underset{20)253 \text{ — } 12.65 \text{ gms.}}{I_2} + \underset{20)496 \text{ — } 24.8 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} \text{ V. S.}}{2(Na_2S_2O_3 + 5H_2O)} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

20 cc. of the $\frac{N}{10}$ V. S. should be required, which represents 20% of metallic iron, or 96.34% of pure ferric chloride (crystallized):

$$0.026975 \times 20 = 0.5395 \text{ gm.}$$

$$\frac{0.5395 \times 100}{0.56} = 93.34\%$$

Liquor Ferri Chloridi (Solution of Ferric Chloride). —This is an aqueous solution of ferric chloride, $Fe_2Cl_6 = \begin{cases} 323.98 \\ *324.4 \end{cases}$, containing about 37.8 per cent. of the anhydrous salt or about 13 per cent. of metallic iron.

0.56 (or .5588) gm. of the solution is introduced into a glass-stoppered bottle (having a capacity of about 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept for half an hour at 40° C. (104° F.), then cooled, and mixed with a few drops of starch T. S. and titrated with $\frac{N}{10}$ sodium thiosulphate V. S. until the blue or greenish color of the liquid is discharged. 0.56 gm. of the solution having been taken, each cc. of the standard solution represents 1 per cent. and 13 cc. should be required. If 1.12 gms. are taken, as the U. S. P. directs, each cc. represents 0.5 per cent. and 26 cc. should be required. The reactions are the same as in ferric chloride, each cc. representing 0.026975 gm. of crystallized ferric chloride, or 0.016199 gm. of anhydrous ferric chloride, or .0056 gm. of metallic iron. To find percentage: Multiply by number of cc. used, then multiply the result by 100 and divide by the quantity of solution taken.

Tinctura Ferri Chloridi (Tincture of Ferric Chloride).—A hydro-alcoholic solution of ferric chloride, $Fe_2Cl_6 = \begin{cases} 323.98 \\ *324.4 \end{cases}$, containing about 13.6 per cent. of anhydrous ferric chloride, and corresponding to about 4.7 (4.69) per cent. of metallic iron.

To estimate this tincture follow the directions given for *liquor ferri chloridi.*

Ferric Citrate, $Fe_2(C_6H_5O_7)_2 = \begin{cases} 488.48 \\ *490 \end{cases}$.—*0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid, with the aid of gentle heat. 1 gm. of potassium iodide is then added,

and the mixture kept for half an hour at a temperature of 40° C. (104° F.). It is then cooled, and a few drops of starch T. S. added. The decinormal sodium thiosulphate V. S. is then delivered in from a burette, until the blue or greenish color of the liquid just disappears. Each cc. of the decinormal solution represents 1 per cent. or 0.0056 gm. of metallic iron, corresponding to 0.024424 gm. of ferric citrate.

$$3Fe_2(C_6H_8O_7)_2 + 6KI = 2Fe_3(C_6H_5O_7)_2 + 2K_3C_6H_5O_7 + 3I_2.$$

Ferric citrate. Ferrous citrate.

$3Fe_2$ 488.48 6)759

6)335.28 3 10)126.5

10) 55.88 6)1465.44 12.65 gms.

5.588 gms. 10) 244.24

(*5.6 gms.) 24.424 gms.

$$I_2 + 2(Na_2S_2O_3, 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

2)253 2)496

10)126.5 10)248

12.65 gms. 24.8 gms. or 1000 cc. $\frac{N}{10}$ sodium thiosulphate.

Thus each cc. represents 0.01265 gm. of iodine, which corresponds to 0.024424 gm. of ferric citrate or *0.0056 gm. metallic iron.

$$16 \text{ cc.} = 16 \times 0.0056 = .0896 \text{ gm. metallic iron.}$$

$$\frac{.0896 \times 100}{0.56} = 16\%$$

$$16 \times 0.024424 = 0.390784 \text{ gm. ferric citrate.}$$

$$\frac{0.390784 \times 100}{0.56} = 69.9\%$$

Liquor Ferri Citratis (Solution of Ferric Citrate). —This is an aqueous solution of ferric citrate, corresponding to about 7.5 per cent. of metallic iron.

*0.56 (0.5588) gm. of the solution is introduced into a glass-stoppered bottle (having a capacity of about 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour; it is then cooled and mixed with a few drops of starch T. S., and decinormal thiosulphate V. S. delivered in from a burette until the blue or greenish color of the liquid is discharged. Each cc. of the volumetric solution indicates 1% of metallic iron. If *1.12 (1.1176) gms. of the liquor are taken, as the U. S. P. directs, each cc. of the V. S. used represents 0.5% of metallic iron.

Iron and Ammonium Citrate (Ferri et Ammonii Citras).—The precise chemical constitution of this preparation is not determined. Therefore the metallic iron only is estimated, of which it should contain 16 per cent.

Ammonio-ferric Tartrate (Ferri et Ammonii Tartras).—The exact chemical composition of this compound is not known. It is, theoretically, $2(FeO)\text{-}NH_4C_4H_4O_6.3H_2O$). It should contain 17 per cent. of metallic iron.

Potassio-ferric Tartrate (Ferri et Potassii Tartras).—There is some difference of opinion as to the composition of this salt. It is probably a double salt, consisting of one molecule of ferric tartrate, $Fe_2(C_4H_4O_6)_3$ and one of potassium tartrate, $K_2C_4H_4O_6$, with one of H_2O. It should contain 15 per cent. of metallic iron.

Soluble Ferric Phosphate (Ferri Phosphas Solubilis).—This salt is called soluble ferric phosphate in order to distinguish it from the true ferric phosphate. It is not a definite chemical compound, but a mixture

of citrate and phosphate of sodium and iron It should contain 12 per cent of metallic iron.

The foregoing four salts being of indefinite chemical composition, are tested for metallic iron only, as follows:

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept at 40° C. (104° F.) for half an hour, then cooled, a few drops of starch T. S. added, and decinormal sodium thiosulphate V. S. delivered in slowly from a burette until the blue or greenish color of the liquid is completely discharged. Each cc. of $\frac{N}{10}$ V. S. represents 1 per cent. of metallic iron, if 0.56 (0.5588) gm. of the salt is taken.

Iron and Quinine Citrate (Ferri et Quininæ Citras).—The U. S. P. gives an assay process for quinine and one for iron to be applied to this salt.

ESTIMATION OF THE QUININE.

1.12 (1.1176) gms. of the salt are dissolved in a capsule in 20 cc. of water, with the aid of gentle heat.

The solution is poured into a separator, the capsule is rinsed with a little water, and the rinsings added to the liquid in the separator; when this has become cool, add 5 cc. of ammonia water and 10 cc. of chloroform, and shake. Allow the liquids to separate, draw off the chloroformic layer, and add to the residual liquid a second and a third portion of 10 cc. of chloroform added, shaking after each addition, and drawing off the chloroformic solution. The combined chloroformic

solutions are evaporated spontaneously in a tared capsule, and the residue dried at 100° C. (212° F.) to a constant weight. It should weigh not less than 0.1288 gm.

$$\frac{0.1288 \times 100}{1.1176} = 11.5\% \text{ of dried quinine.}$$

In the above assay the ammonia water precipitates the quinine and the chloroform dissolves it. Then by evaporating the chloroformic solution the quinine is obtained.

ESTIMATION OF THE IRON.

The aqueous liquid from which the quinine has been removed, as above described, is heated on a water-bath until the odor of chloroform and ammonia has disappeared; allow the liquid to cool, and dilute it with water to the volume of 50 cc. Take 25 cc. of this, put it in a glass-stoppered bottle (having a capacity of 100 cc.), add 2 cc. of hydrochloric acid and 1 gm. of potassium iodide, and digest at 40° C. (104° F.) for half an hour. Allow it to cool, add a few drops of starch T. S. and titrate with decinormal sodium thiosulphate V. S. until the blue or greenish color is discharged.

Each cc. of the volumetric solution represents 0.0056 (.005588) gm. of metallic iron, or 1 per cent. 14.5 cc. should be required.

$$0.0056 \times 14.5 = 0.0812 \text{ gm.}$$

$$\frac{0.0812 \times 100}{0.56} = 14.5\%$$

Soluble Citrate of Iron and Quinine (Ferri et Quininæ Citras Solubilis).—This salt is assayed for

quinine and iron in the manner above described under *Ferri et Quininæ Citras*, and should respond to the requirements for the latter.

Iron and Strychnine Citrate (Ferri et Strychninæ Citras).—This salt should be tested quantitatively for strychnine and iron.

ESTIMATION OF THE STRYCHNINE.

*2.24 (2.2352) gms. of the salt are dissolved in a separator in 15 cc. of water, 5 cc. of ammonia water are then added and 10 cc. of chloroform, and the mixture shaken. Set aside so as to allow the liquids to separate, draw off the chloroformic layer, add a second and a third portion of 10 cc. of chloroform, shaking each time and drawing off the chloroformic solution. The chloroformic extracts are then mixed, and allowed to evaporate spontaneously in a tared capsule. The residue is then dried at 100° C. (212° F.) to a constant weight.

This residue should not weigh less than 0.02 gm. nor more than 0.0224 gm., corresponding to not less than 0.9 nor more than 1 per cent. of strychnine.

$$\frac{.0224 \times 100}{2.24} = 1\%$$

ESTIMATION OF THE IRON.

The aqueous liquid from which the strychnine has been removed in the manner described above, is heated on a water-bath until the chloroform and ammonia are entirely volatilized. This is then allowed to cool, and diluted with water to the volume of 100 cc. 25 cc. of

this are transferred to a glass-stoppered bottle (having a capacity of 100 cc.), 2 gms. of hydrochloric acid and 1 gm. of potassium iodide are then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour. After it has been allowed to cool add a few drops of starch T. S., and titrate with decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid is entirely discharged. 16 cc. of the $\frac{N}{10}$ V. S. should be required to produce this result, each cc. corresponding to 1 per cent. or 0.0056 gm. of metallic iron.

$$0.0056 \times 16 = 0.0896 \text{ gm.}$$

$$\frac{0.0896 \times 100}{0.56} = 16\% \text{ of Fe.}$$

Ammonio-ferric Sulphate (Ferri et Ammonii Sulphas; Ammonio-ferric Alum), $Fe_2(SO_4)_3.(NH_4)_2SO_4 + 24H_2O = \begin{cases} 962.1 \\ *964 \end{cases}$.—This salt has a definite chemical composition, and therefore by determining the quantity of metallic iron the quantity of pure salt may be found by calculation.

The U. S. P. process for assay is as follows:

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid, 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour. It is then allowed to cool, and mixed with a few drops of starch T. S., and titrated with decinormal sodium thiosulphate V. S. until the blue or greenish color of the

liquid is discharged. Not less than 11.6 cc. of the $\frac{N}{10}$ V. S. should be required, each cc. corresponding to 1 per cent, or .0056 gm. of metallic iron, or 0.0482 gm. of the salt. See the following equations:

$$(Fe_2)\quad \underbrace{Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O}\ + 2KI$$

2)112
10) 56
5.6 gms.

2)*964
10) 482
48.2 gms.

$$= 2\,FeSO_4 + K_2SO_4 + (NH_4)_2SO_4 + I_2 + 24H_2O.$$

2)253
10)126.5
12.65 gms.

Then

$$I_2 + 2(Na_2S_2O_3.5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

2)253
10)126.5
12.65 gms.

2)496
10)248
24.8 gms. or 1000 cc. $\frac{N}{10}$ V. S.

Thus it is seen that 1 cc. of $\frac{N}{10}$ V. S. represents 0.01265 gm. of iodine, and this corresponds to 0.0482 gm. of ammonio-ferric sulphate, or 0.0056 gm. of metallic iron.

$$0.0482 \times 11.6 = 0.55912 \text{ gm.}$$

$$\frac{0.55912 \times 100}{11.6} = 99.8\% \text{ of the pure salt.}$$

$$0.0056 \times 11.6 = .06496 \text{ gm.}$$

$$\frac{.06496 \times 100}{0.56} = 11.6\% \text{ of Fe.}$$

Soluble Ferric Pyrophosphate (Ferri Pyrophosphas Solublilis).—This is estimated according to the U. S. P. in the following manner:

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 10 cc of water, then 10 cc. of hydrochloric acid and subsequently 40 cc. of water are added. Then 1 gm. of potassium iodide is put into the solution and the temperature kept at 40° C. (104° F.) for half an hour. The liquid is then cooled and a few drops of starch T. S. added, and the $\frac{N}{10}$ sodium thiosulphate V. S. delivered in from a burette, until the blue or greenish color is completely discharged. Each cc. of the $\frac{N}{10}$ V. S. represents 1 per cent. or 0.0056 gm. of metallic iron.

True ferric pyrophosphate has the chemical composition $Fe_4(P_2O_7)_3 + 9H_2O$. The soluble ferric pyrophosphate of the U. S. P. is a mixture of ferric pyrophosphate and sodium citrate.

The reaction with potassium iodide is expressed as follows:

$$Fe_4(P_2O_7)_3 + 4KI = 2Fe_2P_2O_7 + K_4P_2O_7 + 2I_2$$

$4)746$
$10)186.5$
18.65 gms.

$4)506$
$10)126.5$
12.65 gms.

Thus 18.65 gms. of ferric pyrophosphate cause the liberation of 12.65 gms. of iodine, and since each cc. of $\frac{N}{10}$ sodium thiosulphate V. S. will absorb, and consequently represent, .01265 gm. of iodine, it corresponds to 0.01865 gm. of pure ferric pyrophosphate.

10 cc. of the decinormal solution is the quantity which the U. S. P. requires should be used.

$$0.01865 \times 10 = 0.1865 \text{ gm.}$$

$$\frac{0.1865 \times 100}{0.56} = 33.3\%$$

of ferric pyrophosphate, which corresponds to 10% of metallic iron in the U. S. P. salt.

Ferric Valerianate (Ferri Valerianas), $Fe_2(C_5H_9O_2)_6 = \{*718$.—The true ferric valerianate is illustrated by the above formula, but the U. S. P. salt is of variable composition, and should contain not less than 15%, nor more than 20%, of iron in combination.

The estimation is conducted as follows: *0.56(0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 2 cc. of hydrochloric acid. This decomposes the salt, forming ferric chloride and liberating valerianic acid. 15 cc. of water are now added, together with 1 gm. of potassium iodide, and the mixture heated to 40° C (104° F.) and kept at that temperature for half an hour; it is then cooled, and the liberated iodine estimated with decinormal sodium thiosulphate V. S., using starch T. S. as indicator.

Not less than 15 cc. nor more than 20 cc. of the $\frac{N}{10}$ V. S. should be required to discharge the color of starch iodide. Each cc. corresponds to 1% of metallic iron. The reactions are expressed by the following equations:

$$Fe_2(C_5H_9O_2)_6 + 6HCl = Fe_2Cl_6 + 6HC_5H_9O_2; \quad . \quad . \quad (1)$$

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2; \quad . \quad . \quad (2)$$

$$I_2 + 2(Na_2S_2O_3 \cdot 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O. \quad (3)$$

Liquor Ferri Acetatis (Solution of Ferric Acetate).—This is an aqueous solution, containing about 31% of anhydrous ferric acetate ($Fe_2(C_2H_3O_2)_6 = \left\{ {}^{*}\frac{464.92}{466} \right.$, corresponding to 7.5% of iron. 1.12 (1.1176) gms. of the solution are introduced into a glass-stoppered bottle (having a capacity of 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid.

1 gm. of potassium iodide is then added and the mixture kept at a temperature of 40° C. (104° F.) for half an hour; then cooled, and, after adding a few drops of starch T. S., pass into it from a burette decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid has completely disappeared.

Each cc. of the decinormal solution thus consumed represents 0.5% of metallic iron.

If 0.56 (0.5588) gm. of the solution is used instead of 1.12 (1.1176) gm., and treated as described above, each cc. of the $\frac{N}{10}$ V. S. represents 1% of metallic iron, or 0.0056 gm.

The principal reaction is expressed by the following equation:

$$Fe_2(C_2H_3O_2)_6 + 2KI = 2Fe(C_2H_3O_2)_2 + 2KC_2H_3O_2 + I_2.$$

2)464.92
10)232.46
23.246 gms.

2)253
10)126.5
12.65 gms.

Thus each cc. of the $\frac{N}{10}$ V. S. also represents 0.023246 gm. of ferric acetate.

15 cc. of the $\frac{N}{10}$ V. S. should be required if 1.12 gms. of solution are taken.

$$0.023246 \times 15 = 0.34869 \text{ gm.}$$

$$\frac{0.34869 \times 100}{1.12} = 31.1\% \text{ of ferric acetate.}$$

7.5 cc. the $\frac{N}{10}$ V. S. should be consumed if 0.56 gm. is taken.

$$0.023246 \times 7.5 = 0.17434 \text{ gm.}$$

$$\frac{0.17434 \times 100}{0.56} = 31.1\%$$

Liquor Ferri Nitratis (Solution of Ferric Nitrate).—An aqueous solution containing about 6.2% of anhydrous ferric nitrate ($Fe_2(NO_3)_6 = \begin{cases} 483.1 \\ *484 \end{cases}$, and corresponding to about 1.4% of metallic iron.

Introduce into a glass-stoppered bottle (having a capacity of 100 cc.) 1.12 (1.1176) gms. of the solution, together with 15 cc. of water and 2 cc. of hydrochloric acid. Then add to the mixture 1 gm. of potassium iodide, and keep it at a temperature of 40° C. (104° F.) for half an hour. Allow the mixture to cool, and estimate the liberated iodine with decinormal sodium thiosulphate V. S., using starch T. S. as indicator. When the blue or greenish color of starch iodide has entirely disappeared, the reaction is completed.

2.8 cc. of the $\frac{N}{10}$ V. S. should be required, each cc. corresponding to 0.5% of metallic iron.

The reaction between the ferric nitrate and potassium iodide is as follows:

$$Fe_2(NO_3)_6 + 2KI = 2Fe(NO_3)_2 + 2KNO_3 + I_2.$$

2)483.1
10)241.5
24.15 gms.

2)253
10)126.5
12.65 gms.

or 1000 cc. $\frac{N}{10}$ V. S.

Thus each cc. of the decinormal sodium thiosulphate V. S. represents 0.02415 gm. of ferric nitrate.

Liquor Ferri Subsulphatis (Solution of Basic Ferric Sulphate; Monsel's Solution).—An aqueous solution of basic ferric sulphate of variable composition, chemically corresponding to about 13.6% of metallic iron.

1.12 (1.117) gms. of the solution are introduced into a flask (having a capacity of 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added and the mixture digested for half an hour at a temperature of 40° C. (104° F.). It is then cooled, and after adding a few drops of starch T. S., it is titrated with decinormal sodium thiosulphate V. S. When the blue or greenish color of the liquid disappears, the reaction is completed. 27.2 cc. should be required to complete the reaction, each cc. corresponding to 0.5% or 0.0056 gm. of metallic iron.

$$0.0056 \times 27.2 = 0.15232 \text{ gm.}$$

$$\frac{0.15232 \times 100}{1.12} = 13.6\%$$

Liquor Ferri Tersulphatis (Solution of Ferric Sulphate).—An aqueous solution of normal ferric sulphate $\left(Fe_2(SO_4)_3 = \begin{cases} 399.2 \\ *400 \end{cases}\right)$ containing about 28.7 per cent. of the salt, and corresponding to about 8 per cent. of metallic iron.

1.12 (1.1176) gms. of the solution are introduced into a 100-cc. glass-stoppered bottle, together with 15 cc. of water and 2 cc. of hydrochloric acid; 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour, then allowed to cool, and the liberated iodine estimated in the usual way with $\frac{N}{10}$ sodium thiosulphate V. S., using starch T. S. as indicator.

About 16 cc. of the $\frac{N}{10}$ V. S. should be required.

The following equation illustrates the reaction:

$$\underset{\substack{2)399.2 \\ 10)199.6 \\ 19.96 \text{ gms.}}}{Fe_2(SO_4)_3} + 2KI = 2FeSO_4 + K_2SO_4 + \underset{\substack{2)253 \\ 10)126.5 \\ 12.65 \text{ gms. or}}}{I_2}.$$

the equivalent of 1000 cc. of $\frac{N}{10}$ thiosulphate V. S.

Thus each cc. represents 0.01996 gm. of ferric sulphate, which corresponds to 0.5 per cent. or 0.0056 gm. of metallic iron.

If 16 cc. are used, the solution of ferric sulphate contains $0.01996 \times 16 = 0.31936$ gm.

$$\frac{0.31936 \times 100}{1.12} = 28.5\%$$

of pure ferric sulphate, and

$$0.0056 \times 16 = 0.0896 \text{ gm.},$$

$$\frac{.0896 \times 100}{1.12} = 8\%$$

of metallic iron.

Hydrogen Peroxide, $H_2O_2 = \left\{ {}^{*}\frac{33.92}{34} \right.$.—The iodometric method, which originated with Kingzett, is based upon the fact that iodine is liberated from potassium iodide by hydrogen peroxide, in the presence of sulphuric acid, and that this liberation of iodine is in direct proportion to the available oxygen contained in the peroxide.

Then by determining the amount of iodine liberated, the available oxygen is readily found.

$$\underset{\frac{2)34}{17 = 1 \text{ available O} = \frac{2)16}{8}}}{H_2O_2} + H_2SO_4 + 2KI = K_2SO_4 + 2H_2O + \underset{\frac{2)253}{126.5}}{I_2}.$$

This shows that 126.5 gms. of iodine are liberated by 17 gms. of absolute peroxide, which are equivalent to 8 gms. of available oxygen.

Thus 1000 cc. of $\frac{N}{10}$ sodium thiosulphate V. S., which absorb and consequently represent 12.65 gms. of iodine, are equivalent to 1.7 gms. of H_2O_2 or 0.8 gm. of available oxygen.

Each cc. of this $\frac{N}{10}$ V. S., then, represents, of H_2O_2 *0.0017 gm., of available oxygen *0.0008 gm.

The coefficients for weight of H_2O_2 and of oxygen, it is seen, are identical with those used in the permanganate process. Therefore the coefficient for volume is also the same in this method as in the other, namely, 0.5594.

The process is carried out as follows: Take 2 or 3 cc. of sulphuric acid, dilute it with about 30 cc. of water, add an excess of potassium iodide (about 1 gm.), and then 1 cc. of hydrogen peroxide. After the mixture has been allowed to stand five minutes starch T. S. is added, and the titration with $\frac{N}{10}$ sodium thiosulphate begun.

Note the number of cc. required to discharge the blue color, and multiply this number: by 0.0017 gm. to find the quantity, by weight, of H_2O_2; by 0.0008 gm. to find the weight of available oxygen; by 0.5594 cc. to find the volume of available oxygen.

If 18 cc. are required, the solution is of $0.5594 \times 18 = 10.0683$ volume strength.

$$0.0017 \times 18 = .0306 \text{ or } 3.06\% \ H_2O_2.$$
$$0.0008 \times 18 = .0144 \text{ or } 1.44\% \text{ of oxygen.}$$

With this method the author has always obtained satisfactory results. The lack of uniformity in the reaction, which is frequently reported, is doubtless due to the use of insufficient acid.

TABLE OF SUBSTANCES, ESTIMATED BY DECINORMAL SODIUM THIOSULPHATE V. S.

Name.	Formula.	Molecular Weight.	Factors.
			Gm.
Chlorine	Cl_2	70.68	.003537
Ferric acetate	$Fe_2(C_2H_3O_2)_6$	464.92	.023446
Ferric chloride	$Fe_2Cl_6 + 12H_2O$	539.5	.026975
Ferric citrate	$Fe_2(C_6H_5O_7)_2$	488.48	.024424
Ferric nitrate	$Fe_2(NO_3)_6$	483.1	.02415
Ferric phosphate	$Fe_2(PO_4)_2$	*302	.0151
Ferric pyrophosphate	$Fe_4(P_2O_7)_3$ anhydrous	*746	.01865
Ferric sulphate	$Fe_2(SO_4)_3$	399.2	.01996
Ferric and ammonium sulphate	$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$	*964.0	.0482
Ferric valerianate	$Fe_2(C_5H_9O_2)_6$	*718	.0359
Hydrogen peroxide	H_2O_2	33.92	.001696
Iodine	I_2	253	.01265
Iron, in ferric salts	Fe_2	111.76	.005588
Oxygen, available, weight	O_2	*32	.0008
Oxygen, available volume	O_2	*32	.5594 cc.

PART II.

CHAPTER XV.

ACETIC ACID AND ACETATES.

Vinegar.—Vinegar is impure diluted acetic acid. Its strength may be estimated in the same manner as acetic acid. Phenolphthalein must be used as an indicator. Litmus will give only approximate results, because potassium and sodium acetate both have a slightly alkaline reaction with litmus, but show no reaction with phenolphthalein.* The absence of mineral acids must be assured before the volumetric test is applied.

The strength of vinegar may also be estimated by distilling 110 cc. until 100 cc. come over. The 100 cc. will contain 80% of the whole acetic acid present in the 110 cc., and may be titrated ; or the specific gravity of the distillate may be taken, and, by consulting the table below, the per cent strength of the distillate found. By adding 20% to this the strength of the original vinegar is obtained.

Vinegar usually contains from 3% to 6% of acetic acid.

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* Even dark-colored vinegar may be titrated in this way when diluted. If the color, however, is too dark, litmus-paper or phenolphthalein paper may be used by bringing a drop of the liquid in contact with the paper from time to time during the titration.

ACETIC ACID TABLE.

Per cent of Absolute Acetic Acid.	Specific Gravity at 15° C. / 59° F.	Per cent of Absolute Acetic Acid.	Specific Gravity at 15° C. / 59° F.	Per cent of Absolute Acetic Acid.	Specific Gravity at 15° C. / 59° F.
1	1.0007	26	1.0363	51	1.0623
2	1.0022	27	1.0375	52	1.0631
3	1.0037	28	1.0388	53	1.0638
4	1.0052	29	1.0400	54	1.0646
5	1.0067	30	1.0412	55	1.0653
6	1.0083	31	1.0424	56	1.0660
7	1.0098	32	1.0436	57	1.0666
8	1.0113	33	1.0447	58	1.0673
9	1.0127	34	1.0459	59	1.0679
10	1.0142	35	1.0470	60	1.0685
11	1.0157	36	1.0481	61	1.0691
12	1.0171	37	1.0492	62	1.0697
13	1.0185	38	1.0502	63	1.0702
14	1.0200	39	1.0513	64	1.0707
15	1.0214	40	1.0523	65	1.0712
16	1.0228	41	1.0533	66	1.0717
17	1.0242	42	1.0543	67	1.0721
18	1.0256	43	1.0552	68	1.0725
19	1.0270	44	1.0562	69	1.0729
20	1.0284	45	1.0571	70	1.0733
21	1.0298	46	1.0580	71	1.0737
22	1.0311	47	1.0589	72	1.0740
23	1.0324	48	1.0598	73	1.0742
24	1.0337	49	1.0607	74	1.0744
25	1.0350	50	1.0615	75	1.0746

ESTIMATION OF FREE MINERAL ACIDS IN VINEGAR.

Mr. Hehner has devised the method given below, which has the merit of being speedy, scientific, and accurate.

The method is based upon the fact that acetates of the alkalies are always present in commercial vinegar, and when vinegar is evaporated to dryness, and the ash ignited, the acetates of the alkalies are converted into carbonates. If the ash has an alkaline reaction no free mineral acid is present. If, however, the ash is

neutral or acid some free mineral acid must be present.

The quantitative process in detail is as follows: 50 cc. of vinegar are mixed with 25 cc. of $\frac{N}{1}$ soda or potash V. S. The liquid is evaporated to dryness on a water-bath, and the residue carefully incinerated at the lowest possible temperature, to convert the acetates into carbonates. When cooled, 25 cc. of $\frac{N}{10}$ sulphuric acid V. S. are added, the mixture heated to expel CO_2 and filtered. The filter is washed with hot water, phenolphthalein T. S. added, and the filtrate and washings carefully titrated with $\frac{N}{10}$ alkali. Each cc. of $\frac{N}{10}$ alkali used represents 0.0049 gm. H_2SO_4 or 0.003637 gm. HCl.

Mohr's Method for Estimating Acetic Acid in Vinegar.—Take 20 gms. of the vinegar, add an excess of pure precipitated calcium carbonate (say 3 gms.), set aside until reaction is complete, shaking occasionally, and then boil to drive off the CO_2.

Now separate the residual calcium carbonate by filtration, wash it thoroughly with boiling water, and dissolve in a measured excess of $\frac{N}{1}$ hydrochloric acid, say 35 cc., and titrate back with $\frac{N}{1}$ sodium hydroxide, using phenolphthalein as indicator. Assuming that 4 cc. were used, then $35 - 4 = 31$, the number of cc. of $\frac{N}{1}$ hydrochloric acid which reacted with the residual calcium carbonate. Thus we have $31 \times .05$ gm. $= 1.55$ gms. of residual calcium carbonate. Deduct this from the 3 gms. taken, and we arrive at the

quantity which was taken up by the acetic acid, namely, 1.45 gms.

Therefore the 20 gms. of vinegar contain $1.45 \times 1.2 = 1.74$ gms. of pure acetic acid, or 8.7%. The reactions are as follows:

$$\underset{100}{CaCO_3} + 2\underset{120}{HC_2H_3O_2} = Ca(C_2H_3O_2)_2 + H_2O + CO_2.$$

Hence 1 gm. of calcium carbonate represents 1.2 gms. of acetic acid.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

$$\frac{2)100}{50} \quad \frac{2)72.8}{36.4} = 1000 \text{ cc. } \frac{N}{1} \text{ HCl V. S.}$$

$$0.050 = 1 \text{ cc. } \text{“} \quad \text{“} \quad \text{“}$$

This process answers well for dark-colored liquids and is especially useful for impure brown pyroligneous acid.

Pettenkofer's Method.—A measured excess of standard barium hydroxide solution is added to the acetic acid or the vinegar, and titrated back with decinormal acid, using turmeric paper as indicator.

ESTIMATION OF METALLIC ACETATES.

Acetates of lead, iron, etc., are treated with an excess of normal alkaline carbonate, which precipitates the metal as carbonate while an alkaline acetate is formed in the solution. The mixture is boiled, filtered, and the precipitate thoroughly washed on the filter with hot water. The filtrate and washings are mixed and made up to a definite volume. An aliquot portion is taken out and titrated with $\frac{N}{1}$ acid solution.

The difference between the quantity of acid used and that of the alkaline carbonate originally added is calculated into acetate by multiplying by 0.06 gm. If other salts than acetates are present, proceed as follows: Add excess of alkaline carbonate solution to precipitate the metal, exactly neutralize the filtrate with hydrochloric acid, evaporate to dryness, ignite the residue to convert the acetate into carbonate, and then titrate with normal acid solution in the usual way.

Any other organic acid present will of course be recorded as acetic.

CHAPTER XVI.

BORIC ACID AND BORATES.

Free Boric Acid may be estimated by means of barium hydroxide, as suggested by Will. The method is said to be fairly accurate.

The boric acid solution is titrated with a barium hydroxide solution of known strength, until the turbidity appearing at first is completely and exactly removed.

The equation is as follows:

$$4H_3BO_3 + Ba(OH)_2 = BaB_4O_7 + 7H_2O.$$

Thompson's Method (*Jour. Soc. Chem. Ind.*, XII. 432).—The addition of glycerine to a boric acid solution to the extent of 30 per cent develops the acidity of the acid to a great degree. It may then be titrated with standard sodium hydroxide solution, using phenolphthalein as indicator.

Boric Acid in Borax may be estimated as follows:

Add methyl orange solution (on which H_3BO_3 has no effect) to the solution of borax, and then just sufficient standard sulphuric acid solution to acidulate. Boil and exactly neutralize with standard sodium hydroxide. All the boric acid is now in a free state; sufficient glycerine is now added so that the solution contains at least 30 per cent, and the titration with

standard sodium hydroxide is begun, in the presence of phenolphthalein.

$$1 \text{ cc. } \frac{N}{1} \text{ NaOH} = 0.0620 \text{ gm. } H_3BO_3;$$
$$\text{“ “ “} = 0.0505 \text{ gm. } Na_2B_4O_7.$$

E. F. Smith's Process (*Amer. Chem. Jour.*, 1882). —Take 10 cc. of borax solution containing 0.1 gm.; add 10 cc. of solution of manganese sulphate, containing 0.06 gm. of $MnSO_4$, and finally 20 cc. of strong alcohol. A white flocculent precipitate of MnB_4O_7 separates. Set aside for half an hour to settle, filter, wash the precipitate with alcohol, and evaporate the filtrate and washings to dryness. Then dissolve the residual manganese in water, add some strong solution of zinc sulphate, heat to near the boiling point, and titrate with potassium permanganate until a permanent pink is produced. Each cc. of the permanganate represents 0.00324 gm. of $MnSO_4$.

In the above titration 6.4 cc. were required = 0.0207 gm.

This deducted from the 0.06 gm. added gives us 0.0393 gm., the amount which combined.

$$151 \text{ gm. } MnSO_4 = 202 \text{ gm. } Na_2B_4O_7;$$
$$\text{“ “ “} = 140 \text{ gm. } B_2O_3.$$

Thus the 0.1 gm. of borax analyzed contained

$$0.0525 \text{ gm. of pure } Na_2B_4O_7 = 52.5\%,$$
or $$0.0364 \text{ gm. of } B_2O_3 = 36.4\%.$$

CHAPTER XVII.

CARBONIC ACID AND CARBONATES.

ALKALINE carbonates may be accurately estimated by titration with standard acid solutions, as described on page 63.

They may also be estimated by precipitation with calcium or barium chloride and the precipitated carbonate then treated with an excess of standard acid, and retitrated with standard alkali.

Calcium chloride is preferred where it can be used, because the physical characters of the calcium carbonate are such as to render it more rapidly and thoroughly washed than is the case with barium carbonate. If caustic alkalies are present, however, barium chloride must be used, as calcium hydrate is very insoluble, and is in consequence precipitated with the carbonate.

If ammonia is present, the precipitation of calcium carbonate or barium carbonate is not complete. In this case it is necessary to heat the mixture for several hours.

Example.—The carbonate is dissolved in water, heated and treated with calcium or barium chloride in excess, and the mixture boiled for a few minutes, filtered and the precipitate rapidly washed with several portions of hot water. The precipitate together with the filter is placed in a flask and a measured excess of normal acid added, and the mix-

ture boiled until the precipitate is dissolved and the CO_2 expelled.

Phenolphthalein is then added, and lastly normal alkali from a burette until a faint pink appears.

The quantity of normal alkali used is deducted from the acid added, and the quantity of the latter which went into combination with the precipitate found. The reactions are written thus:

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl;$$

then $$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

The factors for the alkaline carbonates are the same as when estimated by direct titration with acid, which see. See also the gasometric method, page 471.

CARBONIC ACID IN INSOLUBLE CARBONATES.

This may be estimated by decomposition with an acid, and conducting the CO_2 into strong ammonia-water which absorbs it completely. The CO_2 is then precipitated by calcium chloride and estimated as explained under soluble carbonates. The ammonia-water must be free from CO_2. If any be present, it must be removed by means of calcium chloride. The decomposition is effected in the apparatus shown in Fig. 43. The carbonate and some water is put in *A*, hydrochloric acid in *b*, ammonia-water in *B*, and some pieces of broken glass

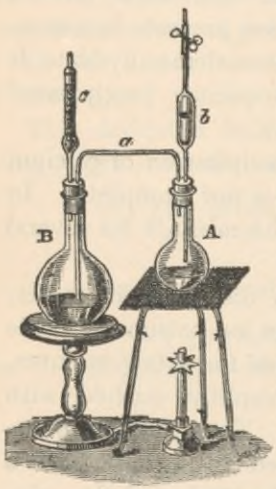

FIG. 43.

in *c*, through which the ammonia is poured into the flask.

The flask containing the ammonia-water is heated until it is filled with its fumes. Then the hydrochloric acid is run into the carbonate by opening the pinch-cock, and when decomposition of the carbonate is complete the liquid is boiled, and finally a slow current of air free from CO_2 is drawn through the apparatus to carry over the last traces of the gas.

The apparatus is then disconnected, *c* is rinsed into *B*, calcium chloride added and the solution boiled for some time, and the precipitated carbonate treated as explained in the foregoing process. In either of the foregoing processes the precipitated barium or calcium carbonate may be dissolved in hydrochloric acid, evaporated to dryness and the amount of chlorine, as chloride, found by means of $\frac{N}{10}$ silver nitrate solution in presence of chromate.

1 cc. $\frac{N}{10}$ acid or silver = 0.0022 gm. CO_2;

" " " " " = 0.0053 gm. Na_2CO_3.

CHAPTER XVIII.

CHLORATES, BROMATES, AND IODATES.

THESE may be estimated by titrating with $\frac{N}{10}$ silver nitrate solution after ignition. They are reduced by heat to chlorides, bromides, and iodides respectively.

(*a*) $KClO_3 + \text{heat} = KCl + O_3$.

(*b*) $KCl + AgNO_3 = AgCl + KNO_3$.

$$\underset{7.438 \text{ gms.}}{10)74.38} \qquad \underset{16.97 = 1000 \text{ cc.}}{10)169.7} \quad \frac{N}{10} AgNO_3 \text{ V. S.}$$

Thus each cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. represents 0.007438 gm. of KCl = 0.012237 gm. $KClO_3$. The factor is $\frac{1}{10000}$ the molecular weight in grammes of any univalent chlorate, bromate or iodate and $\frac{1}{20000}$ that of bivalent salts.

Chlorates, Bromates, and Iodates may also be estimated by digestion with excess of hydrochloric acid in the presence of potassium iodide. In each case the liberated chlorine acts upon the potassium iodide and sets free an equivalent of iodine, the amount of which is then estimated by means of $\frac{N}{10}$ sodium thiosulphate.

(*a*) $\underset{122.4}{KClO_3} + 6KI + 6HCl = \underset{759}{7KCl} + 3H_2O + I_6$.

(*b*) $I_2 + 2(Na_2S_2O_3 . 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O$.

2)253 2)496
10)126.5 10)248
12.65 gms. 24.8 gms. or 1000 cc. $\frac{N}{10}$ V. S.

Each cc. of $\frac{N}{10}$ $Na_2S_2O_3 = 0.01265$ gm. of iodine = 0.0020432 gm. of $KClO_3$.

CHAPTER XIX.

CITRIC ACID AND CITRATES.

Citrates of the Alkalies and Earths may be estimated by treating with a solution of lead nitrate or acetate. The resulting precipitate of lead citrate is then washed with a mixture of equal parts of alcohol and water, and then suspended in water and treated with H_2S gas until all the lead is precipitated as sulphide. The lead sulphide is separated and the clear solution boiled to expel H_2S, and then titrated with normal alkali solution.

Each cc. of the latter used = 0.070 gm. of crystallized citric acid.

This method may be employed for estimating solutions of citrate of magnesia.

Lime-juice or Lemon-juice, the chief constituent of which is citric acid, may be estimated by titrating with $\frac{N}{1}$ potassium hydroxide V. S. in the same manner as other acid solutions.

Lime-juice contains on an average 7.84%, rarely as much as 10%, and very seldom as little as 7% of citric acid.

Commercial lime-juice frequently contains sulphuric, hydrochloric, or tartaric acid. Therefore before applying this test the absence of notable quan-

tities of these acids must be insured by qualitative tests.

Warington's Method (*Jour. Chem. Society*, 1875, 934).—20 cc. of ordinary juice or 4 cc. of concentrated juice are neutralized with normal sodium hydroxide solution and diluted to about 50 cc. The mixture is heated to boiling and a small excess of calcium chloride solution added. The boiling is continued for about half an hour, the precipitate collected on a filter and washed with hot water.

The filtrate and washings are mixed and concentrated to about 15 cc.; a few drops of ammonia-water are added and the precipitate produced collected separately and washed.

Both filters and their precipitates are then dried and incinerated at a low red heat and the residue titrated with $\frac{N}{1}$ hydrochloric acid.

The process depends upon the formation of sodium citrate, which is precipitated as calcium citrate. This is converted by ignition into carbonate, which is finally titrated with the normal acid.

Each cc. represents 0.07 gm. of $H_3C_6H_5O_7, H_2O$. See also page 93.

CHAPTER XX.

HYDROCYANIC ACID AND CYANIDES BY SULPHOCYANIDE SOLUTION.

A WEIGHED quantity of the cyanide is treated with a measured excess of decinormal silver nitrate solution in order to unite the cyanogen entirely with the silver as silver cyanide; the mixture is then made up to a certain volume by the addition of distilled water, thoroughly shaken and a portion filtered through a dry filter. An aliquot portion of the whole solution is then removed by means of a pipette, some ammonio-ferric sulphate solution added, then strongly acidulated with nitric acid, and titrated for the excess of silver nitrate with $\frac{N}{10}$ potassium sulphocyanide solution. The quantity of silver being found in the aliquot portion, it is multiplied by the proper figure and the quantity of silver in the entire solution is ascertained. This deducted from the quantity originally added gives the quantity which went into combination with the cyanogen.

Each cc. of $\frac{N}{10}$ $AgNO_3$ V.S. = 0.002598 gm. CN.
" " " " " " = 0.002698 " HCN.
" " " " " " = 0.006501 " KCN.
" " " " " " = 0.004897 " NaCN.
" " " " " " = 0.011289 " $Hg(CN)_2$.

This is essentially the method of Volhard, described under Analysis by Precipitation in Part I. The end reaction is known by the appearance of a red color. In estimating cyanides by this method the above-described procedure must be carefully followed.

The following precautions must be taken, which are not necessary when the halogens are estimated by this method, namely:

The cyanogen must be completely combined with the silver and under no circumstances must the solution be acidulated before the silver solution is added, otherwise the cyanide will be converted into hydrocyanic acid, as the equation shows:

$$KCN + HNO_3 = KNO_3 + HCN.$$

This would not only cause a loss by volatilization, but would seriously endanger the health or even the life of the analyst.

Furthermore, the sulphocyanide solution must not be added to the solution which contains the silver cyanide in suspension as is done in the case of the halogens, because the sulphocyanide will react with silver cyanide, which is not the case with the haloid salts of silver. Hence it is directed to filter the liquid and operate upon an aliquot portion.

In the estimation of solutions containing free HCN, such as bitter-almond water, a weighed quantity of the latter is poured directly into the silver nitrate solution in order to lose as little as possible of the hydrocyanic acid.

Cyanides insoluble in water are treated with an acid in order to set free the hydrocyanic acid, which is distilled over and received in a solution of potassa.

If potassium ferrocyanide is to be estimated in this way it is treated with sulphuric acid; but it must be remembered that only half of the contained cyanogen distils over, the rest remains in combination with potassium and iron.

Care must be taken in distilling hydrocyanic acid, inasmuch as it is partially decomposed into formic acid and ammonia in the presence of much free acid. To

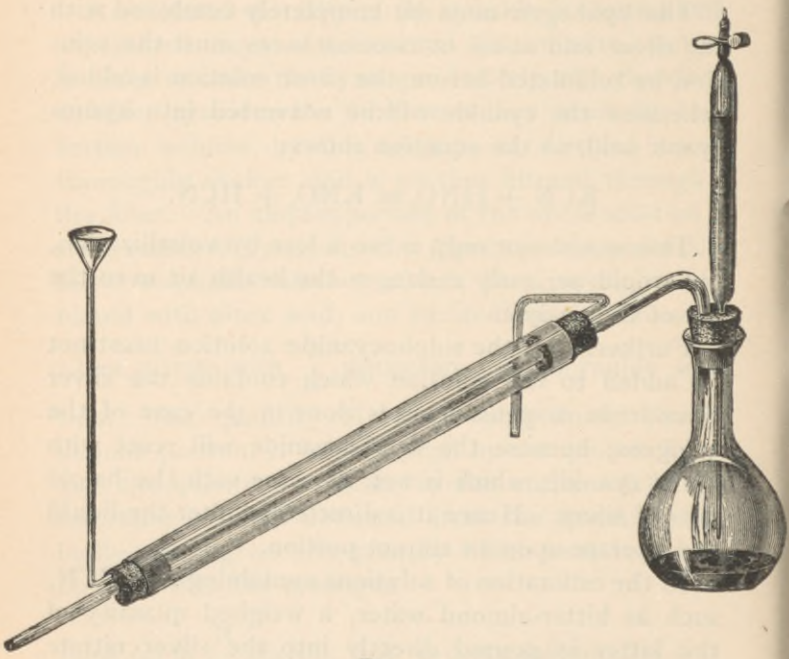

FIG. 44.

overcome this the distilling apparatus shown in Fig. 44 is used. The hydrochloric acid is contained in the pipette. The cyanide together with some water is placed in the flask. The water in the flask is heated

to boiling, and the hydrochloric acid allowed to flow in slowly, drop by drop. In this way the hydrocyanic acid formed by each drop of hydrochloric acid distils over immediately with the vapor of water, and is condensed by means of the Liebig's condenser.

Cyanides may also be estimated by means of iodine solution in the presence of alkaline carbonate. Free alkaline hydroxides must not be present; if they are, the addition of strong carbonated water will convert them into carbonates.

The reaction is as follows:

$$KCN + I_2 = KI + CNI.$$

Thus each cc. of $\frac{N}{10}$ iodine V. S. represents

0.0013 gm. CN;
0.003259 gm. KCN.

CHAPTER XXI.

FERRO- AND FERRICYANIDES.

Ferrocyanides.—Alkaline ferrocyanides may be estimated by potassium permanganate or dichromate. The reaction is as follows:

$$5K_4Fe(CN)_6 + KMnO_4 + 4H_2SO_4 = 5K_3Fe(CN)_6 + MnSO_4 + 3K_2SO_4 + 4H_2O.$$

The ferrocyanide is thus oxidized to ferricyanide. The former is yellow in color, the latter red. Therefore the end reaction is the appearance of a red color, but much practice is required in order to recognize the first appearance of a red, which is very difficult in the greenish-yellow solution. The end reaction may also be found by bringing a drop of the solution in contact, on a white slab, with a drop of ferric chloride solution; when a blue color is no longer produced by this contact the end point is reached.

The process is conducted as follows: 2 gm. of the ferrocyanide are dissolved in sufficient water to make 1 litre of solution. 100 cc. of this, representing 0.2 gm. of the salt, is acidulated with sulphuric acid placed in a white porcelain dish and titrated with the permanganate. 1 cc. of the permanganate represents

0.0368 gm. of $K_4Fe(CN)_6$,
or 0.0422 gm. of $K_4Fe(CN)_6 + 3H_2O$.

Ferricyanides.—These salts may be estimated after reduction to ferrocyanides by titrating with permanganate as described in the preceding.

The ferricyanide is treated with an excess of potassa or soda and boiled while small quantities of strong solution of ferrous sulphate are added from time to time, until the precipitate produced is black in color. The solution is then diluted to a convenient quantity, say 300 cc.

100 cc. of this solution are then taken out, acidified strongly with sulphurric acid, and titrated with $\frac{N}{10}$ permanganate, as directed for the estimation of ferrocyanides.

The process is based upon the fact that ferrous sulphate reduces the ferricyanide to ferrocyanide, in the form of a blue precipitate, Turnbull's blue ($Fe_3Fe_2(CN)_{12}$), as the equation shows:

$$K_6Fe_2(CN)_{12} + 3FeSO_4 = Fe_3Fe_2(CN)_{12} + 3K_2SO_4.$$

This blue precipitate when boiled with an alkali is immediately reduced to magnetic oxide (Fe_3O_4), and the alkaline ferrocyanide goes in solution, as shown by equation:

$$Fe_3Fe_2(CN)_{12} + 8KOH = Fe_3O_4 + 2K_4Fe(CN)_6 + 4H_2O.$$

In the analysis, whatever quantity of permanganate is used must be multiplied by three, because only one third of the entire solution is titrated.

Each cc. of permanganate represents

0.0368 gm. of $K_4Fe(CN)_6$,

which equals

0.0329 gm. of $K_3Fe(CN)_6$.

Most of the insoluble ferricyanides are converted into potassium ferricyanide by boiling with KOH.

The reduction of ferricyanide may be effected by means of nascent hydrogen developed from zinc and potassa, or by means of sodium amalgam. De Haen employs lead oxide for this purpose in alkaline solution, the reaction being expressed thus:

$$2K_3Fe(CN)_6 + PbO + 2KOH = 2K_4Fe(CN)_6 + PbO_2 + H_2O.$$

CHAPTER XXII.

PHOSPHORIC ACID AND PHOSPHATES.

Phosphoric Acid may be estimated by Stolba's method, as *Ammonio-magnesian Phosphate.*

0.2 gm. of phosphoric acid is supersaturated with ammonia water, so as to convert all of the acid into ammonium phosphate and leave an excess of the alkali.

$$\underset{98}{H_3PO_4} + 2NH_4OH = \underset{132}{(NH_4)_2HPO_4} + 2H_2O.$$

An excess of magnesia mixture* is now added in order to precipitate all of the phosphoric acid in the form of ammonio-magnesian phosphate.

$$\underset{132}{(NH_4)_2HPO_4} + MgSO_4 = \underset{137}{Mg(NH_4)PO_4} + NH_4HSO_4$$

The precipitate is washed, first with ammonia water, and then the ammonia is entirely removed by washing with alcohol of 50% or 60% strength.

The precipitate is now dissolved in a measured *excess* of $\frac{N}{10}$ hydrochloric acid V. S., a few drops of methyl-orange T. S. added, and the excess of acid

* **Magnesia Mixture.**—Dissolve 10 gms. of magnesium sulphate and 20 gms. of ammonium chloride in 80 cc. of water, add 42 cc. of ammonia water, set aside for a few days in a well-stoppered bottle, and filter. It should never be used freshly made.

found by titrating back with $\frac{N}{10}$ potassium hydrate. The difference between the number of cc. of $\frac{N}{10}$ HCl added and the quantity of $\frac{N}{10}$ KOH used gives the quantity of HCl which went into combination with the ammonia-magnesian phosphate.

$$\underset{137}{Mg(NH_4)PO_4} + \underset{72.8}{2HCl} = NH_4H_2PO_4 + MgCl_2.$$

By consulting the equations given, it will be seen that 72.8 gms. of HCl are equivalent to 137 gms. of $Mg(NH_4)PO_4$, or 132 gms. of $(NH_4)_2HPO_4$, or 98 gms. of H_3PO_4.

This means that 1000 cc. of a decinormal $\left(\frac{N}{10}\right)$ solution of HCl, containing 3.64 gms. of the acid, represents $\frac{1}{10}$ of each of these quantities; and one cc. of $\frac{N}{10}$ HCl thus represents 0.0049 gm. of phosphoric acid.

In this estimation care must be taken that all free ammonia is removed from the precipitate, and that the whole of the ammonia-magnesian phosphate is decomposed by the acid before titration with the $\frac{N}{10}$ alkali. This may be insured by using a rather large excess of the acid and warming.

Example.—To the precipitate of ammonia-magnesian phosphate obtained from 0.2 gm. of phosphoric acid, 50 cc. of $\frac{N}{10}$ HCl are added. In titrating back 15.3

cc. of $\frac{N}{10}$ KOH are required. Hence 34.7 cc. of the acid went into combination with the double salt.

Then $34.7 \times .0049 = 0.17003$ gm.,

and $\frac{.17003 \times 100}{.2} = 85.01\%$ of absolute phosphoric acid. This method is said to give good results.

Estimation of Phosphates by Uranic Nitrate.—

The solutions required are:

1. A standard uranium solution.
2. A standard phosphate solution.
3. A solution of sodium acetate in dilute acetic acid.
4. A freshly prepared solution of potassium ferrocyanide.

Standard Uranium Solution.—Either the acetate or nitrate of uranium may be employed.

35 gms. of the salt are dissolved in about 1000 cc. of water. The solution keeps better if about 25 cc. of glacial acetic acid are included.

Standard Phosphate Solution.—5.886 gms. of crystallized non-effloresced microcosmic salt (ammonio-sodic phosphate) are dissolved in water and diluted to one litre.

50 cc. of this solution will represent 0.1 gm. of P_2O_5.

The Sodium Acetate Solution is made by dissolving 100 gm. of sodium acetate in water, adding 50 cc. of glacial acetic acid, and diluting to one litre.

The standard uranium solution is titrated against the above standard phosphate solution and diluted so

that 20 cc. of the uranium solution will be equivalent to 50 cc. of the phosphate solution. 50 cc. of the phosphate solution are placed in a beaker, 5 cc. of sodium acetate solution are added, and the mixture heated to nearly boiling. The uranium solution is then delivered in from a burette, until a drop of the hot solution brought in contact on a white porcelain plate with a drop of the freshly prepared ferrocyanide solution produces a brown color (uranic ferrocyanide). A second and third titration should always be made so as to ascertain the exact strength of the uranium solution, which is then diluted so that 20 cc. correspond to 50 of the phosphate solution. If 18.7 cc. were required, then each 18.7 cc. must be diluted to 20, or 935 to 1000.

In estimating phosphoric acid by standard uranium solution it is absolutely essential that all the above conditions should be present. That is, the bulk of fluid should be the same, the quantity of phosphate acted upon should be nearly the same, 0.1 gm. in 50 cc., the same relative amount of sodium acetate, and the same depth of color in testing.

In the analysis, the phosphate is dissolved in water, if no ammonia is present, 1 cc. of 10 per cent solution is added and neutralized with the least possible quantity of acetic acid; then 5 cc. of sodium acetate, and water to make 50 cc. The solution is then heated to near boiling, and the uranium solution run in as described.

Several titrations should be made; the first will give roughly the amount required, and that may be taken as a guide.

Each cc. of uranium solution = 0.005 gm. of P_2O_5 = 0069H_3PO_4. This method depends upon the

fact that when uranic nitrate is added to a solution of an orthophosphate the whole of the P_2O_5 is precipitated as yellow uranyl phosphate. If ammonia is present, the P_2O_5 is precipitated as uranyl-ammonium phosphate.

If a mineral acid is present, as when phosphate is dissolved by the use of hydrochloric or nitric acid, a corresponding amount of ammonium acetate and ammonia-water in excess must be added, followed by acetic acid to neutralize. The reactions may be expressed as follows:

$$Na_2HPO_4 + UO_2(NO_3)_2 = UO_2HPO_4 + 2NaNO_3,$$

or

$$Na(NH_4)HPO_4 + UO_2(NO_3)_2 = (UO_2)(NH_4)PO_4 + NaNO_3 + HNO_3.$$

R. Segalle's Modification of Glückmann's Method (*Zeit. f. Anal. Chem.*, 1895).—To the solution of phosphoric acid add a measured excess of normal ammonia solution; then sufficient of a neutral solution of magnesium sulphate to cause the precipitation of all of the phosphoric acid as ammonio-magnesium phosphate. The mixture is then made up to a definite volume, shaken vigorously, and immediately filtered.

The excess of ammonia is then determined by titration with normal acid solution. The number of cc. of acid solution used is deducted from the quantity of normal ammonia added, and the difference represents the phosphoric. The reactions which take place are represented by the following equations:

$$H_3PO_4 + 3NH_3 = (NH_4)_3PO_4;$$
$$(NH_4)_3PO_4 + MgSO_4 = NH_4MgPO_4 + (NH_4)_2SO_4.$$

Thus it is seen that one molecule of phosphoric acid is neutralized by three molecules of ammonia.

$$H_3PO_4 + 3NH_3.$$

$$3)98 \qquad 3)51$$

$$32.6 \text{ gm.} = 17 \text{ gm. or } 1000 \text{ cc. } \frac{N}{1} \text{ V. S.}$$

$$0.0326 \text{ gm.} = 1 \text{ cc. } \frac{N}{1} \text{ V. S.}$$

The presence of the magnesium sulphate does not interfere in the least with the titration of the ammonia.

Pemberton's Molybdic Method (*Ch. News*, XLVI. 4).—This process is based upon the fact that if an aqueous solution of ammonium molybdate be added to a hot solution of a phosphate in the presence of a large quantity of ammonium nitrate and a small excess of nitric acid, the phosphoric acid will be completely precipitated in the form of ammonium phospho-molybdate.

The standard molybdate solution is made by dissolving 89.543 gm. of the crystallized salt in about 900 cc. of water, and if the solution is not quite clear a few drops of ammonia-water are added, and it is then diluted with water to 1000 cc.

The solution should be standardized with a solution of phosphate of known strength.

The Analysis.—Take a quantity of the phosphate not containing more than 0.1 gm. of P_2O_5, add a small quantity of water, then 2 cc. of nitric acid (sp. gr. 1.4) and 10 gm. of granular ammonium nitrate, and heat the solution to 140° F. or over. Then run in some of the standard molybdate solution, stirring constantly; set aside in a warm place for a few minutes in order to allow the yellow precipitate to settle and leave the supernatant liquid, not clear,

but containing widely disseminated particles, in which the yellow cloud produced by the further addition of molybdate solution may be readily seen.

When the precipitation is thought to be nearly complete, the titration is continued carefully, with the aid of a Beale's filter (Fig. 54). By means of the Beale's filter a small portion is taken out of the solution at intervals, and tested with a drop or two of the molybdate solution. If a precipitate is produced the solution is washed back into the beaker with a little hot water, and the titration continued until a portion of the filtered solution tested as above no longer yields a precipitate.

If the end point has been overstepped, a measured quantity of phosphate solution of known strength is added, and the titration with molybdate continued, the quantity of phosphate thus added being deducted from the amount found.

Each cc. of the molybdate solution represents 0.003 gm. of P_2O_5 or 0.004 gm. H_3PO_4.

About three titrations should be made: the first shows about how much of the molybdate solution is required, the second gives approximate results, the third will give exact results.

The process is not reliable in the presence of silicates, organic matter, or organic acids.

Pemberton's New Molybdic Method as Modified by H. B. McDonald (Bulletin No. 49, U. S. Dept. Agriculture).—This method depends upon the precipitation of ammonium phospho-molybdate, and then titrating the precipitate alkalimetrically. The process requires great delicacy of manipulation, but gives excellent results.

The solutions required are:

Molybdic Solution.—Dissolve 100 gms. of molybdic acid in 400 gms. or 417 cc. of ammonia-water sp. gr. 0.96, and pour the solution thus obtained into 1500 gms. or 1250 cc. of nitric acid sp. gr. 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from the sediment and preserve it in glass-stoppered vessels. For use add to 100 cc. of this solution 5 cc. of nitric acid sp. gr. 1.42. Filter each time before using.

Standard Potassium Hydroxide Solution. — This solution contains 18.17106 gms. of potassium hydroxide to the litre. It is prepared by diluting 323.81 cc. of normal potassium hydroxide (which has been freed from carbonates by barium hydroxide) to one litre. One cc. of this is equal to .001 of P_2O_5, or 1 per cent if 0.1 gm. of the substance is taken for analysis.

Standard Nitric Acid Solution. — This solution should correspond in strength to the standard alkali solution, or may be one half that strength. It is standardized by titrating against that solution, using phenolphthalein as indicator.

The Process.—If a soluble phosphate is to be analyzed, dissolve 1 gm. in sufficient water to make 250 cc. 25 cc. of this solution, representing 0.1 gm. of the substance, is taken for analysis. If the phosphate is in an insoluble compound or organic substance, 2 gms. are treated with 40 cc. strong nitric acid and a little hydrochloric acid and boiled. It is then made up to a definite volume and an aliquot portion, corresponding to 0.4 gm. of the substance,

is taken for analysis; half of this amount if more than 5 per cent of P_2O_5 be present.

In either case add ammonia in slight excess, then nitric acid in slight excess, and warm to about 50° C.

Now add the molybdic solution slowly and with stirring, using an excess, about 75 to 80 cc. for each 0.1 gm. of P_2O_5 present, and in no case less than 10 cc.; stir well, let stand for about 30 minutes at 40° to 50° C., stirring several times at intervals; filter through good filter-paper about 9 cm. in diameter, on an ordinary funnel without suction; wash precipitate with water at ordinary temperature, first by decantation and then on the filter; when filtrate measures 250 cc. test filtrate, as it drops through the funnel, with a small strip of litmus-paper; wash once more, stirring the precipitate with the water-jet, and test again. When two successive tests show no acidity of filtrate, the washing is sufficient.

Remove filter and contents to the same beaker in which the precipitation was performed; add standard potassium hydroxide solution in excess and stir till precipitate is dissolved and titrate with standard nitric acid solution, using phenolphthalein as indicator.

The volume of the acid is deducted from that of the alkali used, and the remainder multiplied by .001 gm. gives the quantity of P_2O_5 in the sample taken. If 0.1 gm. of the sample was taken, each cc. of the alkali solution required will represent one per cent of P_2O_5.

CHAPTER XXIII.

SULPHATES.

THE sulphate is dissolved in water, acidified with hydrochloric acid, heated to boiling, and decinormal barium chloride carefully added until no further precipitation occurs.

The end of the reaction may be determined by the use of Beale's filter, Fig. 54, or by placing a drop of the clear solution on a plate of black glass or a mirror, and bringing in contact with it a drop of barium chloride solution.

A better plan is to add an excess of the barium chloride solution and heat to boiling, then add some ammonia-water and titrate the excess of barium chloride with decinormal potassium dichromate. The latter is added in small portions, boiling after each addition until the fluid above the precipitate is of a faint yellow color. The decinormal potassium dichromate solution is made by dissolving 7.35 gms. of the salt in sufficient water to make 1000 cc.

The reactions are as follows:

(*a*) $K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl$;

(*b*) $2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$.

Each cc. of $\frac{N}{10}$ barium chloride solution represents

0.0087 gm. of K_2SO_4;
0.0049 " " H_2SO_4.

By Precipitation as Lead Sulphate.—A decinormal solution of lead nitrate is prepared by dissolving 16.518 gms. of pure dry lead nitrate in sufficient water

to make 1000 cc. The sulphate is dissolved in water and titrated with the lead nitrate solution until precipitation is complete. A solution of potassium iodide may be used as indicator. The reaction is known to be completed when a drop of the solution brought in contact with a drop of the indicator on a porcelain slab gives a yellow color, due to the formation of lead iodide. The reaction is:

$$K_2SO_4 + Pb(NO_3)_2 = PbSO_4 + 2KNO_3$$

$$\begin{array}{rr} 2)174 & 2)330.36 \\ 10)87 & 10)165.18 \\ 8.7 & 16.518 = 1000 \text{ cc. } \frac{N}{10} \text{ V. S.} \end{array}$$

Each cc. = 0.0087 gm. of K_2SO_4;
" " = 0.0049 " " H_2SO_4.

CHAPTER XXIV.

SULPHIDES—BY STANDARD ZINC SOLUTION.

THE standard zinc solution is made by dissolving 14.35 gms. of pure crystallized zinc sulphate in water, making strongly alkaline with ammonia-water, and diluting to 1000 cc. The indicator is nickel protochloride or alkaline lead solution.

The sulphide is dissolved in water and titrated with the zinc solution until no dark color is produced when a drop of the solution is brought in contact with a drop of the nickel protochloride indicator on a porcelain tile.

Each cc. of the zinc solution used represents

0.0016 gm. of sulphur;
0.0039 gm. of sodium sulphide;
0.00551 gm. of potassium sulphide;
0.0034 gm. of ammonium sulphide.

CHAPTER XXV.

ALUMINUM.

ALUM AND ALUMINUM SALTS.

THE salt is dissolved in water, phenolphthalein added and then a measured excess of $\frac{N}{1}$ sodium hydroxide. This makes the solution red.

$$Al_2(SO_4)_3 + 6NaOH = Al_2(OH)_6 + 3Na_2SO_4.$$

The $Al_2(OH)_6$ dissolves in the excess of NaOH.

Normal acid solution is now added until the red color disappears, the quantity of the acid solution used is deducted from the alkali added, and the remainder multiplied by the factor.

Each cc. $\times$ 0.017 gm. $= Al_2O_3$;
$\times$ 0.057 gm. $= Al_2(SO_4)_3$.

The Ph. Germ. directs the following procedure for estimating aluminum sulphate:

1 gm. of the salt is dissolved in 10 cc. of water and 1.2 gm. of barium chloride added. Then a few drops of phenolphthalein T. S. are added and the mixture titrated with $\frac{N}{1}$ potassium hydroxide until red color appears.

The process depends upon the fact that the acid

combined with aluminum behaves toward the indicator as though it were in a free state. The red color does not appear until the aluminum is completely precipitated. In the case of sulphate of aluminum, however, the addition of alkali hydroxide solution is apt to cause the precipitation of basic sulphate of aluminum.

Hence in this process barium chloride is added in order to convert the sulphate into chloride of aluminum, which can be accurately titrated with the alkali solution.

The reactions are:

$$Al_2(SO_4)_3 + 3BaCl_2 = Al_2Cl_6 + 3BaSO_4;$$

then

$$Al_2Cl_6 + 6KOH = Al_2(OH)_6 + 6KCl.$$

Aluminum sulphate is apt to have some free acid, and this is of course included in the calculation together with the combined acid.

Hence not more than 8.7 cc. of $\frac{N}{1}$ KOH V. S. should be used; any quantity above that would indicate free acid.

Each cc. of $\frac{N}{1}$ alkali = 0.057 gm. of $Al_2(SO_4)_3$.

The free acid may be estimated by the use of tropæolin O. O., which reacts only with free acid.

CHAPTER XXVI.

AMMONIUM.

AMMONIUM SALTS may be estimated by distilling them with potassium or sodium hydroxide, and receiving the ammonia (NH_3) which distils over, in a known volume of normal or decinormal acid. After the distillation is completed the ammonia is found by titrating back with normal or decinormal alkali. The apparatus illustrated in Fig. 43 may be used for this purpose.

The ammonium salt in solution, is put into flask *A*; *b* contains strong solution of sodium hydroxide. The receiving-flask *B* contains a measured quantity of normal hydrochloric acid, which is poured in through the tube *c*, containing fragments of glass.

The pinch-cock upon *b* is opened, which allows the sodium hydroxide solution to run into the flask, and the solution is then gently boiled until all the ammonia is driven over and absorbed by the normal acid.

Care must be taken not to heat too strongly, or some of the fixed alkali may be projected up into the connecting-tube and carried over into the acid in flask *B*.

After the distillation is completed the acid adhering to the broken glass in *c* is washed into the flask, phenolphthalein added and the excess of acid found by titrating with normal alkali. The amount of

normal alkali used is deducted from the quantity of normal acid added, and the remainder is the acid which combined with the ammonia.

$$NH_3 + HCl = NH_4Cl.$$

17 36.4 = 1000 cc. $\frac{N}{1}$ V. S.

.017 .0364 = 1 cc. $\frac{N}{1}$ V. S.

Thus 1 cc. $\frac{N}{1}$ HCl = 0.014 gm. N;

" " " = 0.017 gm. NH_3;

" " " = 0.018 gm. NH_4;

" " " = 0.0534 gm. NH_4Cl.

Indirect Method.—In the case of pure ammoniacal salts or solutions free from acid, the following method may be employed.

To a weighed quantity of the salt a measured quantity of normal sodium hydroxide is added, and the mixture boiled in an open vessel until all the ammonia is expelled.

The residual alkali in the flask is then titrated with normal acid, and the difference between the normal acid used and the normal soda added gives the quantity of the latter which reacted with the ammonium salt.

The reaction is thus expressed:

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3;$$

each cc. of $\frac{N}{1}$ NaOH = 0.0534 gm. NH_4Cl;

" " " " " = 0.066 " $(NH_4)_2SO_4$.

CHAPTER XXVII.

ANTIMONY.

Antimonous Oxide, or any of its compounds, is estimated in the same manner as described for tartar emetic (page 186).

Solution of the oxide is first effected by means of tartaric acid, and any excess of the latter neutralized by sodium carbonate. Then for every 0.1 gm. of Sb_2O_3, 10 cc. of a cold saturated solution of sodium bicarbonate are added then starch solution, and finally titrated with $\frac{N}{10}$ iodine.

Each cc. of $\frac{N}{10}$ iodine V. S. = 0.0060 gm. Sb;

" " " " " " = 0.0072 gm. Sb_2O_3.

Antimonic Acid and its Salts are dissolved and strongly acidified with hydrochloric acid, a strong solution of sodium sulphite is then gradually added, the mixture boiled to drive off the SO_2, a drop of phenolphthalein solution added, and then KOH until slightly alkaline, as shown by red color. Then a small excess of tartaric acid is added and the process completed as for antimonous acid.

1 cc. $\frac{N}{10}$ iodine V. S. = 0.0060 gm. Sb.

CHAPTER XXVIII.

ARSENICUM.

Arsenous Oxide, As_2O_3.—The estimation of arsenous oxide by iodine is described in Chapter XIII. It may also be estimated as follows:

By Oxidation with Potassium Dichromate.—0.1 gm. of the substance is dissolved in about 10 cc. of water with the aid of hydrochloric acid. Then 20 cc. of hydrochloric acid, sp. gr. 1.12, and 80 cc. of water are added. An excess of $\frac{N}{10}$ potassium dichromate (say 30 cc.) is now introduced, the mixture allowed to react for a few minutes and then retitrated with a ferrous sulphate solution which corresponds in strength with the dichromate. A freshly prepared solution of potassium ferricyanide is used as the indicator. The difference between the quantities of the ferrous sulphate and dichromate solutions used gives the quantity of the latter which reacted with the arsenous oxide. In order to find the end reaction more accurately, it is advised to add another $\frac{1}{2}$ or 1 cc. of the dichromate and again retitrate with the ferrous sulphate solution.

The reaction is as follows:

$$3As_2O_3 + 2K_2Cr_2O_7 = 2K_2CrO_4 + 3As_2O_5;$$

2)593.04	2)587.56
6)296.52	6)293.76
10)49.42	10)48.96
4.942 gm.	4.896 gm. = 1000 cc. $\frac{N}{10}$ dichromate.

$$1 \text{ cc. } \frac{N}{10} \text{ dichromate} = 0.004942 \text{ gm. } As_2O_3.$$

The reaction between the ferrous sulphate and the dichromate is shown on page 156.

In the above estimation the volume of hydrochloric acid must not be less than one sixth nor more than one third that of the solution.

This process may also be employed in the estimation of antimonous salts, in the absence of organic matter and organic acids.

Arsenic Oxide, As_2O_5.—This may be estimated by iodine as directed for As_2O_3, if it be first reduced to the latter form by boiling with potassium iodide in the presence of hydrochloric acid in large excess until the iodine vapors are entirely dissipated. It is then cooled, neutralized with sodium carbonate, then bicarbonate added in excess and starch paste and titrated with $\frac{N}{10}$ iodine as directed for As_2O_3.

$$1 \text{ cc.} = 0.00575 \text{ gm. } As_2O_5.$$

Arsenic oxide and arsenates may also be estimated by means of magnesia mixture in exactly the same way as described for phosphoric acid.

Each cc. of $\frac{N}{10}$ hydrochloric acid V. S. represents 0.00575 gm. As_2O_5.

Arsenic Oxide by Precipitation with Uranium Solution.—Arsenic acid forms with uranic nitrate or acetate a precipitate which is analogous in composition to that produced by phosphoric acid. The estimation is conducted in exactly the same way as that of phosphoric acid.

The arsenic must be in the state of As_2O_5. If it is in the form of As_2O_3 it may be oxidized to As_2O_5 by evaporation with strong nitric acid, neutralizing with an alkali, and then dissolving in acetic acid.

ESTIMATION OF ARSENIC IN SMALL QUANTITIES, AS IN CASES OF POISONING.

Houzeau's Method (*Comp. Rend.*, LXXV.).—The substance containing the arsenic is placed in a Marsh's apparatus, and the arseniuretted hydrogen given off is passed into a measured amount of $\frac{N}{10}$ silver nitrate solution. A part of the silver nitrate is reduced to metallic silver, which may be separated by filtration and the filtrate titrated with $\frac{N}{10}$ sodium chloride. The loss of silver corresponds to the arsenic.

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3.$$

6)75 6)1018.2
10)12.5 10)169.7
100)1.25 1000)16.97
.00125 .01697 = 1000 cc. $\frac{N}{10}$ V. S.

The number of cc. of sodium chloride deducted from the number of cc. of $\frac{N}{10}$ $AgNO_3$ solution first taken gives the number of cc. of the latter which was reduced by the AsH_3.

Each cc. thus reduced represents 0.00125 gm. of As, or 0.00408 gm. As_2O_3.

CHAPTER XXIX.

BARIUM.

BARIUM SALTS may be titrated by precipitation with potassium dichromate.

The dichromate solution used for this purpose is a decinormal solution, but it differs in strength from that used as an oxidizing solution.

The reaction is as follows:

$$2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O$$

4)273.8 — 10)68.45 — 6.845 gm.

4)294 — 10)73.5 — 7.35 gm. = 1000 cc. $\frac{N}{10}$ V. S.

$$= 2BaCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

Each cc. of $\frac{N}{10}$ dichromate = 0.006845 gm. of $Ba(C_2H_3O_2)_2$.

In the analysis the barium compound is dissolved in water, ammonia-water free from carbonate is added, the mixture heated to 70° C., and titrated with the dichromate solution so long as a precipitate is formed.

Soluble barium salts may also be estimated by precipitation with sulphuric acid. The process is the converse of that for sulphuric acid and sulphates (Chapter XXIII. See also page 109).

CHAPTER XXX.

BISMUTH.

THE bismuth in nitric acid solution is treated with a strong solution of oxalic acid in considerable excess, and the mixture shaken up and then set aside to settle.

The supernatant liquid is then poured off and the precipitated oxalate boiled for five or ten minutes with successive quantities of about 50 cc. of water, which converts it into the basic oxalate.

So soon as the supernatant liquid ceases to show an acid reaction the transformation is complete.

The precipitate is then dissolved in dilute sulphuric acid and titrated with $\frac{N}{20}$ potassium permanganate V. S.

The original bismuth solution must be free from hydrochloric acid and must contain just sufficient nitric acid to prevent the precipitation of basic nitrate before the oxalic acid solution is added.

One molecule of oxalic acid corresponds to one atom of bismuth, or $126 = 208$.

The reaction may be represented as follows:

$$Bi(NO_3)_3 + H_2C_2O_4 + H_2O = Bi(OH)C_2O_4 + 3HNO_3.$$

Each cc. of the $\frac{N}{20}$ permanganate solution represents 0.0052 gm. of Bi.

CHAPTER XXXI.

CALCIUM.

ANY calcium salt soluble in water or acetic acid may be estimated as follows:

Dissolve in water and add ammonium hydroxide until the solution is alkaline, and then ammonium chloride and ammonium oxalate. Heat gently until the calcium oxalate has completely separated, collect on a filter, wash thoroughly, dissolve in warm dilute sulphuric acid, and estimate the oxalic acid liberated by means of $\frac{N}{10}$ permanganate. In case the calcium salt is insoluble in water but soluble in dilute acetic acid, it is to be dissolved in the smallest possible quantity of the latter, and the calcium precipitated as oxalate without previous addition of ammonium hydroxide.

Another way is to add to the solution of calcium salt a known volume in excess of a solution of ammonium oxalate, dilute to 200 cc., allow the precipitate to settle, take out 50 or 100 cc. by means of a pipette, and determine the excess of oxalic acid by acidifying with sulphuric acid and titrating with $\frac{N}{10}$ permanganate.

Each cc. of permanganate = 0.0020 gm. Ca;
" " " " = 0.0050 gm. $CaCO_3$;
" " " " = 0.0028 gm. CaO.

Calcium sulphate is estimated by dissolving in water, adding dilute hydrochloric acid, and titrating with $\frac{N}{10}$ barium chloride solution.

Each cc. of $\frac{N}{10}$ $BaCl_2$ V. S. = 0.0068 gm. $CaSO_4$.

Soluble calcium salts may also be estimated as described on page 105.

CHAPTER XXXII.

COPPER.

THIS may be estimated by precipitation as cuprous iodide.

The copper solution, which must be free from nitric or hydrochloric acids, is treated with potassium iodide. The following reaction occurs:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

The cuprous iodide precipitates and the free iodine is titrated with $\frac{N}{10}$ thiosulphate solution.

Each cc. of $\frac{N}{10}$ thiosulphate = 0.01265 gm. of iodine = 0.0159 gm. of $CuSO_4$.

The copper solution should contain at least one per cent of Cu in order to estimate it. If it contains free nitric acid or hydrochloric acid, it must be neutralized by means of sodium carbonate and acetic acid added.

By Sodium Sulphide.

In Ammoniacal Solution. — The sodium sulphide solution should be checked against a solution of copper sulphate of known strength. The titration should be performed between the temperatures of 60° and 80° C., at which temperature the precipitate of oxysulphide (CuO,CuS) subsides readily. The CuS which forms at lower temperature subsides very

slowly. The end point is reached when the further addition of sodium sulphide fails to produce a precipitate, or when the blue color of the titrated liquid is discharged.

In Acid Solution.—The copper solution is diluted to about 200 cc. with hot water in a stoppered flask, acidulated with HCl, and the standard sulphide solution added little by little, replacing the stopper and shaking after each addition until the end point is reached. The CuS formed here subsides quickly.

CHAPTER XXXIII.

GOLD.

THE gold must be in the form of chloride ($AuCl_3$).

To the solution of gold chloride a measured excess of $\frac{N}{1}$ oxalic acid solution is added and the mixture set aside for 24 hours.

The solution is then made up to a definite volume (say 300 cc.). Then by means of a pipette 100 cc. are removed, and the excess of oxalic acid found by titrating with $\frac{N}{10}$ permanganate V. S. in the presence of sulphuric acid.

The reaction is:

$$2AuCl_3 + 3H_2C_2O_4 = 2Au + 6HCl + 6CO_2.$$

Each cc. of $\frac{N}{1}$ oxalic acid solution = 0.0655 gm. of Au, or 0.10101 gm. of $AuCl_3$.

CHAPTER XXXIV.

IRON.

Ferric Salts may be estimated by means of potassium permanganate or dichromate, but they must first be reduced to the ferrous state. The reduction may be accomplished in various ways, as follows:

The ferric salt in solution may be percolated through a column of zinc dust, which reduces it to the ferrous state and the iron may then be estimated in the usual way with permanganate.

Another way for reducing ferric salts is to treat the solution with small pieces of metallic zinc or magnesium and a little sulphuric acid. The reduction is known to be complete when the solution ceases to give a red color with potassium sulphocyanate. The change of color of the ferric solution from dark to light is also an indication of reduction.

When zinc or magnesium are used the metal must be entirely dissolved before titration is begun.

Stannous chloride solution is also employed for reducing ferric salts. This solution is made by dissolving 10 gm. of pure tin in 200 cc. of strong hydrochloric acid and diluting to 1000 cc. It should be freshly made when needed.

After reduction by stannous chloride the titration may be performed with dichromate.

Ammonium bisulphide may also be used as a reducing agent when the titration is to be performed with dichromate.

After reduction by any method the titration should be started without delay, because the iron is rapidly reoxidized upon exposure.

Ferric salts may also be estimated by direct titration with sodium thiosulphate.

ESTIMATION OF METALLIC IRON IN REDUCED IRON.

Professor E. Schmidt, of Marburg, recommends the following process:

Weigh accurately 0.4 gm. of reduced iron, and place in a 100-cc. flask with 10 cc. of water, and add 2 gm. of pure dry iodine.

The iodine combines with metallic iron, but does not react with any ferric oxide which may be present.

$$Fe_2 + 2I_2 = 2FeI_2.$$

Now rinse down the iodine left in the neck of the flask with some water, and add 1 gm. of potassium iodide; when all of the iodine has dissolved, add sufficient water to make 100 cc.; shake the flask and allow to stand for several hours.

Then measure off 50 cc. of the clear liquid and titrate the free iodine with decinormal sodium thiosulphate V. S., using starch as an indicator.

The reaction is thus expressed:

$$I_2 + 2Na_2S_2O_3, 5H_2O = Na_2S_4O_6 + 2NaI + 10H_2O.$$

$$\begin{array}{lll} 2)253 & 2)496 & \\ 10)126.5 & 10)248 & \\ 12.65 \text{ gm.} & 24.8 \text{ gm.} & \text{or } 1000 \text{ cc. } \frac{N}{10} \text{ V. S.} \\ .01265 \text{ gm.} & .0248 \text{ gm. } \text{“} & 1 \text{ cc. } \text{“ } \text{“} \end{array}$$

Example.—Assuming that 9 cc. of the decinormal solution were employed in titrating the 50 cc., then 18 cc. would be required by the entire quantity.

As seen in the above equation, each cc. of the decinormal solution represents 0.01265 gm. of iodine; hence if 18 cc. are employed we have 18×0.01265 gm. $= 0.2277$ gm., the quantity of free iodine.

Then by subtracting this amount from the quantity of iodine taken (2 gms.) we ascertain the quantity which went into combination with the iron, namely, 1.7723 gms. All that is now necessary is to ascertain by calculation the quantity of metallic iron represented by the above weight of iodine.

$$\underset{56}{Fe} + \underset{253}{I_2} = FeI_2;$$

$$\frac{1.7723 \times 56}{253} = 0.3922 + \text{gm.}$$

Thus the 0.40 gm. of reduced iron taken contained 0.3922 + gm. of metallic iron, or 98 per cent.

CHAPTER XXXV.

LEAD.

Lead Oxide or Carbonate are estimated by dissolving in a measured excess of normal nitric acid solution, and then titrating back with normal sodium carbonate or hydroxide solution until a faint milkiness appears, or phenolphthalein which has been added turns red. The quantity of normal alkali solution used is deducted from the quantity of normal acid added, and the remainder multiplied by the factor for the lead salt examined.

Pb = 0.1032 gm.;
PbO = 0.1112 gm.;
$PbCO_3$ = 0.1332 gm.

Lead salts may also be estimated by precipitation with a standard solution of potassium dichromate. The end point is reached when a further addition of a drop of the dichromate solution fails to produce a precipitate. Beale's filter may here be employed, or a neutral solution of silver nitrate may be used as an indicator, by contact on a porcelain slab. The dichromate solution used for precipitating lead is the same as that used for the estimation of barium containing 7.35 gms. in a litre.

The reaction is as follows:

$$2Pb(C_2H_3O_2)_2 + H_2O + K_2Cr_2O_7 = 2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

The lead solution must not contain much free acid. Sufficient sodium acetate is added to saturate the mineral acid and set free an equivalent of acetic acid.

Each cc. of $\frac{N}{10}$ dichromate = 0.01032 gm. Pb;

" " " " = 0.01112 gm. PbO.

Lead may also be estimated by precipitating as oxalate, and then titrating the oxalate with permanganate, or by adding an excess of oxalic acid, and then retitrating with permanganate in an aliquot portion of the supernatant liquid. The lead should be in the form of a soluble salt, such as acetate or nitrate.

A better method is the converse of that described for sulphates (Chapter XXIII). In this the lead salt in solution is titrated with a decinormal solution of potassium sulphate until precipitation is complete or until a drop of the solution ceases to produce a yellow spot upon paper impregnated with potassium iodide and sodium thiosulphate.

The lead should be in the form of nitrate. If any free nitric acid is present this should be neutralized by means of ammonia water. Before applying a drop of the solution to the test paper it is important to allow the suspended lead sulphate to settle, because this will also react with the potassium iodide. The decinormal factors are the same as those given above.

CHAPTER XXXVI.

MAGNESIUM.

MOST magnesium compounds may be converted into the sulphate by evaporating, treating with concentrated sulphuric acid, evaporating to dryness and heating to dull redness to drive off the excess of acid. The heat must not be raised higher than dull redness, otherwise some of the sulphate is apt to be decomposed. Dissolve the residue in water, add a few drops of hydrochloric acid, and determine the sulphuric acid by means of $\frac{N}{10}$ barium chloride V. S.

Each cc. of $\frac{N}{10}$ barium chloride = 0.0012 gm. Mg;
" " " " " = 0.0020 " MgO;
" " " " " = 0.0042 " $MgCO_3$;
" " " " " = 0.0060 " $MgSO_4$.

Estimation as Phosphate.

Magnesium salts may be precipitated as ammonio-magnesium phosphate and the precipitate then titrated with $\frac{N}{10}$ hydrochloric acid, or with uranium solution as directed under estimation of phosphoric acid.

The magnesium in the form of a soluble salt is dissolved in a small quantity of water, at least twice the

quantity of ammonium chloride is added, and then ammonia-water to make strongly alkaline. Then sodium phosphate solution is added in excess, and the mixture allowed to stand twelve hours. The magnesium is thus completely precipitated as ammonio-magnesium phosphate.

This precipitate is separated by filtration and washed, first with a mixture of water, 3 parts and ammonia water, 1 part, and then with 50 or 60 per cent. alcohol to remove the ammonia.

The precipitate is then dissolved in a measured excess of $\frac{N}{10}$ hydrochloric acid V. S., a few drops of methyl orange added, and the excess of acid found by retitrating with $\frac{N}{10}$ potassium hydroxide. The difference between the quantities of acid and alkali solutions used is the quantity of the former which reacted with the ammonio-magnesium phosphate.

Each cc. of $\frac{N}{10}$ hydrochloric acid = 0.0012 gm. Mg;

" " " " " = 0.0020 " MgO.

Or, the precipitate of ammonio-magnesium phosphate may be dissolved in acetic acid and estimated by uranium solution as directed under phosphoric acid.

Each cc. of uranium solution = 0.001695 Mg;

" " " " " = 0.002817 MgO.

CHAPTER XXXVII.

MANGANESE.

A DILUTE, neutral, or faintly acid solution of manganese salt is heated to 80° C., and $\frac{N}{10}$ potassium permanganate solution added, so long as a brownish-red precipitate of hydrated MnO_2 forms and until the occurrence of the characteristic rose color of permanganate in excess. In neutral solution the reaction is exact, but a larger excess of hydrochloric or sulphuric acid causes irregularity. Iron and chromium must also be absent. The manganese compound may be dissolved in nitro-muriatic acid, if necessary boiled, and the excess of acid neutralized. The reaction is written thus:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = K_2SO_4 + 5MnO_2 + 2H_2SO_4;$$

1 cc. of $\frac{N}{10}$ permanganate = 0.00165 gm. of Mn.

Manganese Dioxide, MnO_2.—The estimation of manganese dioxide depends upon the fact that when it is boiled with oxalic acid in the presence of sulphuric acid a definite reaction takes place, as the equation shows:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

In the estimation a measured excess of oxalic acid solution is added, together with some sulphuric acid, and the mixture heated until solution is complete.

The excess of oxalic acid is then found by retitration with standard permanganate solution. It is well to use a normal oxalic acid solution and a decinormal permanganate solution.

0.5 gm. of the dioxide is a convenient quantity to operate upon. Each cc. of decinormal solution represents 0.00433 gm. of MnO_2.

Example.—0.5 gm. of MnO_2 is treated with sulphuric acid and 10 cc. of normal oxalic acid solution, which is equivalent to 100 cc. of decinormal oxalic acid solution, the mixture treated as described above, and upon retitrating 25 cc. of decinormal permanganate are required. Thus:

$$100 \text{ cc.} - 25 \text{ cc.} = 75 \text{ cc.}$$

of $\frac{N}{10}$ oxalic acid went into reaction with the MnO_2. Then

$$75 \times 0.00433 = 0.32475 \text{ gm.};$$

$$\frac{.32475 \times 100}{.5} = 64.95\%.$$

Manganese dioxide may also be estimated by the following method:

0.2 gm. of the substance is placed in a 250-cc. flask, an excess of potassium iodide solution added, and then strongly acidulated with hydrochloric acid. The flask is stoppered, and allowed to stand until the manganese dioxide is completely dissolved. The solution is then diluted with water to the 250-cc.

mark, and 25 cc. of it taken out and titrated with centinormal sodium thiosulphate, using starch solution as the indicator. The method depends upon the fact that MnO_2 when treated with HCl gives off two atoms of chlorine for each molecule of MnO_2, and in the presence of an iodide the chlorine liberates an equivalent of iodine. Hence two atoms of iodine represent one molecule of MnO_2. The reaction is thus expressed:

$$MnO_2 + 4HCl + 2KI = MnCl_2 + 2KCl + I_2 + 2H_2O.$$

Thus each cc. of $\frac{N}{100}$ sodium thiosulphate represents .0012653 gm. of iodine, which is equivalent to 0.004336 gm. of manganese dioxide.

CHAPTER XXXVIII.

MERCURY.

Mercurous Nitrate.—A weighed quantity of the solution is treated with a measured excess of $\frac{N}{10}$ sodium chloride, which precipitates all the mercury as mercurous chloride. The mixture is filtered, the precipitate well washed, and the mixed filtrates titrated with $\frac{N}{10}$ silver nitrate solution, using potassium chromate as indicator. The solution must be neutral.

The quantity of silver solution used is deducted from the quantity of sodium chloride solution added, and the difference is the quantity of the latter which reacted with the mercurous nitrate. This multiplied by 0.0262 gm. gives the quantity of $Hg_2(NO_3)_2$ in the solution taken.

Mercurous Chloride (Calomel).—The mercurous chloride is treated with potassium iodide and $\frac{N}{10}$ iodine solution until it is completely dissolved. The reaction is as follows:

$$Hg_2Cl_2 + 6KI + I_2 = 2HgK_2I_4 + 2KCl.$$

Starch solution is then added, which gives a blue color with the excess of iodine. The mixture is then

titrated with $\frac{N}{10}$ thiosulphate until the blue color disappears, and lastly with $\frac{N}{10}$ iodine until the blue color returns. Subtract the cc. of thiosulphate from the total quantity of iodine added, and the remaining cc. will be the measure of the mercury.

Each cc. $\frac{N}{10}$ iodine = 0.0200 gm. Hg;

" " " " = 0.0235 gm. Hg_2Cl_2.

In the analysis, take to 1 gm. of calomel about 2.5 gms. of potassium iodide and 100 cc. of $\frac{N}{10}$ iodine.

Mercurous Salts other than the chloride may be converted into the chloride by precipitation with sodium chloride, the precipitate well washed, and treated as directed for mercurous chloride.

Mercuric Salts may be converted into mercurous chloride by adding sodium chloride, an excess of ferrous sulphate, and sodium hydroxide to alkaline reaction. The mixture is allowed to stand for a short time, shaking frequently. Then hydrochloric acid is added until the solution becomes clear, and the mercurous chloride white, and free from iron. The precipitate is then separated, washed, and treated as directed under mercurous chloride. The reaction is as follows:

$$2HgSO_4 + 2NaCl + 2FeSO_4 + 6NaOH = Hg_2Cl_2 + Fe_2(OH)_6 + 4Na_2SO_4.$$

Mercuric salts may also be estimated by Personne's method, described under estimation of iodides, page 122.

The mercuric solution must be added to the potassium iodide solution; a reversal of the process is not reliable.

The mercuric salt must be in the form of a neutral solution of mercuric chloride, and it should be considerably diluted, say to 300 or 500 cc., and as a preliminary trial 20 cc. of decinormal potassium iodide solution should be taken, and titrated with the mercuric solution. Two or more titrations should be made, the first will give the approximate figure.

The decinormal solution used in this process contains 33.2 gm. of potassium iodide to the litre, and each cc. represents 0.01 gm. Hg, and 0.0135 gm. $HgCl_2$.

CHAPTER XXXIX.

SILVER.

Silver Salts in neutral solutions may be accurately estimated by means of standard solution of sodium chloride with neutral chromate as indicator. See page 137.

The method of Volhard, in which standard solution of sulphocyanate is used, in the presence of ammonio-ferric sulphate, and nitric acid may also be employed. Its advantage is that it can be used in the presence of nitric acid, which is not the case in the foregoing unless the indicator be left out. The decinormal potassium sulphocyanate solution is made as described on page 129.

CHAPTER XL.

STRONTIUM.

Strontium Oxide and Hydroxide may be estimated by dissolving in water and titrating with decinormal hydrochloric acid in the presence of an indicator. A better way is by residual titration, i.e., adding a measured excess of $\frac{N}{10}$ hydrochloric acid, and retitrating with $\frac{N}{10}$ NaOH in the presence of phenolphthalein after boiling the acid solution.

1 cc. $\frac{N}{10}$ hydrochloric acid = 0.004377 gm. Sr;

" " " " = 0.006077 " $Sr(OH_2)$.

Strontium Carbonate may be estimated by residual titration as above described.

1 cc. $\frac{N}{10}$ hydrochloric acid = 0.007377 gm. $SrCO_3$.

Strontium Chloride may be estimated by precipitating the metal as sulphate by means of potassium sulphate, and then titrating the filtrate containing potassium chloride with decinormal silver nitrate solution, and chromate as indicator.

$$SrCl_2 + K_2SO_4 = SrSO_4 + 2KCl;$$

then

$$KCl + AgNO_3 = AgCl + KNO_3.$$

1 cc. $\frac{N}{10}$ silver nitrate solution = 0.00792 gm. $SrCl_2$.

The same method may be employed for strontium iodide and bromide. These haloid salts may also be titrated direct with silver nitrate, as described on page 119.

Strontium Nitrate may be estimated by adding to its solution an excess of sodium carbonate, thoroughly washing the resulting precipitate of strontium carbonate with hot water, and then estimating the carbonate as described for that salt.

All soluble strontium salts may be estimated by precipitation as oxalate, in the absence of calcium, barium, and other metals precipitable by oxalic acid.

A strong solution of oxalic acid is added in excess, then an equal volume of alcohol. Let stand over night, filter through sand, dry the precipitate thoroughly to expel the alcohol, wash it into a beaker, add dilute sulphuric acid to decompose the oxalate, and titrate with $\frac{N}{10}$ permanganate.

1 cc. $\frac{N}{10}$ permanganate = 0.004377 gm. Sr.

CHAPTER XLI.

TIN.

Metallic Tin or its stannous salt if not already in solution is dissolved in hydrochloric acid, and a tolerable quantity of Rochelle salt is added, and then a strong solution of sodium bicarbonate, until the solution is alkaline. If the solution becomes cloudy upon addition of the sodium bicarbonate, more Rochelle salt must be added. Starch solution is then added and $\frac{N}{10}$ iodine solution from a burette until the blue color appears. See equation below.

Stannous Chloride of Commerce is estimated according to Dietze (*Ph. Ztg.*, 1897, 191) as follows:

One gm. is dissolved in water, a few drops of hydrochloric acid added, and the solution diluted to 100 cc. 25 cc. of this solution are mixed with 1 gm. of tartaric acid, 2 or 3 gms. of sodium bicarbonate, and a few drops of starch solution, and the mixture titrated with $\frac{N}{10}$ iodine solution until a blue color appears. 21.9 cc. to 22.1 cc. of the latter should be employed.

Each cc. of $\frac{N}{10}$ iodine = 0.01125 gm. of $SnCl_2 + 2H_2O$.

The cc. used multiplied by 4 and then by the factor gives the quantity in the 1 gm. taken. This multiplied by 100 gives the per cent. The reaction is as follows:

$$SnCl_2 + 2H_2O + 2HCl + I_2 = SnCl_4 + 2H_2O + HI.$$

CHAPTER XLII.

ZINC.

Zinc Oxide and Carbonate.—Benedikt and Cantor (*Zeit. Angew. Chem.*, 1888, 236, 237) show that the above compounds can be accurately titrated by adding a measured excess of normal acid solution and titrating back with normal alkali, using methyl-orange as indicator.

$$\underset{\substack{2)81\\ 40.5}}{ZnO} + \underset{\substack{2)98\\ 49 = 1000\text{ cc.}\frac{N}{1}\text{ V. S.}}}{H_2SO_4} = ZnSO_4 + H_2O;$$

$$\underset{\substack{2)125\\ 62.5}}{ZnCO_3} + \underset{\substack{2)98\\ 49 = 1000\text{ cc.}\frac{N}{1}\text{ V. S.}}}{H_2SO_4} = ZnSO_4 + H_2O + CO_2.$$

1 cc. $\frac{N}{1}$ H_2SO_4 = 0.0325 gm. Zn;
" " " = 0.0405 " ZnO;
" " " = 0.0625 " $ZnCO_3$.

Zinc as Oxalate.—The zinc salt, in solution preferably as sulphate and neutral in reaction, is treated with an excess of a strong solution of oxalic acid, and then a volume of strong alcohol equal in bulk to the zinc solution is added. This is allowed to stand 12 hours, and then the precipitated zinc oxalate separated by filtration through a plug of asbestos, and thoroughly

washed with alcohol, and dried in air-bath. The asbestos plug and precipitate are placed in hot dilute sulphuric acid, by which the oxalate is dissolved, and the mixture titrated with $\frac{N}{10}$ potassium permanganate solution.

Each cc. of $\frac{N}{10}$ permanganate = .003258 gm. of Zn;

" " " " = .004058 " of ZnO;

" " " " = .008058 " of $ZnSO_4$.

Zinc Dust.—Zinc dust is generally a mixture of metallic zinc, zinc oxide, and often some zinc carbonate. It is largely used as a reducing agent, and its value in this respect is proportionate to the metallic zinc it contains. Hence it is important to be able to estimate the quantity of free metal in a sample. This may be done as follows:

A weighed portion of the zinc dust, free from lumps, is introduced into a flask provided with a ground-glass stopper, and a measured excess of a centinormal solution of iodine added and the mixture digested for some time. The metallic zinc is acted upon by the iodine, and zinc iodide is formed; the oxide is not affected.

When the reaction is completed, the excess of iodine is determined by retitration with centinormal sodium thiosulphate solution, and the quantity required deducted from the quantity of iodine added.

Each cc. of $\frac{N}{100}$ iodine V. S. = 0.0003244 gm. of metallic zinc.

PART III.

CHAPTER XLIII.

SANITARY ANALYSIS OF WATER.

In collecting samples of water great care must be exercised in order to secure a fair representation of the water and to avoid the introduction of foreign matters.

The samples should be collected in clean glass-stoppered bottles having a capacity of from 2 to 5 pints.

It is well to completely fill the bottle with water, then empty it, and again fill with the water to be analyzed.

In taking samples from lakes, reservoirs, or slow streams the bottle should be submerged, so as to avoid collecting any water that has been in direct contact with the air.

In collecting from pump-wells a few gallons should be pumped out before taking the sample in order to remove that which has been standing in the pump.

If the public water-supply is to be analyzed, take the water from a hydrant communicating directly with the street main, and not from a cistern.

At the time of collecting, a record should be made of those surroundings and conditions which might influ-

ence the character of the water, such as proximity of cesspools, sewers, stables, and factories.

It should also be noted whether the sample is from a deep or shallow well, a river, spring, or artesian well.

The nature of the soil and the different strata of the locality must also be taken into account.

The sample should be kept in the dark and analyzed with as little delay as possible.

Color.—This may be taken by looking down through a column of water in a colorless glass tube about two feet long, standing upon a piece of white paper.

A comparison is made with a second tube containing distilled water.

Another way of determining the color is by the use of a colorless glass tube two feet long and two inches in diameter, closed at each end, with disks of colorless glass cemented on, but having a small opening at one end for filling and emptying the tube.

To use this tube, it is half filled with the water to be examined and placed in a horizontal position. A piece of white paper is held at one end of the tube, and then by looking through from the other end the color of the liquid is observed, and a comparison of tint made between the lower half of the tube containing the water and the upper half containing air.

Odor.—Three or four ounces of water are placed in a small flask fitted with a cork through which is passed a thermometer; the flask is placed in a water-bath and heated to 100° F. The flask is then shaken, the cork withdrawn, and the odor immediately observed.

In this way, satisfactory and uniform tests are obtained, and a practised nose can frequently detect pollution.

Reaction.—This may be determined by the use of a neutral solution of litmus. If an acid reaction is obtained, the water should be boiled in order to determine if it is due to carbonic acid; if the red color disappears upon boiling, the acid reaction is due to carbonic acid.

Phenolphthalein or lacmoid may also be used for this purpose.

Suspended Matter.—A litre of the turbid water is passed through a dried and weighed filter. The filter is then again dried and weighed, and the increase in weight represents the suspended matter in one litre of the water.

TOTAL SOLIDS.

A platinum dish having a capacity of about 120 cc. is heated to redness, then cooled under a desiccator, and weighed. 100 cc. of the water is then introduced and evaporated over a low-temperature burner at a moderate heat. When the residue appears dry the heat may be increased by placing the dish in an air oven kept at a temperature of about 212° F. until it ceases to lose weight; finally cool under a desiccator, and weigh. In waters of exceptional purity it may be advisable to use larger quantities, such as 250 cc.

The increase in weight of the dish represents approximately the total solids contained in the water taken.

If the solid residue does not exceed 57 parts per 100,000, no reason is afforded for rejecting the water for domestic use. It has been found that the figure for total solids obtained thus, does not truly represent the sum of the organic and mineral matters in all cases.

Experiments have been made with urea dissolved in

varying quantities of water. Where the solution contained 1 gm. of urea the residue after evaporation varied from 0.98 to 0.007 gm.

Besides the possible loss of organic matter during the evaporation, some of the mineral constituents may retain with great obstinacy, large quantities of water in the form of water of crystallization, which would cause an error in the opposite direction.

Thus the determination of total solids is only an approximation.

ORGANIC AND VOLATILE MATTER—LOSS ON IGNITION.

Though the mineral matter in a water must to some extent be taken into account in judging of a water, the organic matter is of far greater importance. The really injurious matters are more probably the organic.

It is therefore important to determine as near as possible their quantity and nature.

It was naturally supposed that by igniting the residue obtained from evaporation of the water, the organic matter would be burned out, and that the loss of weight would then represent the organic matter. But as waters ordinarily contain some earthy carbonates, which upon ignition are deprived of carbonic-acid gas and converted into oxides, it was customary to add a few drops of carbonic-acid water or ammonium carbonate to the ash, and then dry and weigh the residue.

Ignition, however, decomposes other salts which may be contained in water, and may even volatilize some wholly; therefore the loss on ignition cannot be truly called the organic matter. Hence the expressions "Organic and Volatile Matter," and "Loss on Ignition."

Frankland recommends ignition as a rough qualita-

tive test for the presence of organic matter, the degree of blackening which takes place, giving some idea of the probable amounts of organic matter present.

CHLORINE

may be estimated by the use of decinormal or centinormal silver-nitrate solution; but analysts generally use a solution of such strength that 1 cc. will represent 0.001 gm. of chlorine.

Standard Silver-nitrate Solution. — Dissolve 4.794 gms. of pure recrystallized silver nitrate in sufficient water to make 1000 cc.

Potassium-chromate Solution.—Five gms. of neutral potassium chromate are dissolved in 100 cc. of water and a weak solution of silver nitrate added, drop by drop, until a slight permanent red precipitate is produced, which is allowed to settle in the bottle, or separated by filtration.

The Process.—Measure out 100 cc. of the water to be analyzed into a beaker or white basin; add a few drops of the potassium-chromate solution; then run in slowly from a burette, the silver-nitrate solution until a slight red tint appears. Note the number of cc. of silver solution used. Each cc. represents 0.001 gm. (1 milligramme). If the chlorine is present in small quantity, about 250 cc. of the water should be evaporated to about one fifth before titrating with the silver-nitrate solution.

Example.—100 cc. of water taken, 4 cc. of silver solution consumed; thus showing that the 100 cc. of water contained 0.004 gm. of chlorine, or 100,000 cc. contained 4 gms.

Multiplied by 10 gives parts per million.

The water must be perfectly neutral before titration. If acid, it must be shaken with a little pure precipitated calcium carbonate.

AMMONIA.

When organic matter decomposes spontaneously, it first forms ammonia, then nitrites, and finally nitrates. Thus the presence of ammonia in water is generally conceded to indicate decomposing organic matter, and hence its determination is an important part of the sanitary examination of water.

The ammonia is generally spoken of as free ammonia and albuminoid ammonia, or, more properly, as ammonium salts and ammonia from organic nitrogen.

The sanitary examination of a water should always include a quantitative determination of nitrogen in both compounds.

The process requires several solutions and considerable care in manipulation. The solutions required are:

1. *Nessler's Solution*, made by dissolving 35 gms. of potassium iodide in 100 cc. of water and 17 gms. of mercuric chloride in 300 cc. of water. The liquids may be heated to aid solution, but if so, must be again cooled. When solution is complete, add the latter to the former until a permanent precipitate is produced; then dilute with a 20% solution of sodium hydroxide to 1000 cc. Now add mercuric-chloride solution again until a permanent precipitate is formed. Let the mixture stand until settled, then decant off the clear solution for use. The bulk of the solution should be kept in a well-stoppered bottle, and a small quantity transferred from time to time to a small bottle, from which it should be used. This solution

improves on keeping, and reacts with extremely minute quantities of ammonia.

2. *Sodium-carbonate Solution.*— A 20% solution of pure freshly-ignited sodium carbonate in water free from ammonia.

3. *Standard Ammonium-chloride Solution.*—Dissolve 0.3138 (*.314) gm. of pure ammonium chloride in water to 100 cc. For use dilute 1 cc. of this solution with 99 cc. of distilled water free from ammonia. Each cc. of this solution contains 0.00001 gm. of ammonia.

4. *Alkaline Potassium-permanganate Solution.*—Dissolve 200 gms. of pure potassium hydroxide and 8 gms. of pure potassium permanganate in sufficient ammonia-free water to make 1000 cc.

5. *Ammonia-free Water.*—If the distilled water of the laboratory gives a reaction with Nessler's solution, it should be treated with sodium carbonate, about 1 gm. to the litre, and boiled until one fourth has been evaporated.

A good clear hydrant water when treated with sodium carbonate and distilled yields ammonia-free water. The first portion which comes over has of course some ammonia in it, and small portions of the distillate should be tested with Nessler's reagent until no more reaction is obtained; the remainder, except the very last portion, should be collected.

Ammonia-free water may also be obtained by distilling water acidulated with sulphuric acid. In the first two processes the ammonia is converted into a volatile salt and is easily dissipated, or appears in the first distillate; in the last process it is converted into a non-volatile salt, which does not distil over.

Apparatus Required.—A still, consisting of a glass

retort, having a capacity of about 700 cc., which is connected with a Liebig's condenser by an air-tight joint.

The heat is applied by means of a low-temperature burner, the iron ring of which is removed, so that the retort rests directly upon the gauze. (See Fig. 45.)

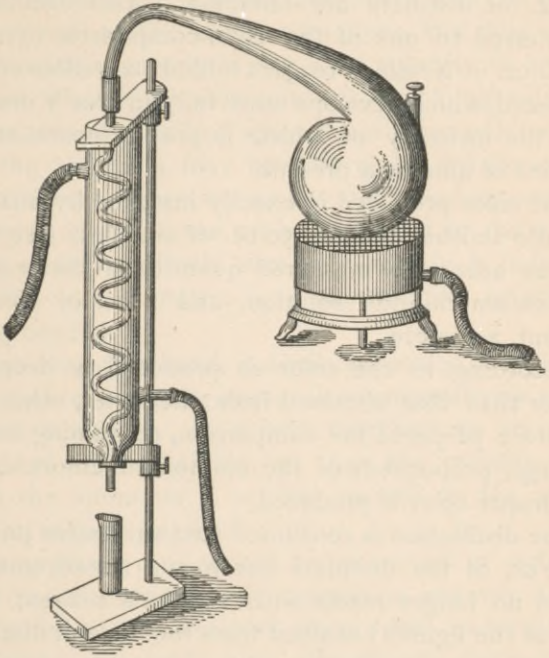

FIG. 45.

Cylinders for Comparative-color Tests.—These cylinders are made of pure colorless glass, about one inch in diameter, having a capacity of about 100 cc. and graduated at 50 cc. These should either have a milk-glass foot, or should stand upon white paper. Two or more of these are required.

The Process.—The retort and condenser are thoroughly rinsed out with ammonia-free water. Then 500 cc. of the water to be tested are introduced, and about 5 cc. of sodium-carbonate solution added to make the water alkaline. The water is then gently boiled until 50 cc. of distillate are obtained. This distillate is transferred to one of the color-comparison cylinders and 2 cc. of Nessler's reagent added; a yellow color is produced, which develops more fully in 3 or 5 minutes, and the intensity of which is proportionate to the amount of ammonia present.

The color produced is exactly matched by introducing into another cylinder 50 cc. of ammonia-free water and an accurately measured quantity of the standard ammonium-chloride solution, and 2 cc. of Nessler's reagent, as before.

According as the color so produced is deeper or lighter than that obtained from the water, other solutions are prepared for comparison, containing smaller or larger proportions of the ammonium chloride, until the proper color is produced.

The distillation is continued, and successive portions of 50 cc. of the distillate taken and tested, until the liquid no longer reacts with Nessler's reagent. The sum of the figures obtained from the several distillates gives the total ammonia, existing in ammonium compounds, in the 500 cc. of water taken.

The residue in the retort serves for the determination of the nitrogen of the organic matter, which is converted by the alkaline permanganate into ammonia (*albuminoid ammonia*).

50 cc. of the alkaline permanganate are placed in a porcelain dish of about 150 cc. capacity, the dish nearly

filled with distilled water, and then the liquid boiled down to 50 cc.

This is added to the residue in the retort, the distillation resumed, and the ammonia estimated in each 50 cc. of the distillate, as before described.

It is the practice of some analysts to mix the distillates of each of the above operations, and thus make determinations merely of the total quantity of ammonia and albuminoid ammonia. By so doing valuable information may be lost, since it has been pointed out that the ammonia may be differently distributed in the distillates, according to the state, decomposing or otherwise, in which the ammonia exists in the water. If the ammonia distils over very rapidly, it indicates that the organic matter is in a putrescent or decomposing condition.

If, on the other hand, it distils gradually, it indicates the presence of organic matter in a comparatively stable or fresh condition. It is best, therefore, to keep the record of each distillate, so that the rapidity with which the ammonia is set free, as well as the actual amount, may be known.

The greatest care should be exercised in order to avoid the introduction of ammonia in any way during the course of the analysis, since small quantities of ammonia compounds and nitrogenous matters are everywhere present. All measuring-vessels, cylinders, etc., should be thoroughly rinsed before using.

NITROGEN AS NITRATES.

Solutions Required.—*Acid Phenyl Sulphate.*—18.5 cc. of strong sulphuric acid are added to 1.5 cc. of

water and 3 gms. of pure phenol. This should be preserved in a tightly-stoppered bottle.

Standard Potassium Nitrate.—0.722 gm. of pure potassium nitrate, previously heated to a temperature just sufficient to fuse it, is dissolved in water, and the solution made up to 1000 cc. 1 cc. of this solution will contain .0001 gm. of nitrogen.

The Process.—A measured volume of water is evaporated just to dryness in a platinum or porcelain dish, 1 cc. of the acid phenyl sulphate added and thoroughly mixed with the residue by means of a glass rod, then 1 cc. of water and three drops of strong sulphuric acid, and the dish gently warmed. ,The liquid is then diluted with about 25 cc. of water, a slight excess of ammonium hydroxide added, and the solution made up to 100 cc.

The reactions are:

$$\underset{\text{Acid phenyl sulphate.}}{HC_6H_5SO_4} + 3HNO_3 = \underset{\text{Trinitrophenol (picric acid).}}{HC_6H_2(NO_2)_3O} + H_2SO_4 + 2H_2O$$

$$HC_6H_2(NO_2)_3O + NH_4OH = \underset{\text{Ammonium picrate.}}{NH_4C_6H_2(NO_2)_3O} + H_2O.$$

The nitric acid used in the above equation is derived from the potassium nitrate by the action of sulphuric acid.

The ammonium picrate imparts a yellow color to the solution, the intenstiy of which is proportional to the amount present.

Five cc. of the standard potassium-nitrate solution are now similarly evaporated in a platinum basin, treated as above, and made up to 100 cc. The color produced

is compared to that given by the water; and one or the other of the two solutions diluted until the tints agree.

The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate present, as the following example will show. Five cc. of the standard nitrate are treated as above, and made up to 100 cc. Each cc. represents 0.0001 gm. of nitrogen.

$$\begin{array}{r} .0001 \\ 5 \\ \hline .0005 \text{ gm. N per 100 cc.} \\ 10 \\ \hline .0050 \text{ gm. N per 1000 cc.} \end{array}$$

Suppose 100 cc. of water similarly treated are found to require dilution to 150 cc. before the tint will match that of the standard; then

$$100 : 150 :: .005 : x. \quad x = 0.0075.$$

That is, the water contains 7.5 milligrams of nitrogen as nitrate per litre.

Care should be taken that the same quantity of acid phenyl sulphate is used for the water and for the comparison liquid, otherwise different tints instead of depths of tints are produced.

With river or spring waters 25 to 100 cc. should be evaporated for the test, but with subsoil and other waters which probably contain much nitrates 10 cc. will be sufficient.

The Copper-zinc Process.—500 cc. of the water are acidulated with oxalic acid, and half of this is poured into each of two wide-mouthed bottles. Into one of these is put a copper-zinc couple, made by taking a piece of sheet zinc (4 × 6 in.) and rolling it into a loose coil and immersing it in a 1.5-per-cent. solution of copper sulphate until the surface is covered with an even layer of copper.

Cork both bottles and let stand 24 hours. Remove 50 cc. from each bottle and Nesslerize as directed under Ammonia.

The difference between the two readings gives the ammonia due to the reduction of the nitrates and nitrites present. The nitrogen in the nitrites, which is separately determined, must be subtracted, when the remaining nitrogen will be that from the nitrates.

NITROGEN AS NITRITES.

Solutions Required.—1. *Naphthylammonium Chloride* (*Naphthalamin Hydrochlorate*).—Saturated solution in water free from nitrites. It should be colorless (0.5 gm. dissolved in 100 cc. of boiling water). This solution should be kept in a glass-stoppered bottle with a little animal charcoal, which will keep the solution colorless.

2. *Sulphanilic Acid* (*Para-amido-benzene—Sulphonic Acid*).—A saturated solution in water free from nitrites (1 gm. in 100 cc. of hot water).

Hydrochloric Acid.—25 cc. of concentrated pure hydrochloric acid mixed with 75 cc. of water free from nitrites.

Standard Sodium Nitrite.—0.275 gm. pure silver nitrite is dissolved in pure water, and a dilute solution of pure sodium chloride added until a precipitate ceases to form. It is then diluted with pure water to 250 cc. and allowed to stand until clear. For use 10 cc. of this solution are diluted to 100 cc. It must be kept dark. One cc. of the dilute solution is equivalent to .00001 gm. of nitrogen.

A standard solution of silver nitrite is used by some chemists, but the above is said to give better results.

The Process.—100 cc. of the water is placed in one of the color-comparison cylinders, the measuring-vessels and cylinder having previously been rinsed with the water to be tested. By means of a pipette introduce into the water 1 cc. each of the solutions of sulphanilic acid, dilute hydrochloric acid, and naphthylammonium-chloride solution in the order named. It is convenient to have three pipettes—one for each of these solutions, and to use them for no other purpose. In all cases the pipettes should be rinsed with ammonia-free water before using them. Into another clean comparison-cylinder introduce 1 cc. of the standard nitrite solution and make up to 100 cc. with pure water; then add the same reagents as were added to the water in the other cylinder.

A pink color is produced in the presence of nitrites, which requires in dilute solutions half an hour for complete development. At the end of that time the darker solution is diluted with water until the tints are matched, and the calculation made as explained under nitrates.

The reactions are explained by the following equations:

$$\underset{\text{Sulphanilic acid.}}{C_2H_4NH_2HSO_3} + HNO_2 = \underset{\text{Para-diazo-benzene-sulphonic acid.}}{C_6H_4N_2SO_3} + 2H_2O;$$

$$C_6H_4N_2SO_3 + \underset{\substack{\text{Naphthammonium}\\ \text{chloride.}}}{C_{10}H_7NH_2Cl} = \underbrace{C_{10}H_6(NH_2)NNC_6H_4HSO_3}_{\substack{\text{Azo-alpha-amido-naphthalene-}\\ \text{parazo-benzene-sulphonic acid.}}} + HCl.$$

The last-named body gives the color to the liquid.

Example.—Suppose that 100 cc. of the water require dilution to 125 cc. in order to bring it to the same tint as that produced by 1 cc. of the standard nitrite solution, which contains .00001 gm. of nitrogen as nitrite.

100 : 125 :: .00001 : x. 0.0000125 gm. in 100.

That is, 100 cc. of water contain 0.0000125 gm. of N; 0.0125 gm. in 100,000 cc.

OXYGEN-CONSUMING POWER.

Potassium permanganate readily yields up its oxygen, especially in the presence of a strong mineral acid, as sulphuric. It oxidizes many salts, and organic matter.

This property led to the idea that this salt may be used for burning up (chemically speaking) the organic matter in water, and that the quantity of permanganate used could be relied upon as a means of measuring the organic matter in water.

This method does not distinguish between animal and vegetable matter, nor does the quantity of

permanganate consumed represent only the organic matter.

The organic matters in water are very variable in character and condition, and their oxidability is subject to much difference.

Nevertheless as a high oxygen-consuming power certainly indicates pollution by organic matter, the process is of considerable value.

The following is a convenient method for approximating the oxygen-consuming power of a water:

Solutions Required.—*Potassium Permanganate.*—0.395 gm. of pure potassium permanganate is dissolved in distilled water, and the solution made up to 1000 cc. 1 cc. of this solution will yield under favorable circumstances 0.0001 gm. of oxygen.

Diluted Sulphuric Acid.—50 cc. of pure sulphuric acid are mixed with 100 cc. of water, and then just sufficient of the permanganate solution added to give the mixture a faint pink color, which remains after standing in a warm place four hours.

The Process.—Five stoppered bottles having a capacity of 500 cc. are thoroughly cleansed with strong sulphuric acid and then carefully rinsed with pure water, and 250 cc. of the water to be tested put into each one. 10 cc. of the dilute sulphuric acid is then added to each, together with regularly increasing quantities of the standard permanganate, say 2, 4, 6, 8, and 10 cc., respectively.

At the end of an hour they should be examined, to see which, if any, are decolorized. At the end of the fourth hour they should again be examined, and again at the expiration of twenty-four hours.

If all of the bottles are decolorized at or before the

fourth hour an additional 10 cc. of the permanganate solution should be added to each bottle.

With ordinary waters the first and probably the second bottle will be decolorized, while a little color will remain in the third, and the color in the fourth and fifth will be but little diminished. In this way an approximate figure for the oxygen-consuming power of the water may be obtained, which in most cases is all that is necessary. If a closer figure is desired, the experiment may be repeated, using quantities of permanganate intermediate between those marking the limits of the reaction.

Thus if the second bottle is decolorized and a faint color still remains in the third, repeat the experiment with 5 cc. of the permanganate.

This method of procedure has an advantage over some of the other processes, because the rate of oxidation can easily be seen. This is considered by some to be of more importance than the actual amount of oxygen consumed.

It must be remembered that nitrites, ferrous salts, sulphides, etc., consume oxygen as well as organic matter. It is therefore important to boil water containing hydrogen sulphide in order to drive the latter off. Nitrites may be removed by treating the water with sulphuric acid, and boiling. The nitrite is thus converted into nitrous acid, which is driven off by the heat. Or the oxygen required to convert the nitrites present into nitrates may be deducted from the total amount of oxygen consumed. 14 parts of nitrogen as nitrite require 16 parts of oxygen for oxidation into nitrate.

PHOSPHATES.

Solutions Required.—*Ammonium Molybdate.*—Made by dissolving 10 gms. of molybdic anhydride in a mixture of 15 cc. of concentrated ammonia (sp. gr. .900) and 25 cc. of water. This solution is poured slowly, and with constant stirring, into a mixture of 65 cc. of concentrated nitric acid (sp. gr. 1.4) and 65 cc. of water, and allowed to stand until clear. It should be kept dark.

The Process.—One litre of the water is evaporated to about 50 cc.; a few drops of a dilute solution of ferric chloride are added, followed by a slight excess of ammonia. Ferric hydroxide is thus precipitated, which carries down with it all the phosphate. This precipitate is separated by filtration, dissolved on the filter in the smallest possible quantity of hot dilute nitric acid, and a little water passed through the filter. The filtrate and washings should not exceed 5 cc., and should, if more, be evaporated to this bulk.

The solution is now heated nearly to boiling and 2 cc. of the ammonium-molybdate solution added. If after half an hour an appreciable precipitate is formed, it is collected on a small weighed filter and its weight found after thorough drying. This weight, multiplied by 0.05 gives the amount of PO_4. If the quantity is too small to be collected and weighed in this manner, it is usually reported as "traces," "heavy traces," or "very heavy traces."

HARDNESS.

The hardness of water, that is, its soap-destroying power, is due principally to the presence of calcium salts; but salts of magnesium, iron, and other metals may also contribute to this effect.

Two kinds of hardness are recognized:

1. "Temporary," which is due to the presence in water of the acid carbonates of calcium, magnesium, etc. By boiling, these salts are decomposed, the carbonic-acid gas being driven off, and the neutral carbonate formed, which is precipitated. Thus the water loses its hardness upon boiling.

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

2. "Permanent" hardness is due to the presence in water of salts of the above-mentioned metals which are not removed by boiling, such as the sulphates.

Hardness is estimated by means of a standard soap solution.

Many samples of water possess both temporary and permanent hardness, and it is sometimes desirable to estimate them separately.

The total hardness is estimated in one sample, and the hardness in another sample is determined after boiling and filtering off the precipitated calcium carbonate.

The hardness found after boiling is the permanent hardness, and is the most objectionable form. The difference between the total and permanent hardness is the temporary hardness. To express the hardness in some tangible form, the usual custom in this country and in England is to give results in the corresponding amounts of calcium carbonate, i.e., practically to determine the amount of soap destroyed by a measured quantity of water, and then to state the results as the amount of calcium carbonate which would destroy that quantity of soap.

The reaction which takes place when soap is added to a hard water, is illustrated in the following equations:

$$\underset{\text{Acid calcium carbonate.}}{CaH_2(CO_3)_2} + 2\underset{\text{Sodium stearate (Soap).}}{NaC_{18}H_{35}O_2} = \underset{\text{Calcium stearate.}}{Ca(C_{18}H_{35}O_2)_2} + Na_2CO_3 + H_2O + CO_2;$$

or,

$$\underset{\text{Calcium sulphate.}}{CaSO_4} + 2NaC_{18}H_{35}O_2 = Ca(C_{18}H_{35}O_2)_2 + Na_2SO_4.$$

The calcium stearate, which is an insoluble calcium soap, is precipitated in both cases as a white curd-like mass.

The method for estimating hardness in water by the use of soap solution is known as Clark's method.

Solutions Required.—*Standard Soap Solution.*—Dissolve 10 gms. of shavings of air dried Castile soap in a litre of dilute alcohol. Filter the solution if it is not clear, and keep it in a tightly-stoppered bottle.

Standard Calcium Chloride Solution.—Dissolve 1 gm. of pure calcium carbonate in the smallest excess of hydrochloric acid, then carefully neutralize with ammonia water, and add sufficient water to make up to one litre.

One cc. of this solution will contain the equivalent of 0.001 gm. of calcium carbonate. This solution is used for determining the strength of the soap solution, which is done as follows:

Measure out 10 cc. of this solution, add 90 cc. of distilled water, and run in the soap solution, drop by drop, from a burette until a lather is formed, which remains

for five minutes. Note the number of cc. of soap solution used.

We now repeat the experiment with 100 cc. of distilled water. The amount of the soap solution required to produce a permanent lather with the distilled water must be deducted from the amount used in the first test. Usually it will be about one half or one cc.

The 10 cc. of the calcium chloride solution contained the equivalent of 0.010 gm. of $CaCO_3$. Suppose in the above-mentioned test 8.5 cc. of the soap solution were used to produce a permanent lather, and 0.5 cc. were used by the distilled water. Then 8 cc. were used to precipitate 0.010 gm. of $CaCO_3$. Thus each cc. of this soap solution will represent $\frac{1}{8}$ of .010 gm. = .00125 of calcium carbonate.

The soap solution may either be used as it is, or it may be diluted with dilute alcohol so that about 10.5 or 11 cc. of it will be required to produce a permanent lather with 10 cc. of the standard calcium chloride solution. If so diluted each cc. will represent 0.001 gm. of $CaCO_3$.

This is a convenient strength, because if 100 cc. of water are operated upon, each cc. of the soap solution used will represent 1 part of $CaCO_3$ in 100,000 parts of water.

Measure 100 cc. of the water into a well-stoppered bottle having a capacity of about 250 or 300 cc. Add the soap solution gradually from a burette, one cc. at a time at first, and smaller quantities towards the end of the operation, shaking well after each addition until a soft lather is obtained, which if the bottle is placed at rest on its side, remains continuous over the whole surface for five minutes.

The soap should not be added in large quantities at a time, even if the volume required is approximately known.

If magnesium salts are present, a kind of scum (simulating a lather) will be seen before the reaction is completed. The character of this scum must be carefully watched, and the soap solution added very carefully, with an increased amount of shaking after each addition. The point when the false lather due to the magnesium salt ceases and the true persistent lather is produced is comparatively easy to distinguish.

If more than 23 cc. of the soap solution are consumed by the 100 cc. of water, a smaller quantity of water should be taken (say 50 or 25 cc.) and made up to 100 cc. with distilled water, recently boiled. In such case the quantity of soap solution used must be multiplied by 2 or 4.

If the first-mentioned soap solution is used each cc. represents 0.00125 gm. If the second solution is used each cc. represents 0.001 gm. of $CaCO_3$, and if 100 cc. of water are acted upon each cc. represents 1 part of $CaCO_3$ in 100,000.

If 70 cc. of water are acted upon, instead of 100 cc., each cc. of soap solution used represents 1 gm. per 70,000 cc., which corresponds to 1 gr. per imperial gallon (70,000 grs.) or 1 degree of hardness.

These estimations are, however, only approximate, for the lather does not form until the reaction between the soap and the calcium in the water is completed, and then the quantity of soap solution required to produce the lather depends upon its strength.

Dr. Clark, the originator of this method, has shown that 1000 grains of distilled water (free from hardness)

require 1.4 measures of soap solution, each measure being the volume of 10 grains of distilled water at 16° C.

For Permanent Hardness.—To determine the hardness after boiling, a measured quantity of water must be boiled briskly for half an hour, adding distilled water from time to time to make up the loss by evaporation. At the end of the half-hour allow the water to cool, make up to its original volume with recently boiled and cooled distilled water, filter rapidly, and test in the same manner as described above. One half or one cc. is deducted from the soap solution used, for the calculation.

Among German chemists it is customary to designate the soap-destroying power equivalent to 1 part of CaO in 100,000, as one degree of hardness.

Among French chemists each degree of hardness represents 1 part of $CaCO_3$ in 100,000.

INTERPRETATION OF RESULTS.

Statement of Analysis.—The composition of water is generally expressed in terms of a unit of weight in a definite volume of liquid, but no fixed standard is used, the proportions being expressed by some analysts in parts per million, by others in parts per hundred thousand. Sometimes, generally by English chemists, the figures are given in grains per imperial gallon of 70,000 grains; less frequently, in grains per U. S. gallon of 58,328 grains.

In order to pass judgment upon the analytical results from a sample of water, the analyst must know to which class of water it belongs—whether river-water, well-water, or artesian-well water. He must know something of the soil and geological character of the locality from which the water is obtained, as well as

other conditions of the locality which might affect the quality of the water, such as proximity of stables, cesspools, sewers, factories, etc.

Color.—Water of the highest purity is clear, colorless, odorless, and nearly tasteless. But the color of water is no indication of its quality. A turbid or colored water is not necessarily a dangerous one, neither is a clear, colorless water always a safe water.

Odor.—For comfort, if for nothing else, potable water should be free from odor. Water sometimes has an unpleasant odor and taste, yet it may be used with perfect safety for domestic purposes. At other times the odor may give rise to suspicions which a subsequent examination may confirm. Thus by the odor alone the safety of the water cannot be told.

Total Solids.—This is intended to represent the total solid matters dissolved in the water; but since much of the organic matter as well as some of the inorganic matter is volatilized by evaporation, the total solids obtained by this method are only the total non-volatile solids. The indication is thus lower than it should be. On the other hand, certain salts, especially calcium sulphate, retain water of crystallization, thus producing an effect in the opposite direction.

The total solids so obtained, contain both organic and inorganic matters, either of which may be injurious or not. Mineral waters contain large quantities of inorganic salts. Much smaller quantities of total solids in other waters might indicate pollution.

Large quantities of mineral solids, especially of marked physiological action, are known to render water non-potable; but no *absolute* maximum or minimum can be assigned as the limit of safety. An arbitrary

limit has, however, been fixed by sanitary authorities of 60 parts per 100,000; and if the solid residue does not exceed 57 parts per 100,000, there is no reason for rejecting a water. Many waters, especially artesian waters, which are in constant use, contain much larger quantities.

The loss on ignition should never reach 50 per cent of the total residue.

Chlorine in potable waters is very largely derived from sodium and potassium chlorides of urine and sewage.

Food contains considerable amounts of chlorides, and still more is added by way of condiment in the shape of salt. The chlorine thus taken into the system is again thrown off in the excreta, and thus appears in the sewage; hence the presence of large quantities of chlorine in water is taken as an indication of pollution. Urine contains about 500 parts of chlorine per 100,000. The average quantity found in sewage is about 11.5 parts per 100,000. Over 5 parts per 100,000 of chlorine in a water may be considered, in most cases, to be due to pollution of the water by sewage or animal excretions. The chlorine itself is not a dangerous constituent of water, but its presence in large quantities is an unfavorable indication. Nevertheless too much dependence must not be put upon the amount of chlorine in water as a means of judging of its purity, for dangerous vegetable matter may exist in it without its presence being indicated by chlorine. The maximum amount of chlorine per 100,000, given by the Rivers Pollution Commission, is 21.5 parts, the minimum 6.5 parts. Various conditions, however, which affect the proportion of chlorine, such as the

nature of the strata through which the water passes, proximity to the sea, etc., must be taken into account.

Nitrogen in Ammonia.—Ammonium compounds are usually the result of the spontaneous putrefactive fermentation of nitrogenous organic matter; nitrites are then formed, and finally nitrates. Ammonium compounds may also result from the reduction of nitrites and nitrates in the presence of excess of organic matter. Therefore in either case the presence of ammonia suggests contamination.

This fact is so generally conceded that the estimation of ammonia in water, is a very important part of the sanitary examination.

In the water from deep wells an excess of ammonia is nearly always found, but its presence here cannot always be considered an adverse condition, since it is derived largely from the decomposition of nitrates, and shows previous contamination; but the water having undergone extensive filtration and oxidation, its organic matter is presumably converted into harmless bodies.

Rain-water often contains large proportions of ammonium compounds, which it dissolves out of the air in its descent; but here also, this fact cannot condemn the water, since it does not indicate contamination with dangerous organic matter.

An average of 71 samples of rain-water collected in England contained 0.05 parts per 100,000, including an exceptional maximum of 0.21 parts.

Fischer ("Chemische Technologie des Wassers") gives two analyses of typically good wells, containing respectively 0.048 and 0.044 parts per 100,000, and of

two typically bad shallow wells, containing respectively 0.084 and 2.227 parts per 100,000.

Albuminoid Ammonia.—If water yields no albuminoid ammonia it is free from recently added organic contamination. If it contain more than 0.01 part per 100,000 it is looked upon as suspicious, and when it reaches 0.015 parts per 100,000 it is to be condemned. When free ammonia is present in considerable quantity, then the albuminoid ammonia becomes suspicious when it reaches 0.005 parts per 100,000. An opinion should not, however, be formulated without a knowledge of the source of the water; for, as has been said before, free ammonia may exist in large quantities in deep wells without indicating contamination. Wanklyn gives the following standards:

High purity.....	.000	to	.0041	of albuminoid ammonia	per	100,000
Satisfactory purity	.0041	to	.0082	" "	"	"
Impure	over		.0082	" "	"	"

In the absence of free ammonia he does not condemn a water unless the albuminoid ammonia exceeds .0082 parts per 100,000; but he condemns a water yielding 0.0123 parts of albuminoid ammonia, under all circumstances.

Nitrogen as Nitrates.—Nitrates are normally present in all natural waters, and are derived chiefly from the oxidation of *animal* matters. The nitrogen of organic matters liberated by putrefaction, is first converted into ammonia; then this is oxidized into nitrous, and finally into nitric acid. These changes are due partially to direct oxidation and partially to certain microorganisms which have the power of converting nitrogenous organic matter into nitrites and nitrates.

Nitrates and nitrites in themselves, in the quantity in which they exist in water, are perfectly harmless. They are, however, an indication of previous contamination; and many analysts believe that a water which has once been contaminated is always open to suspicion. Others consider them of little importance in determining the impurity of a water. Water which is laden with organic matter is purified by percolating through the ground, the nitrogenous matter being converted into nitrates; therefore deep wells may contain large quantities of nitrates without being essentially impure, while the water from shallow wells should be condemned if the nitrates are excessive.

Certain strata, as the chalk formation, yield large amounts of nitrates to water. If the nitrogen as nitrates exceeds 0.6 parts per 100,000 the water is suspected.

Nitrogen as Nitrites.—Some chemists regard the presence of nitrites as an indication that the oxidation of the dangerous compounds has probably been incomplete, and accordingly condemn water in which nitrites are found. Leeds places the nitrites in American rivers at .03 per 100,000. The average in good waters is placed at about .0014 per 100,000. When the quantity exceeds .02 parts per 100,000 it is considered an indication of previous contamination.

Oxygen Consuming Power.—This is intended to represent the oxidizable organic matter in the water. But there are other substances in water besides organic matters which absorb oxygen, namely, nitrites, which are thus oxidized to nitrates; ferrous salts, which are oxidized into ferric salts; etc. Thus the oxygen-consuming power does not represent the organic matter

alone. However, a water having a high oxygen-consuming power may be considered as polluted.

The following basis for interpreting results of this method are given by Frankland and Tidy:

	Oxgen absorbed in 3 hours.
High organic purity.....	.05 parts per 100,000
Medium purity.....	.05 to .15 " " "
Doubtful.....	.15 to .21 " " "
Impure.....	over .21 " " "

Phosphates.—Sewage contains large amounts of phosphates, but water usually contains alkaline or earthy carbonates, which precipitate the phosphates; therefore the absence of phosphates does not indicate purity. But their presence *may* indicate sewage contamination. .06 parts per 100,000 is regarded with suspicion (calculated as PO_4).

Hardness.—On account of the presence of considerable amounts of calcium compounds in our food sewage is usually very hard, containing especially calcium sulphate. The hardness of water, therefore, has some bearing upon the question as to whether the water is probably polluted with sewage or not. But water may be hard, yet otherwise perfectly pure. The test for the degree of hardness is therefore of little importance in determining sewage, as the figures below show that water uncontaminated by sewage may be very hard.

	Temporary.	Permanent.
Rain-water, average.....	0.3	1.7
Highest from different geological formations...	38.6	48.5
From 272 samples of water from shallow and polluted wells:		
Minimum.....	0	3.8
Maximum.....	52	164.3
Average.....	19	31.5

The above figures are parts in 100,000. The hardness has, however, much significance from an economic point of view. Hard water is objectionable for domestic purposes in washing, because of its soap-destroying power, and for manufacturing purposes in boilers. It has no bad effect upon the health, but is by some considered wholesome.

Standards.—Certain standards have been fixed by some chemists for determining the purity or impurity of water, according to which if certain figures are exceeded the water is to be condemned.

Dr. Tidy's classification depends upon the amount of oxygen consumed, from potassium permanganate, after standing three hours.

1. Great organic purity..... 0 to 0.05
2. Medium purity..... 0.05 " 0.15
3. Doubtful..... 0.15 " 0.21
4. Impure..... over 0.21

These standards are applied to waters other than upland surface-waters, in which larger quantities of oxygen may be absorbed.

Wanklyn's standard is based upon the indications of the amounts of free and albuminoid ammonia, as follows:

1. Extraordinary purity..... 0 to 0.005 part albuminoid NH_3.
2. Satisfactory purity..... 0.005 to 0.010 " " "
3. Dirty..... over 0.010 " " "

If the albuminoid ammonia exceeds 0.005 parts per 100,000 the free ammonia must be taken into account. If the free ammonia is in large quantity it is a suspicious sign. If it is in small quantity or altogether absent, the water should not be condemned, unless the

albuminoid ammonia is something like 0.010 parts per 100,000; while over 0.015 should condemn the water absolutely.

The following is a list of analyses of waters which were pronounced good. The results are given in parts per 100,000.

	I.	II.	III.	IV.
Chlorine	0.877	1.333	9.294	1.578
Free ammonia	0.0004	none	0.002	0.0002
Albuminoid ammonia	none	0.0006	0.005	0.0022
Oxygen absorbed (in 3 hours)	0.0054	0.0016	0.0255	0.0008
N in nitrates and nitrites	0.2525	0.3376	0.0107	0 2633
Total hardness	19.23	14.0000	13.33	2.079
Permanent hardness	3.715	3.934	3.060	1.980
Organic and volatile matters	1.5	1.7	trace	2.100
Total solids (dried at 230° F.)	24.4	27	37.40	9.40

The following were pronounced bad:

	I.	II.	III.	IV.
Chlorine	0.316	62.43	4.208	28.230
Free ammonia	0.0196	0.278	none	0.0105
Albuminoid ammonia	0.0678	0.0030	0.0105	0.0395
Oxygen absorbed (in 3 hours)	0.2912	0.133	0.0165	0.2110
N in nitrates and nitrites	0.0283	none	0.247	0.6210
Total hardness	6.940	27.72	13.068	50.00
Permanent hardness	3.5	23.76	2.574	32.670
Organic and volatile matters	0.5	19.5	trace	8.00
Total solids (dried at 230° F.)	15.60	156.20	30.50	146.50

I, Back of slaughter-house; II, Drive-well on beach; III, Well; IV, Well 30 feet deep.

CHAPTER XLIV.

MILK.

MILK is the nutritive secretion of glands (the mammary glands) which are characteristic of the mammalia.

This secretion takes place as a result of pregnancy and delivery, and continues for a variable period, constituting the entire food of the young animal until it is able to live upon other foods.

The milk of different animals contains qualitatively identical or analogous ingredients to that of the cow, namely, fat (which is held in suspension), nitrogenous matters such as casein and albumen, milk sugar, inorganic salts, and water.

The average composition of cow's milk is as follows:

Fat	3.65	per cent.
Proteids	4.40	" "
Lactose	4.25	" "
Inorganic salts	0.75	" "
Total solids	13.05	" "
Water	86.95	" "
	100.00	

In the milk of different animals, however, these ingredients are in different proportions, as the following table shows:

	Human.	Goat.	Mare.	Ass.
	per cent.	per cent.	per cent.	per cent.
Fat	3.40	5.2	1.1	1.0
Proteids	2.45	3.8	2.2	2.7
Lactose	5.75	4.3	5.8	5.3
Inorganic salts	0.35	0.7	0.3	0.4
Water	88.05	86.0	90.6	90.6
	100.00	100.0	100.0	100.0
Total solids	11.95	14.0	9.4	9.4

Milk is a perfect natural emulsion. The casein appears to be the emulsifying agent, a film of which envelops each globule of fat, thus preventing cohesion.

The inorganic salts are chiefly the phosphates of sodium and calcium, and the chlorides of sodium and potassium, but magnesium and iron are also generally present.

The proteids consist mainly of casein with some albumen, the proportion being about as 6 to 1.

Besides the above-mentioned constituents milk also contains a very small quantity of peptone, kreatin, leucin, etc. Also gases, such as CO_2, O, and N.

Colostrum is the milk secreted in the early stages of lactation; it is rich in proteids, often containing as much as 20 per cent, and contains a few corpuscles of a peculiar character, which look like epithelium-cells, called *colostrum corpuscles*.

Reaction.—The reaction of the milk of herbivorous animals is generally alkaline, that of carnivora is generally acid. The reaction of cow's milk is generally neutral, sometimes slightly acid, rarely alkaline.

Specific Gravity.—This varies in normal cow's milk from 1.029 to 1.035. It should not be below 1.029.

An excess of fat lowers the specific gravity and the removal of fat raises it. Thus skimmed milk has a higher specific gravity than normal milk.

These facts are made use of for the detection of the ordinary adulterations.

Determinations of the specific gravity of milk should always be made at the temperature of 60° F., and may be made by any of the ordinary methods. See table of corrections for temperatures other than 60° F., page 320. A special hydrometer known as the *lactometer* is, however, generally used. The lactometer is graded from 0° at the top to 120° at the bottom. In taking the specific gravity with this instrument the temperature of the milk must be 60° F.

For every $2\frac{1}{2}$° of temperature above the 60° standard, one degree is to be added to the reading of the lactometer; below 60° F. a similar subtraction is to be made.

On the lactometer scale 0° = 1.000, the specific gravity of pure water; at 60° F. 100 = 1.029, the specific gravity of the poorest possible milk at the same temperature.

If in a sample of milk the lactometer stands at 80° the sample contains about 80 per cent of standard milk and 20 per cent of water. If the lactometer stands at 90°, the sample contains about 10 per cent of water.

Lactometer Reading.	Specific Gravity.	Lactometer Reading.	Specific Gravity.
0	**1.0000**	70	1.0203
10	1.0029	80	1.0232
20	1.0058	90	1.0261
30	1.0087	**100**	**1.0290**
40	1.0116	110	1.0319
50	1.0145	120	1.0348
60	1.0174		

TABLE FOR CORRECTING THE SPECIFIC GRAVITY OF MILK ACCORDING TO TEMPERATURE.

(From Muter's Analytical Chemistry.)

DIRECTIONS FOR USE.—Find the temperature of the milk in the uppermost horizontal line, and the observed specific gravity in the first and last vertical lines. In the same line with the latter, under the temperature is given the *corrected specific gravity*.

Example.—Supposing the temperature to be 59° and the observed specific gravity 1.032.0, at 60° the specific gravity will be 1.031.9. A specific gravity of 1.032.0 at 66° will be 1.032.9 at 60°.

Observed Specific Gravity.	Degrees of Thermometer (*Fahr.*).																				
	50°	51°	52°	53°	54°	55°	56°	57°	58°	59°	60°	61°	62°	63°	64°	65°	66°	67°	68°	69°	70°
1.020.0	19.2	19.3	19.4	19.4	19.5	19.6	19.7	19.8	19.9	19.9	1.020.0	20.1	20.2	20.2	20.3	20.4	20.5	20.6	20.7	20.9	21.0
1.021.0	20.2	20.3	20.3	20.4	20.5	20.6	20.7	20.8	20.9	20.9	1.021.0	21.1	21.2	21.3	21.4	21.5	21.6	21.7	21.8	22.0	22.1
1.022.0	21.2	21.3	21.3	21.4	21.5	21.6	21.7	21.8	21.9	21.9	1.022.0	22.1	22.2	22 3	22.4	22.5	22.6	22.7	22.8	23.0	23.1
1.023.0	22.2	22.3	22.3	22.4	22.5	22.6	22.7	22.8	22.8	22.9	1.023.0	23.1	23.2	23.3	23.4	23.5	23.6	23.7	23.8	24.0	24.1
1.024.0	23.2	23.3	23.3	23.4	23.5	23.6	23.6	23.7	23.8	23.9	1.024.0	24.1	24.2	24.3	24.4	24.5	24.6	24.7	24.9	25.0	25.1
1.025.0	24.1	24.2	24.3	24.4	24.5	24.6	24.6	24.7	24.8	24.9	1.025.0	25.1	25.2	25.3	25.4	25.5	25 6	25.7	25.9	26.0	26.1
1.026.0	25.1	25.2	25.2	25.3	25.4	25.5	25.6	25.7	25.8	25.9	1.026.0	26.1	26.2	26.3	26.5	26.6	26.7	26.8	27.0	27.1	27.2
1.027.0	26.1	26.2	26.2	26.3	26.4	26.5	26.6	26.7	26.8	26.9	1.027.0	27.1	27.3	27.4	27.5	27.6	27.7	27.8	28.0	28.1	28.2
1.028.0	27.0	27.1	27.2	27.3	27.4	27.5	27.6	27.7	27.8	27.9	1.028.0	28.1	28.3	28.4	28.5	28.6	28.7	28.8	29.0	29.1	29.2
1.029.0	28.0	28.1	28.2	28.3	28.4	28.5	28.6	28.7	28.8	28.9	1.029.0	29.1	29.3	29.4	29.5	29.6	29.8	29.9	30.1	30.2	30.3
1.030.0	29.0	29.1	29.1	29.2	29.3	29.4	29.6	29.7	29.8	29.9	1.030.0	30.1	30.3	30.4	30.5	30.7	30.8	30.9	31.1	31.2	31.3
1.031.0	29.9	30.0	30.1	30.2	30.3	30.4	30.5	30.6	30.8	30.9	1.031.0	31.2	31.3	31.4	31.5	31.7	31.8	32.0	32.2	32.2	32.4
1.032.0	30.9	31.0	31.1	31.2	31.3	31.4	31.5	31.6	31.7	31.9	1.032.0	32.2	32.3	32.5	32.6	32.7	32.9	33.0	33.2	33.3	33.4
1.033.0	31.8	31.9	32.0	32.1	32.3	32.4	32.5	32.6	32.7	32.9	1.033.0	33.2	33.3	33.5	33.6	33.8	33.9	34.0	34.2	34.3	34.5
1.034.0	32.7	32.9	33.0	33.1	33 2	33.3	33.5	33.6	33.7	33.9	1.034.0	34.2	34.3	34.5	34.6	34.8	34.9	35.0	35.2	35.3	35.5
1.035.0	33.6	33.8	33.9	34.0	34.2	34.3	34.5	34.6	34.7	34.9	1.035.0	35.2	35.3	35.5	35.6	35.8	35.9	36.1	36.2	36.4	36.5

The Adulterations of Milk.—The adulterations usually practised are the abstraction of cream (skimming) or the addition of water, or both. Occasionally the addition of some foreign substance, as sodium carbonate, borax, common salt, or sugar, is met with; or preservatives, as boric or salicylic acids.

The detection of adulterations usually depends upon the determination of the specific gravity, the fat, total solids, and the ash.

These ingredients are, however, present in milk in varying proportions, and hence certain limits of allowable variations have been determined upon from time to time.

The standard adopted in many States in this country is, for specific gravity, not less than 1.029, for total solids, not less than 12 per cent., for fat 3 per cent. The total solids may vary legally from 12 to 13.13 per cent., and the solids not fat, from 8.5 to 9.5 per cent.

Estimation of Total Solids and Water.—A small, shallow platinum or porcelain dish about $1\frac{1}{2}$ inches in diameter is heated to redness, allowed to cool, and weighed. About 5 cc. of milk are then put in, and again weighed. The difference between the two weighings gives the weight of the milk taken. Now place the dish on a water-bath and heat until the milk ceases to lose weight. Then cool again and weigh. The weight of the dry residue minus the tare of the dish equals the total solids.

Then by multiplying this by 100, and dividing by the weight of milk taken, the percentage of total solids is found. Thus,

$$\frac{\text{total solids} \times 100}{\text{weight of milk}} = \text{per-cent. of total solids.}$$

This deducted from 100 gives the per-cent. of water.

Fat.—Where great accuracy is unnecessary the fat may be determined by treating the total solid residue with successive portions of warm ether until the fat is completely dissolved out. The ethereal solution is then evaporated and the fat which remains behind is weighed, or the residue in the dish may be again weighed. The loss of weight then represents the fat. The results so obtained are 0.3 to 0.5% too low.

Adams' Method is the officially recognized method for the accurate estimation of fat in milk.

This consists essentially in spreading the milk over absorbent paper, drying, and extracting the fat. The paper used for this purpose must previously have been thoroughly exhausted with alcohol and ether, and should be in long narrow strips.

The procedure is as follows: 5 cc. of the milk are put into a small beaker and weighed. A strip of the absorbent paper which has been rolled into a coil is thrust into the beaker containing the milk. In a few minutes nearly the whole of the milk will be absorbed; the coil is then withdrawn, and stood dry end down upon a sheet of glass.

It is important to take up the whole of the milk from the beaker, as the paper has a selective action, removing the watery constituents by preference over the fat. The beaker is again weighed, and the milk taken found by difference. The paper charged with the milk is now dried in a water-oven and placed in a Soxhlet extraction apparatus (Fig. 53). About 75 cc. of ether are introduced into the tared flask of the apparatus, and heat applied by means of a

water-bath and continued until exhaustion is complete. The flask is then detached, the ether removed by distillation, and the fat which remains is weighed.

The paper may be charged with the milk by spreading the latter over the surface of the paper by means of a pipette.

The Werner-Schmid Method.— This is a satisfactory and at the same time a rapid method for the determination of fat, and is especially suitable for sour milk.

10 cc. of the milk are put into a long tube having a capacity of about 50 cc., and 10 cc. of strong hydrochloric acid are added; or the milk may be weighed in a small beaker and washed into the tube with the acid. The liquids are mixed and boiled for 1½ minutes, or until the liquid turns dark brown, but not black. The tube and contents are then cooled, and 30 cc. of ether are added, shaken, and allowed to stand until the acid liquid and ether have separated. The cork is now taken out and the wash-bottle arrangement inserted (see Fig. 52). The stopper of this should be of cork, not of rubber, since the ether has a solvent action upon the latter. The lower end of the exit tube is adjusted so as to rest immediately above the junction of the two liquids. The ethereal solution of fat is then blown off, and received in a weighed beaker. Two more portions of 10 cc. each are shaken successively with the acid liquid, blown out, and added to the first. The ethereal solution is then heated on a water-bath, and the residue of fat weighed. The results agree quite closely with the Adams method.

Calculation Method.—This rests upon the assumption that every per-cent. of solids not fat, raises the specific gravity by a definite amount, while every per-cent. of

fat lowers it by a definite amount. An accurate determination of the per-cent of total solids and of the specific gravity therefore furnish the necessary data for calculating the amount of fat.

Hehner and Richmond have devised the following formula:

$$F = 0.859T - 0.2186G.;$$

in which F = fat, T = total solids, and G = the last two units of the specific gravity and any decimal. Thus if the specific gravity is 1029, G will be 29; if 1029.5, G will be 29.5.

Example.—Let us assume in the examination of a certain milk that the specific gravity was 1030, and that it contained 12 per cent. of total solids. We then have

$$\text{Fat} = 0.859 \times 12 - 0.2186 \times 30 = 3.75\%$$

When the per-cent. of fat is known, the formula may be transposed so as to calculate the total solids, as follows:

$$T = \frac{F + 0.2186G}{0.859}.$$

Example.—A sample of milk is found to contain 3.75 per cent. of fat, and its specific gravity is 1030; then

$$\text{Total solids} = \frac{3.75 + 0.2186 \times 30}{0.859} = 12\%$$

Ash.—The ash may be determined by igniting at a dull-red heat the residue left after the fat has been extracted from the total solids. The organic matter is thus all burned off, and the residue is weighed and calculated as ash. The ash should be about 0.75 per cent, never below 0.67.

To Calculate the Per-cent. of Pure Milk and of

Added Water, the following formula may be adopted, which is based upon the legal standard of the State of New York, which is based upon the poorest possible natural milk, viz., 3 per cent. of fat, 12 per cent. of total solids, and 9 per cent. of "solids not fat."

If, however, a milk has 3 per cent. of fat and only 8.5 per cent. of "solids not fat," it need not be considered as definitely proved to be adulterated.

The quantity of added water should, however, always be calculated upon the average standard of 9 per cent "solids not fat," provided the milk is certainly well below the limit of 8.5 per cent.

The "solids not fat" are used as a basis for the calculation because they are a fairly constant quantity, the fat being variable. The calculation is made thus:

$$\frac{\text{"Solids not fat"} \times 100}{9} = \text{p. c. of pure milk present;}$$

and the difference between this result and 100 will of course give the added water.

Example.—A sample of milk upon analysis was found to contain 8.1 per cent of solids not fat; then

$$\frac{8.1 \times 100}{9} = \frac{810.0}{9} = 90\%$$

of pure standard milk and 10 per cent of water.

Total Proteids.—*Rittenhausen's Copper Process.*—The solutions required are: (1) Copper-sulphate solution, 34.64 gms. in 500 cc.; (2) Sodium-hydroxide solution, 12 gms. to 500 cc.

10 gms. of the milk are diluted to 100 cc. with distilled water and placed in a beaker; 5 cc. of the copper-sulphate solution are now added and thoroughly mixed.

The sodium-hydroxide solution is now added drop by drop, stirring constantly until the precipitate settles quickly, and the liquid is neutral or feebly acid. It should never be alkaline, as an excess of alkali prevents the precipitation of some of the proteids.

The precipitate which includes the fat carries down all of the copper. It is washed by decantation and collected upon a weighed dry filter, the contents of the filter being washed until the total filtrate measures about 250 cc. This filtrate, which contains no copper, is reserved for the determination of the sugar by Fehling's Solution.

The precipitate is washed once by strong alcohol to remove adhering water; it is then washed several times with ether to remove the fat. The residue on the filter, which consists of the proteids and copper hydroxide, is dried at 265° F. in the air-bath and weighed. It is then transferred to a porcelain crucible and incinerated, and the residue weighed.

The weight of the filter and contents less the weight of the filter and residue after ignition, gives the weight of the proteids.

The Milk-sugar is estimated in the mixed filtrate from the precipitated proteids by the use of Fehling's Solution in the usual way. (See Estimation of Sugar.)

CHAPTER XLV.

BUTTER.

An analysis of butter comprises the estimation of water, fat, casein, ash, sodium chloride, and also volatile fatty acids.

The water is determined by drying to a constant weight: the fat, by extraction with ether; the casein, by heating the residue, after extraction of fat, to just below redness, until the former becomes white. The loss of weight represents casein and the residue ash. In the ash the chlorine may be determined by dissolving in water and titrating with standard silver nitrate solution. Salt is estimated by washing the butter with several portions of hot water and titrating the aqueous solution, with standard silver nitrate solution.

THE ESTIMATION OF VOLATILE ACIDS.

Reichert's Process.—This is undoubtedly the best process for detecting the admixture of foreign fats with butter. This process depends upon the fact that butter contains certain constituents which when appropriately treated yield volatile acids in much larger quantity than is obtained from any of the practicable substitutes for butter. These acids are

principally butyric and caproic. The process consists in saponifying the fat with an alkali, then separating the fatty acids by neutralization, and distilling off the volatile acids for titration with standard alkali. "Reichert's number" is the number of cc. of decinormal alkali solution required to neutralize the acids distilled from 2.5 gms. of fat. The results are, however, often specified for 5 or 10 gms. of the fat.

The operations involved in this process do not admit of any arbitrary variation, and reliable and comparable results can only be obtained by strictly adhering to the prescribed details.

The solutions required are:

Sodium Hydroxide Solution.—100 gms. of sodium hydroxide are dissolved in 100 cc. of distilled water. The alkali should be as free as possible from carbonates, and be preserved out of contact with the air.

Alcohol of about 95 per cent, redistilled with caustic soda.

Diluted Sulphuric Acid.—25 cc. of the strongest sulphuric acid, in water to make 1000 cc.

Standard Barium Hydroxide Solution.—Accurately standardized, approximately decinormal.

The apparatus required are:

Saponification-flasks of from 250 to 300 cc. capacity, of hard, well-annealed glass, capable of resisting the tension of alcohol vapor at 100° C.

A Pipette, Distilling Apparatus, and an *Accurately Calibrated Burette.*

The following method of manipulation, as drawn up by the Association of Official Agricultural Chemists, is recommended as giving accurate results. In this approximately 5 gms. of the butter are taken.

The process:

Weighing the Fat.—The butter or fat to be examined should be melted and kept in a dry, warm place at about 60° F. for two or three hours, until the water and curd have entirely settled out. The clear supernatant fat is poured off and filtered through a dry filter-paper in a jacketed funnel containing boiling water. Should the filtered fat in a fused state not be perfectly clear, it must be filtered a second time. This is to remove all foreign matter and any trace of moisture. The saponification-flasks are prepared by thoroughly washing with water, alcohol, and ether, wiping perfectly dry on the outside, and heating for one hour at the temperature of boiling water. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:

A pipette with a long stem, marked to deliver 5.75 cc., is warmed to a temperature of about 50° C. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, is then taken up in the pipette and the nozzle of the pipette carried to near the bottom of the flask, having been previously wiped to remove any adhering fat, and 5.75 cc. of fat are allowed to flow into the flask. After the flasks have been charged in this way they should be recovered with the silk handkerchief and allowed to stand 15 or 20 minutes, when they are again weighed.

Saponification.—10 cc. of 95 per cent alcohol are added to the fat in the flask, and then 2 cc. of the caustic soda solution. A soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water or steam bath (see Fig. 46). The flask during the saponification, which should last one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up its sides. At the end of an hour the flask, after having been cooled to near the room temperature, is opened.

FIG. 46.

Removal of the Alcohol.—The stoppers having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro.

Dissolving the Soap.—After the removal of the alcohol the soap should be dissolved by adding 100 cc. of recently boiled distilled water, warming on the steam-bath, with occasional shaking until solution of the soap is complete.

Setting Free the Fatty Acids.—When the soap solution has cooled to about 60° or 70°, the fatty acids are separated by adding 40 cc. of the dilute sulphuric acid solution mentioned above.

Melting the Fatty Acid Emulsion.—The flask should now be restoppered as in the first instance, and the fatty acid emulsion melted by replacing the flask on the steam-bath. According to the nature of the fat examined, the time required for the fusion of the fatty acid emulsions may vary from a few minutes to several hours.

The Distillation.—After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flask is cooled to room temperature, and a few pieces of pumice-stone added. The pumice-stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 cc. of the distillate in, as nearly as possible, 30 minutes (see Fig. 47). The distillate should be received in a flask accurately graded at 110 cc.

Titration of the Volatile Acids.—The 110 cc. of distillate, after thorough mixing, are filtered through perfectly dry filter-paper, 100 cc. of the filtered dis-

tillate poured into a beaker holding from 200 to 250 cc., 0.5 cc. phenolphthalein solution added, and decinormal barium hydrate run in until a red color is produced. The contents of the beaker are then returned to the measuring-flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains apparently unchanged for two or three minutes. The number of cubic centimetres of decinormal barium hydroxide required should be increased by one tenth.

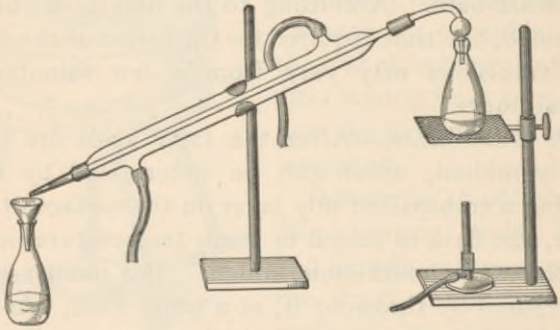

FIG. 47.

When treated as above described, 5 gms. of genuine butter never yields less acidity than is represented by 24 cc. of $\frac{N}{10}$ alkali. It is true, however, that butter made from the milk of a single cow, especially towards the end of her period of lactation, has been known to fall slightly below this figure, but the average butter, as produced from the mixed milk of a herd, usually requires 27 cc. or more. Oleomargarine requires

about 1 cc. beef-fat, and lard about the same. Cacao butter requires about 7 cc.

The percentage of butter-fat in a mixture of fats, 5 gms. being taken: $(n - 0.6) \times 3.65$ = percentage of true butter-fat.

A rapid method for detecting oleomargarine or an admixture of it with butter is to heat the suspected substance in a small tin dish directly over a gas-flame. If it melts quietly, foams, and runs over the dish, it is butter; if it sputters noisily as soon as heated and foams but little, it is oleomargarine.

Another way is to heat the butter for a moment with an alcoholic solution of sodium hydroxide and then empty into cold water. It gives a distinct odor of pineapples (due to ethyl butyrate), while oleomargarine gives only an alcoholic odor.

CHAPTER XLVI.

ESTIMATION OF CARBONIC-ACID GAS IN THE ATMOSPHERE.

THIS is done by Pettenkofer's method. A glass globe or bottle holding from 5 to 10 litres is filled with the air to be tested, by means of a bellows; baryta water of known strength is then introduced in convenient quantity.

The bottle is then securely closed and set aside for about one hour, rotating it at intervals, so that the liquid is spread over the entire inner wall of the bottle.

When the time is up the baryta water is emptied out quickly into a beaker, covered carefully with a watch-glass, and when the barium carbonate has subsided a portion of the clear liquid is withdrawn and titrated with $\frac{N}{10}$ oxalic-acid solution. The difference between the quantity of oxalic-acid solution required to neutralize the barium-hydroxide solution, before and after contact with the air, is the quantity equivalent to the carbonic-acid gas absorbed.

The Baryta-water is made by dissolving about 7 gms. of pure crystallized barium hydroxide in 1000 cc. of distilled water.

This solution, being prone to absorb CO_2 out of the air, must be kept in a special bottle, such as is illustrated in Fig. 40, which prevents access of CO_2 and

admits of the withdrawal of any quantity of solution without inverting the bottle.

The Bottle which is used to collect the air should hold from 5 to 10 litres, and its exact capacity must be known. This may be found by filling the bottle to the bottom of the cork with water and then accurately measuring the water. Before using the bottle it must be absolutely dry.

The Analysis.—Into the bottle, the capacity of which is exactly known,—we will assume it to be 7100 cc.,—is blown the air to be tested, by means of a bellows.

100 cc. of the baryta-water are then introduced, thus leaving 7000 cc. of air in the bottle.

The bottle is now securely closed and set aside for about half an hour, rotating it occasionally so as to spread the liquid over the entire inner wall of the bottle. While waiting for the half-hour to expire, a convenient quantity of baryta-water is taken and its strength compared to decinormal oxalic-acid solution by titrating with the latter, using phenolphthalein as indicator.

50 cc. of baryta-water is a convenient quantity. This is placed in a beaker, a few drops of phenolphthalein added, and then titrated with the $\frac{N}{10}$ acid solution until the color just disappears.

Let us assume that 40 cc. of the latter were consumed; 80 cc. will then be consumed by 100 cc. of baryta-water.

$$Ba(OH)_2 + H_2C_2O_4 + 2H_2O = BaC_2O_4 + 4H_2O;$$

2)170.9 2)126

10) 85.45 10) 63

8.545 gms. 6.3 gms. or 1000 cc. $\frac{N}{10}$ V. S.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

2)170.9	2)44
10) 85.45	10)22
8.545 gms.	2.2 gms.

These equations show that 2.2 gms. of carbon dioxide will neutralize as much barium hydroxide as 1000 cc. of $\frac{N}{10}$ oxalic-acid solution. And thus each cc. of the $\frac{N}{10}$ oxalic-acid solution is chemically equivalent to 0.0022 gm. of carbon dioxide; therefore 100 cc. of the baryta-water is capable of absorbing $80 \times .0022$ gm. $= 0.176$ gm. of CO_2.

The next step is to determine the quantity of CO_2 that was absorbed by the 100 cc. of baryta-water, which was introduced into the bottle of air.

The liquid is poured out of the bottle into a small beaker, carefully covered with a watch-glass, and the barium carbonate allowed to settle. Then 50 cc. of the clear supernatant liquid are drawn out of the beaker by means of a pipette, treated with a few drops of phenolphthalein T. S., and titrated with the $\frac{N}{10}$ oxalic acid V. S. until the red color is just discharged. Note the number of cc. consumed, double it, and deduct this number from 80, the quantity which 100 cc. of baryta-water consumed before being brought in contact with CO_2.

Example.—Assuming that 30 cc. of the oxalic-acid solution were required by the 50 cc. of the baryta-water after exposure, the 100 cc. then would require 60. There is thus a loss of alkalinity equivalent to 20

cc. of $\frac{N}{10}$ oxalic acid V. S. This is due to the absorption of carbon dioxide, which neutralizes the hydroxide by forming a carbonate.

Now since each cc. of $\frac{N}{10}$ oxalic acid V. S. is chemically equivalent to 0.0022 gm. of CO_2, the baryta-water must have absorbed

$$20 \times 0.0022 \text{ gm.} = 0.044 \text{ gm. of } CO_2.$$

Therefore the 7000 cc. of air which the bottle held contained 0.044 gm. of CO_2.

In stating the result of an analysis the quantity of CO_2 by volume in 10,000 cc. of air is generally given.

In the above case 7000 cc. of air contained 0.044 gm. of CO_2; 10,000 cc. of this same air, then, contains

$$\frac{0.044 \times 10{,}000}{7000} \text{ or } \frac{0.044 \times 10}{7} = 0.0628 \text{ gm.}$$

If several bottles are in use it is convenient to mark upon them the multiplier and divisor; thus:

$$\frac{10{,}000}{7000} \text{ or } \frac{10}{7}.$$

In calculating the volume of a gas, the temperature and pressure must be taken into account.

By referring to the following table the volume occupied by 0.001 gm. of CO_2 at different temperatures can be seen.

The volume of 0.0628 gm. of CO_2 at 16° C. is

$$\frac{0.0628 \times 0.53843}{0.001} = 33.81 \text{ cc.}$$

TABLE SHOWING VOLUME OF .001 GM. OF CARBON DIOXIDE AT VARIOUS TEMPERATURES.

C.°	F.°	Cc.	C.°	F.°	Cc.
0	32	0.50863	13	55.4	0.53314
1	33.8	0.51049	14	57.2	0.53471
2	35.6	0.51235	15	59	0.53657
3	37.4	0.51451	16	60.8	0.53843
4	39.2	0.51608	17	62.6	0.54030
5	41	0.51794	18	64.4	0.54216
6	42.8	0.51980	19	66.2	0.54402
7	44.6	0.52167	20	68	0.54589
8	46.4	0.52353	21	69.8	0.54775
9	48.2	0.52539	22	71.6	0.54961
10	50	0.52726	23	73.4	0.55177
11	51.8	0.52912	24	75.2	0.55334
12	53.6	0.53098			

If the pressure remains constant, the volume of a gas increases regularly as the temperature increases, and decreases as the temperature decreases. (Charles' Law.)

This expansion or contraction amounts to $\frac{1}{273}$ of the volume of the gas for each degree centigrade.

Thus by calculation the volume of .001 gm. CO_2 (0.50863 cc.) at any temperature may be found.

$$\frac{1}{273} \text{ of } .50863 = 0.001863.$$

Then to find the volume at any given C. temperature multiply the degree of temperature by 0.001863, and add the answer to 0.50863.

CHAPTER XLVII.

ESTIMATION OF ALCOHOL IN TINCTURES AND BEVERAGES.

THE quantity of alcohol contained in *dilute spirit*, which leaves no residue upon evaporation, may be ascertained by taking the sp. gr. and referring to the alcohol table. When taking the specific gravity, the temperature of the liquid should be 15⅝° C. (60° F.).

In Wines, Beer, Tinctures, and other alcoholic liquids containing vegetable matter, the sp. gr. of the sample is taken at 15⅝° C. (60° F.) and noted. A certain quantity (say 100 cc.) is measured off and evaporated to one half, or till all odor of alcohol has passed off, the evaporation being conducted without ebullition, in order that particles of the material may not be carried off by the steam. The liquid left is then diluted with distilled water, cooled to 60° F. and made up to the original volume (100 cc.), and the sp. gr. taken. Lastly, we calculate: the sp. gr. before evaporating is divided by the sp. gr. after evaporating, and the quotient will be the sp. gr. of the water and alcohol only of the liquor. Then by referring to the alcohol table the percentage of alcohol contained in the liquor is obtained.

Example.—The liquor before evaporating had a sp. gr. of 0.9951; after evaporation and dilution to 100 cc. the sp. gr. was found to be 1.0081.

$\frac{.9951}{1.0081} = 0.987$, the sp. gr. of the contained spirit.

Then by referring to the table we will find that this sp. gr. corresponds to 7.33 per cent., by weight, of absolute alcohol.

Another Way is to boil the liquid in a retort, condense the vapor, and when all the alcohol has passed over add sufficient water to the distillate to make up the original volume, at the temperature of $15\frac{5}{9}°$ C. (60° F.). Then, by taking the sp. gr. of this diluted distillate, the quantity of absolute alcohol is found by reference to the table. This latter method requires the taking of the sp. gr. but once and gives more accurate results.

TABLE FOR ASCERTAINING THE PERCENTAGES RESPECTIVELY OF ALCOHOL BY WEIGHT, BY VOLUME, AND AS PROOF SPIRIT, FROM THE SPECIFIC GRAVITY.

Condensed from the excellent Alcohol Tables of Mr. Hehner in the "Analyst," vol. v. pp. 43–63.

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof, Spirit. Per cent.
1.0000	0.00	0.00	0.00	.9489	35.05	41.90	73.43
.9999	0.05	0.07	0.12	.9479	35.55	42.45	74.39
.9989	0.58	0.73	1.28	.9469	36.06	43.01	75.37
.9979	1.12	1.42	2.48	.9459	36.61	43.63	76.45
.9969	1.75	2.20	3.85	.9449	37.17	44.24	77.53
.9959	2.33	2.93	5.13	.9439	37.72	44.86	78.61
.9949	2.89	3.62	6.34	.9429	38.28	45.47	79.68
.9939	3.47	4.34	7.61	.9419	38.83	46.08	80.75
.9929	4.06	5.08	8.90	.9409	39.35	46.64	81.74
.9919	4.69	5.86	10.26	.9399	39.85	47.18	82.69
.9909	5.31	6.63	11.62	.9389	40.35	47.72	83.64
.9899	5.94	7.40	12.97	.9379	40.85	48.26	84.58
.9889	6.64	8.27	14.50	.9369	41.35	48.80	85.53
.9879	7.33	9.13	15.99	.9359	41.85	49.34	86.47
.9869	8.00	9.95	17.43	.9349	42.33	49.86	87.37
.9859	8.71	10.82	18.90	.9339	42.81	50.37	88.26
.9849	9.43	11.70	20.50	.9329	43.29	50.87	89.15
.9839	10.15	12.58	22.06	.9319	43.76	51.38	90.03
.9829	10.92	13.52	23.70	.9309	44.23	51.87	90.89
.9819	11.69	14.46	25.34	.9299	44 68	52.34	91.73
.9809	12.46	15.40	26.99	.9289	45.14	52.82	92.56
.9799	13.23	16.33	28.62	.9279	45.59	53.29	93 39
.9789	14.00	17.26	30.26	.9269	46.05	53.77	94.22
.9779	14.91	18.36	32.19	.9259	46.50	54.24	95.05
.9769	15.75	19.39	33.96	.9249	46.96	54.71	95.88
.9759	16.54	20.33	35.63	.9239	47.41	55.18	96.70
.9749	17.33	21.29	37.30	.9229	47.86	55.65	97.52
.9739	18.15	22.27	39.03	.9219	48.32	56.11	98.34
.9729	18.92	23.19	40.64	.9209	48.77	56.58	99.16
.9719	19.75	24.18	42.38	.9199	49.20	57.02	99.93
.9709	20.58	25.17	44.12				
.9699	21.38	26.13	45.79	.9198	49.24	57.06	100.00Ps
.9689	22.15	27.04	47.39				
.9679	22.92	27.95	48.98				
.9669	23.69	28.86	50.57	.9189	49.68	57.49	100.76
.9659	24.46	29.76	52.16	.9179	50.13	57.97	101.59
.9649	25.21	30 65	53.71	.9169	50.57	58.41	102.35
.9639	25.93	31.48	55.18	.9159	51.00	58.85	103.12
.9629	26.60	32.27	56.55	.9149	51.42	59.26	103.85
.9619	27.29	33.06	57.94	.9139	51.83	59.68	104.58
.9609	28.00	33.89	59.40	.9129	52.27	60.12	105.35
.9599	28.62	34.61	60 66	.9119	52.73	60.56	106.15
.9589	29.27	35.35	61.95	9109	53.17	61.02	106.93
.9579	29 93	36.12	63.30	.9099	53.61	61.45	107.69
.9569	30.50	36.76	64.43	.9089	54.05	61.88	108.45
.9559	31.06	37.41	65.55	.9079	54.52	62.36	109.28
.9549	31.69	38.11	66.80	.9069	55.00	62.84	110.12
.9539	32.31	38.82	68.04	.9059	55.45	63.28	110.92
.9529	32.94	39.54	69.29	.9049	55.91	63.73	111.71
.9519	33.53	40.20	70.46	.9039	56.36	64.18	112.49
.9509	34.10	40.84	71.58	.9029	56.82	64.63	113.26
.9499	34.57	41.37	72.50	.9019	57.25	65.05	113.99

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.
.9009	57.67	65.45	114.69	.8429	82.19	87.27	152.95
.8999	58.09	65.85	115.41	.8419	82.58	87.58	153.48
.8989	58.55	66.29	116.18	.8409	82.96	87.88	154.01
.8979	59.00	66.74	116.96	.8399	83.35	88.19	154.54
.8969	59.43	67.15	117.68	.8389	83.73	88.49	155.07
.8959	59.87	67.57	118.41	.8379	84.12	88.79	155.61
.8949	60.29	67.97	119.12	.8369	84.52	89.11	156.16
.8939	60.71	68.36	119.80	.8359	84.92	89.42	156.71
.8929	61.13	68.76	120.49	.8349	85.31	89.72	157.24
.8919	61.54	69.15	121.18	.8339	85.69	90.02	157.76
.8909	61.96	69.54	121.86	.8329	86.08	90.32	158.28
.8899	62.41	69.96	122.61	.8319	86.46	90.61	158.79
.8889	62.86	70.40	123.36	.8309	86.85	90.90	159.31
.8879	63.30	70.81	124.09	.8299	87.23	91.20	159.82
.8869	63.74	71.22	124.80	.8289	87.62	91.49	160.33
.8859	64.17	71.62	125.51	.8279	88.00	91.78	160.84
.8849	64.61	72.02	126.22	.8269	88.40	92.08	161.37
.8839	65.04	72.42	126.92	.8259	88.80	92.39	161.91
.8829	65.46	72.80	127.59	.8249	89.19	92.68	162.43
.8819	65.88	73.19	128.25	.8239	89.58	92.97	162.93
.8809	66.30	73.57	128.94	.8229	89.96	93.26	163.43
.8799	66.74	73.97	129.64	.8219	90.32	93.52	163.88
.8789	67.17	74.37	130.33	.8209	90.68	93.77	164.33
.8779	67.58	74.74	130.98	.8199	91.04	94.03	164.78
.8769	68.00	75.12	131.64	.8189	91.39	94.28	165.23
.8759	68.42	75.49	132.30	.8179	91.75	94.53	165.67
.8749	68.83	75.87	132.95	.8169	92.11	94.79	166.12
.8739	69.25	76.24	133.60	.8159	92.48	95.06	166.58
.8729	69.67	76.61	134.25	.8149	92.85	95.32	167.04
.8719	70.08	76.98	134.90	.8139	93.22	95.58	167.50
.8709	70.48	77.32	135.51	.8129	93.59	95.84	167.96
.8699	70.88	77.67	136.13	.8119	93.96	96.11	168.24
.8689	71.29	78.04	136.76	.8109	94.31	96.34	168.84
.8679	71.71	78.40	137.40	.8099	94.66	96.57	169.24
.8669	72.13	78.77	138.05	.8089	95.00	96.80	169.65
.8659	72.57	79.16	138.72	.8079	95.36	97.05	170.07
.8649	73.00	79.54	139.39	.8069	95.71	97.29	170.50
.8639	73.42	79.90	140.02	.8059	96.07	97.53	170.99
.8629	73.83	80 26	140.65	.8049	96.40	97.75	171.30
.8619	74.27	80.64	141.33	.8039	96.73	97.96	171.68
.8609	74.73	81.04	142.03	.8029	97.07	98.18	172.05
.8599	75.18	81.44	142.73	.8019	97.40	98.39	172.43
.8589	75.64	81.84	143.42	.8009	97.73	98.61	172.80
.8579	76.08	82.23	144.10	.7999	98.06	98.82	173.17
.8569	76.50	82.58	144.72	.7989	98.37	99 00	173.50
.8559	76.92	82.93	145.34	.7979	98.69	99.18	173.84
.8549	77.33	83.28	145.96	.7969	99.00	99.37	174.17
.8539	77.75	83.64	146.57	.7959	99.32	99.57	174.52
.8529	78.16	83.98	147.17	.7949	99.65	99.77	174.87
.8519	78.56	84.31	147.75	.7939	99.97	99.98	175.22
.8509	78.96	84.64	148.32				
.8499	79.36	84.97	148.90				
.8489	79.76	85.29	149.44				
.8479	80.17	85.63	150.06		Absolute Alcohol.		
.8469	80.58	85.97	150.67				
.8459	81.00	86.32	151.27				
.8449	81.40	86.64	151.83				
.8439	81.80	86.96	152.40	.7938	100.00	100.00	175.25

CHAPTER XLVIII.

ANALYSIS OF SOAP.

Estimation of Water and Volatile Matters.—(a) 10 gms. of the soap are dried to a constant weight at 100° C. and carefully weighed; the loss of weight = water.

(b) *Free Fats.*—The dried soap obtained as above, is exhausted with petroleum ether of low boiling-point. The petroleum ether is then evaporated off and the residue weighed: this is the weight of the fat contained in 10 gm. of the soap.

(c) *Fatty Acids.*—The residue from (b) which is free from fat and which represents 10 gms. of the soap, is weighed and half of it dissolved in water. Normal nitric acid is then added in excess to liberate the fatty acids. These are collected on a tared filter, dried and weighed. This weight when doubled gives the amount of fatty acids in 10 gms. of the soap. The reaction is illustrated by this equation:

$$\underset{\text{Sodium oleate.}}{NaC_{18}H_{33}O_2} + HNO_3 = \underset{\text{Oleic acid.}}{HC_{18}H_{33}O_2} + NaNO_3.$$

The acid filtrate is now titrated with normal soda or potash, using phenolphthalein as an indicator. The difference between the volumes of acid and alkali solutions used gives roughly the quantity of total alkali.

(d) *Chlorides and Sulphates.*—The residual neutral

liquid from the above, is divided into two equal parts, in one of which chlorine is estimated by $\frac{N}{10}AgNO_3$, using potassium chromate.

In the other sulphuric acid is estimated with barium chloride.

(e) *Free Alkali*, (i.e., the alkali which does not exist as soap).—Ten grammes of the soap are dissolved in hot alcohol, and one drop of phenolphthalein T.S. added; then carbonic-acid gas is passed through the solution until the color disappears. The free alkali is thus converted into sodium carbonate, which is insoluble in alcohol and may be separated by filtration. The residue on the filter is washed with hot alcohol, and then dissolved in a little water and titrated with $\frac{N}{10}$ acid in the presence of methyl-orange. The number of cc. used multiplied by 0.0031 gives the grammes of free alkali, as Na_2O, in the 10 gms. of soap.

Combined Alkali.—The alcoholic solution from the above which contains the combined alkali and the fatty acids, is diluted with a little water, methyl-orange added, and the mixture titrated with decinormal acid. The quantity of combined alkali is thus found. The number of cc. of acid consumed multiplied by 0.0031 gives the quantity as Na_2O.

Another Way is to evaporate the alcoholic solution to dryness, the residue then ignited, and the soap thus converted into alkali carbonate. This is dissolved in water and titrated with normal or decinormal acid in the presence of methyl-orange.

The fatty acids are found by using the factor 0.0282 or 0.282. The number of cc. of decinormal acid used

in the above titration when multiplied by 0.0282, or of normal acid when multiplied by 0.282, gives the quantity of fatty acid as oleic. Soaps, however, contain various fatty acids the molecular weights of which differ.

Therefore in estimating the fatty acids volumetrically, the neutralizing power of the acids liberated from soap, expressed in cc. of standard alkali and called the saponification equivalent, is employed.

Geissler determines the free and combined alkali in soap as follows:

10 gms. of the soap are dissolved in 100 cc. of water, phenolphthalein T. S. added, and the solution titrated with $\frac{N}{1}$ hydrochloric acid solution until the color is just discharged. The quantity of $\frac{N}{1}$ hydrochloric acid solution used represents the free alkali and is calculated as carbonate.

Each cc. of $\frac{N}{1}$ acid = 0.053 gm. of Na_2CO_3 or 0.069 gm. of K_2CO_3.

The $\frac{N}{1}$ acid is now added in excess in order to liberate the fatty acids, and the mixture is heated to melt the fatty acids and cause them to form a clear oily layer on the surface. After the mixture has cooled off, the watery layer is separated and the fatty acids washed with water. The washings are added to the aqueous liquid and titrated with $\frac{N}{1}$ potassium hydroxide until the red color reappears; this gives the

excess of acid, and when deducted from the quantity of acid added after decolorization of the phenolphthalein gives the quantity of the acid which combined with and hence represents the combined alkali of the soap. This is also calculated as carbonate, using the same factors as given above.

CHAPTER XLIX.

ESTIMATION OF STARCH IN CEREALS, ETC.

THE method about to be described depends upon the fact that when barium hydroxide is brought in contact with starch, an insoluble compound is formed, the formula of which is $C_{24}H_{40}O_{20}BaO$. This combination takes place in definite proportions, so that if an excess of barium hydroxide solution is added to the starchy substance, and then the excess estimated, the quantity which combined with and which consequently represents the amount of starch present, is found.

Solutions Required.—1. *Decinormal Hydrochloric Acid.* See page 40 (3.637 gm. to 1 liter.) Each cc. represents .00765 gm. of BaO.

2. *Baryta-water* (barium hydroxide solution), made by dissolving about 7 gms. of pure crystallized barium hydroxide in 1000 cc. of water. Should be kept in a special vessel such as is illustrated in Fig. 40.

The Process.—The sample is finely powdered, and 1 gm. weighed out for analysis. This is rubbed up with successive portions of water (using not more than 50 cc.) and transferred to a flask having a capacity of about 150 cc. The flask and contents are now heated upon a water-bath for half an hour to thoroughly gelatinize the starch. If the substance analyzed contains oil, this must first be extracted in a "Soxhlet" apparatus before the water is added.

If free starch is to be experimented with, 0.2 or 0.3 gm. instead of 1 gm. should be taken.

When the starch is gelatinized, the solution is cooled, and 25 cc. of the baryta-water are added. The flask is corked, and well shaken for two minutes; proof spirit is then added to make about 125 cc., the flask again corked, thoroughly shaken, and set aside to settle. While settling a check is made upon 10 cc. of the baryta-water mixed with 50 cc. of recently boiled distilled water, by titrating with decinormal hydrochloric acid, using phenolphtalein as indicator. The number of cc. of $\frac{N}{10}$ hydrochloric acid V. S. used, is noted, and when multiplied by $2\frac{1}{2}$ the total strength of the 25 cc. of the baryta-water employed in the analysis is obtained.

When the settling of the insoluble compound is completed, 25 cc. of the clear liquid is drawn off (this is $\frac{1}{8}$ of the entire quantity) with a pipette and rapidly titrated with the $\frac{N}{10}$ acid V. S. in the presence of a few drops of phenolphtalein T. S. The number of cc. consumed is noted, multiplied by 5, and then deducted from the number representing the total strength of 25 cc. baryta-water. The difference is the quantity which went into combination with the starch.

Each cc. of the $\frac{N}{10}$ hydrochloric acid V. S. represents 0.00765 gm. of BaO_2, which is equivalent to 0.0324 gm. of starch.

Therefore by multiplying the number of cc. representing the quantity of baryta which combined with

the starch by 0.0324 gm., the quantity of starch present in the sample is obtained.

Example.—1 gm. of substance was taken, mixed with 50 cc. of water, 25 cc. of baryta-water, and sufficient proof spirit to make 125 cc. This is set aside and allowed to settle.

The reaction which takes place is as follows:

$$\underset{\substack{\text{Starch.}\\ 2)648\\ 324}}{2C_{12}H_{20}O_{10}} + \underbrace{BaO,H_2O}_{2)153.0\ \ 76.5} = C_{24}H_{40}O_{20}.BaO + H_2O.$$

While settling, the strength of the baryta-water is determined by titrating with decinormal hydrochloric acid V. S., the following equation being applied:

$$\underbrace{BaO,H_2O}_{\substack{2)153.0\\ 10)\ 76.5\\ 7.65\text{ gms.}}} + 2HCl = BaCl_2 + 2H_2O.$$

$$\underset{\substack{2)72.74\\ 10)36.37\\ 3.67\text{ gms. or 1000 cc. }\frac{N}{10}\text{ V. S.}}}{}$$

Thus each cc. represents 0.00765 gm. of BaO.

10 cc. of the baryta-water are taken, and 8 cc. of the $\frac{N}{10}$ acid solution are required to neutralize this. Therefore 25 cc. of baryta-water will require $2\frac{1}{2} \times 8$ cc. = 20 cc. of $\frac{N}{10}$ acid V. S.

When the settling is completed, 25 cc. of the clear solution is drawn off and titrated with $\frac{N}{10}$ acid V. S. We will assume that 2.5 cc. of the $\frac{N}{10}$ acid V. S. are

required; therefore the entire quantity of solution will neutralize 5×2.5 cc. $= 12.5$ cc.

The difference between 12.5 cc. and 20 cc. $= 7.5$ cc., which is the loss of alkalinity expressed in cc. of $\frac{N}{10}$ acid V. S. Each cc. of alkalinity lost, expressed as $\frac{N}{10}$ acid V. S., indicates that 0.00765 gm. of BaO went into combination with starch; and since 0.00765 gm. of BaO represents 0.0324 gm. of starch, the substance analyzed contains 7.5×0.0324 gm. or 0.243 gm. of starch.

$$\frac{0.243 \times 100}{1} = 24.3\%$$

Another Method for Estimating Starch consists in converting it into glucose and then estimating the glucose with Fehling's Solution.

The starch is weighed and boiled in a flask with water containing hydrochloric acid for several hours; the solution is then cooled, neutralized with potassium hydroxide, and diluted so that 1 part of starch, or rather sugar, shall be contained in 200 parts of water. This is put into a burette and titrated into 10 cc. of Fehling's Solution, as described below under Sugar.

In estimating the starch in baking powder, 2 to 5 gms. of the powder are introduced into an Erlenmeyer flask, 150 to 200 cc. of a 4 per cent solution of hydrochloric acid are added and the solution gently boiled for four hours, after which the flask and contents are cooled, neutralized by adding sodium hydroxide, and made up to a definite volume. It is then ready for testing with Fehling's solution.

CHAPTER L.

ESTIMATION OF SUGARS.

Fehling's Solution.—(a) *The Copper Solution.*—34.64 gms. of carefully selected small crystals of pure cupric sulphate are dissolved in sufficient water to make, at or near 15° C. (59° F.), exactly 500 cc. Keep in small well-stoppered bottles.

(b) *The Alkaline-tartrate Solution.*—173 gms. of potassium and sodium tartrate (Rochelle salt) and 125 gms. of potassium hydroxide, U. S. P., are dissolved in sufficient water to make, at or near 15° C. (59° F.), exactly 500 cc. Keep in small rubber-stoppered bottles.

For use, equal quantities of the two solutions should be mixed at the time required.

10 cc. of the mixed solution is equivalent to

Glucose	.050
Maltose	.082
Inverted cane-sugar	.0475
Inverted starch	.045

The Process.—0.5 gm. or less of the sugar is dissolved in 100 cc. of water. This liquid is placed in a burette. 10 cc. of the Fehling's Solution are mixed with 50 cc. of water and placed in a porcelain dish over a Bunsen burner and heated to boiling. The sugar solution is then run in from the burette, until all blue color is destroyed.

It is always somewhat difficult to determine the exact point at which the blue color disappears, owing to the presence of the precipitated suboxide of copper. This difficulty may be overcome by the addition of some substance which will prevent the precipitation of the cuprous oxide, such as ammonium hydroxide or potassium ferrocyanide. The disappearance of the blue color can then be readily seen, as the solution remains clear to the end, turning from blue to green, and finally brown, which indicates the end of the reaction.

Professor Bartley reports this method as accurate, reliable, and rapid, provided the solution be not boiled during the reduction. He recommends to add to the Fehling's Solution in the porcelain basin 10 cc. of a 10% freshly prepared solution of potassium ferrocyanide and 30 cc. of water. The ferrocyanide does not precipitate the copper in alkaline solution.

If the sugar to be examined be either glucose, maltose, or lactose, it may be titrated directly; but if it be cane-sugar, it must first be inverted. This is done by dissolving the sugar (0.475 gm.) in about 100 cc. of water, adding 3 or 4 drops of strong hydrochloric acid, and boiling briskly for ten or fifteen minutes. This is then allowed to cool, neutralized with potassium hydroxide, and made up to 100 cc. with water.

The Calculation.—10 cc. of Fehling's Solution are always taken; and whatever the quantity of glucose or sugar solution is required to effect reduction, that quantity contains the equivalent of 10 cc. of Fehling's Solution. Thus if 12 cc. of the sugar solution were required to reduce 10 cc. of Fehling's Solution, the 12 cc. contain 0.05 gm. of glucose or 0.082 gm. of maltose,

etc. 100 cc. of the solution therefore contain x gm. of glucose.

$$\frac{.05 \times 100}{12} = 0.416 \text{ gm. glucose.}$$

The sugar in urine may be estimated by this process. The urine is placed in the burette and run into the boiling Fehling's Solution in the usual manner. If it contain a large quantity of sugar, it must be diluted two or three times.

In estimating with Fehling's Solution it is well to attach a rubber tube 8 to 12 inches in length to the lower end of the burette, so that the boiling need not be done directly under the burette, and thus cause incorrect readings through the expansion of the liquid therein.

Pavy's Method.—This consists in adding ammonia-water to the ordinary Fehling's solution, in order to prevent the precipitation of cuprous oxide, which has a tendency to hide the end reaction. Thus the disappearance of the blue color which constitutes the end reaction is distinctly seen.

Pavy's solution is made by dissolving 170 gms. of Rochelle salt and 170 gms. of potassium hydroxide in sufficient water. Then 34.65 gms. of copper sulphate are separately dissolved in water with the aid of heat, and the two solutions are mixed and diluted to 1 litre.

120 cc. of this solution are now taken and mixed with 400 cc. of ammonia-water (sp. gr. 0.88) and diluted with water to 1 litre. This constitutes Pavy's solution, or rather Pavy-Fehling's solution, of which 10 cc. = 1 cc. of Fehling's solution, i.e., 10 cc. of Pavy's solution = 0.005 gm. of glucose.

The process is conducted as follows: 10 cc. of the Pavy's solution are diluted with 20 cc. of water and placed in a small flask, and heated to and kept at the boiling-point, while the glucose solution properly diluted is added from a burette. The glucose solution should be added at about the rate of 100 drops per minute until the blue color is just destroyed. The sugar solution should be so diluted that not less than 4 nor more than 7 cc. are required to produce the decoloration.

In order to avoid the nuisance of filling the laboratory with ammoniacal vapors, the titration may be performed in a small flask provided with a well-fitting cork, having two holes, through one of which the spit of the burette is passed, and through the other an escape-tube which conducts the vapors into a vessel containing water or diluted hydrochloric acid.

Several titrations should always be made in order to obtain exact results, and it is advisable to check the solution against a sugar solution of known strength, since the ratio of reduction is seriously influenced by the amount of potassium hydroxide present and the strength of the ammonia-water.

The calculation is exactly the same as that in the use of Fehling's solution, except that 10 cc. of Pavy = 0.005 gm. glucose.

CHAPTER LI.

PEPSIN.

PEPSIN, the active constituent of the gastric juice, is an albuminous principle secreted by glands imbedded in the lining membrane of the stomach.

Pepsin has never been isolated in a pure state, and its exact chemical composition is not known, therefore pepsin cannot be quantitatively estimated; but the digestive strength of pepsin or its preparations is measured by the amount of egg-albumen it will digest under certain conditions.

A good pepsin should digest 2000 times its own weight of albumen.

The different tests for ascertaining the digestive power of pepsin do not give the actual strength, but serve to show whether a sample is above, below, or near the standard. All the known tests are comparative tests, and must be conducted under like conditions, as slight variations in the manipulation will frequently occasion very different results even with the same pepsin.

In testing pepsin, it is generally assumed that the sample which will so change the largest amount of egg-albumen as to render it soluble is the best.

Coagulated egg-albumen is not readily soluble, but when acted upon by pepsin it is converted into a substance which is soluble.

The value of pepsin as a digestive agent does not, however, lie in its power to convert albumen into a soluble substance, but rather in the amount of a certain soluble and diffusible principle (peptone) which it produces in a given time and under certain conditions.

The function of the gastric juice in the animal economy consists in reducing the proteids of the food to a condition in which they are easily absorbed into the system, and not reducing them to a soluble condition.

This conversion of the indiffusible proteids into soluble and diffusible peptone does not take place at once, but occurs only after they have passed through several successive stages.

The first step in the digestive action of pepsin upon coagulated egg-albumen is the conversion of the latter into soluble acid-albumen, or syntonin, from which state it is subsequently converted into parapeptone, metapeptene, and finally peptone.

The latter is the only one of these products which is highly diffusible, hence the albumen is not digested until it is converted into peptone.

Thus it is seen that in the tests in which the dissolving power of a pepsin is alone taken into account the actual digestive power is not ascertained.

A weak pepsin may dissolve a large quantity of albumen and convert it into syntonin, but will carry the digestion no further, while a stronger pepsin may in the same time convert the same amount of albumen not only into syntonin, but also into peptone. Apparently both samples have done equal work, the albumen being dissolved in both cases, while in reality one is double the strength of the other.

When pepsin is brought in contact with more albu-

men than it can thoroughly digest, the latter is converted principally into syntonin, and little or no peptone is formed; thus in order to determine the real digestive power of a pepsin, it is necessary to find out how much peptone it produces in a certain period.

This may be accomplished by boiling the solution when the time is up, to prevent further action of the pepsin; the solution is then filtered while still hot, and neutralized with sodium carbonate; the syntonin will then be precipitated.

This precipitate should be dried to a constant weight, and weighed; the difference between this weight and the weight of the albumen originally taken will give approximately the quantity of peptone produced. If, however, the albumen was not completely dissolved, that remaining must also be deducted from the quantity first taken.

It must not be forgotten that the conditions of temperature, acidity, time, amount of agitation, etc., must be the same in all cases.

The U. S. P. method for the valuation of pepsin is as follows:

Solutions Required.—(*a*) To 294 cc. of water add 6 cc. of diluted hydrochloric acid.

(*b*) In 100 cc. of solution (*a*) dissolve 0.067 gm. (1 gr.) of the pepsin to be tested.

(*c*) To 95 cc. of solution (*a*) brought to a temperature of 40° C. (104° F.) add 5 cc. of solution (*b*).

The resulting 100 cc. of liquid will contain 0.21 gm. (0.2 cc.) of absolute hydrochloric acid, 0.00335 gm. of the pepsin to be tested, and 98 cc. of water.

Immerse and keep a fresh hen's egg for fifteen minutes in boiling water. Then remove it and place in

cold water. When it is cold, separate the white, coagulated albumen, and rub it through a clean sieve having 30 meshes to the linear inch. Reject the first portion passing through the sieve. Weigh off 10 gms. of the second clean portion, place in a flask of about 200 cc. capacity, and add one half of solution (*c*), and shake to distribute the albumen evenly through the liquid. Then add the other half of solution (*c*) and shake. Place the flask on a water-bath and keep the temperature at about 40° C. (104° F.) for six hours, shaking gently every fifteen minutes. At the expiration of this time the albumen should have disappeared, leaving at most only a few thin, insoluble flakes. The U. S. P. requirement is that the pepsin should be capable of digesting (dissolving) 3000 times its own weight of egg-albumen, coagulated and disintegrated as described above.

The relative proteolytic power of pepsin stronger or weaker than that above described may be determined by ascertaining how much of solution (*b*) made up to 100 cc. with solution (*a*) will be required to exactly dissolve 10 gms. of coagulated and disintegrated albumen under the conditions given above.

This method is somewhat cumbersome and tedious.

The following is Professor Bartley's favorite method. In the hands of the author it has given entirely satisfactory results.

Solutions Required.—(*a*) To 25 gms. of the well-mixed whites of several eggs add enough distilled water to make exactly 250 cc. Mix well by thoroughly shaking with clean fine gravel, and boil for 5 minutes. After cooling, make up the solution to the original volume with water. This solution contains

about 10% of egg-albumen, or about 1.22 gms. of the dry albumen in 100 cc.

(*b*) One gm. of the pepsin to be tested is dissolved in 25 cc. of water. 2 cc. of diluted hydrochloric acid (U. S. P.) are added, and enough water to bring the solution up to 50 cc.

Procedure.—Measure out into a beaker or bottle 50 cc. of the albumen solution, and warm on a water-bath to about 40° C. (104° F.). Add to this 2 cc. of diluted hydrochloric acid, and from 0.5 to 5.0 cc. of the pepsin solution. The more active the pepsin the less the quantity of the pepsin solution is to be taken. It is sometimes necessary with a pepsin of unknown strength to make a preliminary test, to determine the approximate time required by the digestion, as it is best to so regulate the quantity of pepsin and albumen that the digestion shall be complete in two hours or less. The time when the pepsin is added must be carefully noted, and the temperature kept at about 35° to 40° C. (95° to 104° F.). At intervals of 10 minutes a few drops of the solution are drawn out with an ordinary dropper, and floated upon a few drops of pure nitric acid in a narrow test-tube.

Note the *time* when the nitric acid ceases to give a coagulum of albumen, or when the albumen disappears. We thus get for the calculation the weight of the egg-albumen, A; the weight of the pepsin taken, P; and the time consumed, T. We next assume the standard time of 3 hours, the average time of stomach digestion. The relation between the quantities of albumen and pepsin is expressed by the fraction $\frac{A}{P}$; that is, it is

found by dividing the amount of albumen by the weight of the pepsin.

This result gives the amount of albumen digested by one part of pepsin, in the time observed in the experiment.

To calculate what this would digest in the standard time, we must multiply the above ratio by the ratio of the observed time to the standard time; or, to put this in the form of an equation, we have D (or digestive power) $= \frac{A}{P} \times \frac{3}{T}$.

Suppose 50 cc. of solution (*a*) containing 5 gms. of egg-white be taken, and that 1 cc. of solution (*b*) be taken containing 0.02 gms. of pepsin and that the time required for the digestion is 2 hours.

If we substitute these quantities in the above equation, we have $D = \frac{5}{.02} \times \frac{3}{2} = \frac{15}{.04} = 375$ gms. That is, 1 gm. of this pepsin is capable of digesting 375 gms. of egg-albumen in 3 hours, or 750 gms. in 6 hours.

As egg-white contains about 12.2 per cent. of dry albumen, 1 gm. of this pepsin will digest 45.7 gms. of dry albumen in 3 hours.

This method gives an exact statement of results, requires little if any skill in manipulation, requires no shaking, and the results are uniform.

CHAPTER LII.

ESTIMATION OF PEPTONE.

POTASSIUM-BISMUTHOUS IODIDE solution completely precipitates peptone. The precipitate is orange-red and not soluble in excess of the reagent. Let the mixture stand 12 to 24 hours in order that the precipitate may completely form and settle. Collect it on a filter, wash with water slightly acidulated with sulphuric acid, and dry.

In the precipitate the bismuth may be estimated as oxide or as metal (see Chapter XXX.)

1 gm. of peptone = 0.141 to 0.147 gm. of Bi.

This method may be applied to all sorts of peptone-containing solutions with the exception of such as contain alkaloids.

CHAPTER LIII.

DETERMINATION OF THE DIASTASIC VALUE OF MALT EXTRACTS AND PANCREATIC EXTRACTS.

A ONE-PER-CENT. solution of starch-mucilage is employed. This is prepared by boiling 10 gms. of pure starch in water, cooling and making up to 1000 cc.

10 cc. of this standard mucilage is mixed in a beaker with 90 cc. of water. The mixture is then warmed to about 40° C. (104° F.), and a measured amount of the malt extract or pancreatic extract is added, the exact time of adding it being noted. At short intervals, say every half-minute, a drop of the mixture is placed upon a plate or white slab, with a drop of a dilute aqueous solution of iodine. As long as starch is present in the solution a blue color will be produced when brought in contact with a drop of iodine solution.

When all the starch is converted by the pancreatic extract into erythro-dextrin, the blue color no longer appears and a pink or brown color is produced; when all the erythro-dextrin disappears, no color is produced with the iodine. This is termed the *achromic point.* This point should be reached at the end of not less than six minutes, in order that the end reaction may be determined with sharpness. When it takes longer, the change is too gradual to be exactly determined.

In the statement of results we employ the following formula:

$$D = \frac{S}{P} \times \frac{5}{T}.$$

In this,

S = the weight of the starch employed;

P = the weight of pancreatic extract or malt extract employed;

T = the observed time from the addition of the pancreatic or malt extract to the *achromic point*;

5 = the arbitrarily chosen standard of time in minutes.

Example.—10 cc. of starch-mucilage were taken and 0.1 gm. of pancreatic extract was added, and the time required to reach the *achromic point* was three minutes. The above formula would become

$$D = \frac{10}{0.1} \times \frac{5}{3} = \frac{50}{0.3} = 166.66 \text{ cc.}$$

of the starch-mucilage digested by 1 gm. of the extract in five minutes.

As 10 cc. of the solution of starch contains 0.1 gm. of dry starch, 166.66 cc. contain 1.666 gm. This method is equally applicable to malt diastase, salivary diastase, or pancreatic diastase. As malt extract is not official, no standard of strength has been fixed. A good dry extract of malt, however, should digest its own weight of starch in twelve minutes.

Attfield says that 1.5 gm. malt should digest 1 gm. of starch within ½ hour, with the usual quantity of water, at 60° C.

The following standard of a recent German authority is to be preferred. To 0.6 gm. of starch gelatinized with 60 cc. of water and heated to 40° C. there is

added 0.5 gm. of the extract, dissolved in about 12 cc. of water. No color should be produced by iodine in a drop of the solution, at the end of fifteen minutes. If we substitute these numbers in the above formula, we have

$$\frac{0.6}{0.5} \times \frac{5}{15} = \frac{3.0}{7.5} = 0.4 \text{ gm.};$$

or 1 gm. of a fairly good extract by this test should digest 0.4 gm. of starch in five minutes. This is equivalent to the statement that 1 gm. should digest 1 gm. of starch in twelve minutes.

The method used in the laboratory of Parke Davis & Co. is as follows:

Fill six or more two-ounce vials with two ounces of distilled water and two drops of iodine solution. The iodine solution is prepared from 2 gm. of iodine, 4 gm. potassium iodide, 250 gm. of water.

5 gm. of corn-starch are now mixed with 30 gm. of water, and after thoroughly stirring the mixture, in order to have all the starch in suspension, it is poured into 150 cc. boiling water and the mixture brought to the boiling-point, and the boiling continued for a minute, until all the starch-granules have burst, forming a uniform mucilaginous solution; it is then cooled to 100° F.

5 gm. of malt extract are dissolved in 50 cc. of water. 12½ cc. of this solution, representing 1¼ gm. of malt extract, are added to the starch solution, which is placed on a water-bath, and maintained at a temperature of 100° F. during the test. At the expiration of the first five minutes two drops of the mixture are transferred by means of a nipple pipette to one of the

two-ounce vials containing the iodine. The bottle is shaken and the result noted. This is repeated at intervals of *one minute*, until two drops of the solution no longer produce a blue coloration with the dilute iodine solution, nor more than a faint purple from the formation of intermediate products following the conversion of the starch.

The requirement is that the malt shall convert, according to this test, four times its weight of starch in ten minutes.

By Fehling's Solution.—The diastasic value of malt extracts may also be determined by estimating the amount of maltose produced by a given amount of the extract in a given time, when brought in contact with an excess of gelatinized starch solution. It is always necessary to estimate the copper-reducing power of the extracts with Fehling's solution upon a separate sample, and to deduct this from the total reducing power found after treatment with the starch.

The process is briefly as follows: A definite quantity of gelatinized starch, made from the best Bermuda arrowroot, of 3 per cent strength, is placed in a flask and heated to 100° F. A weighed amount of the malt extract is then added, and the temperature kept at 100° F., for exactly half an hour. At the end of this time some sodium hydroxide solution is added in order to check the further action of the diastase upon the starch. The solution is then diluted to a definite volume with water and the dextrose produced, estimated by Fehling's solution in the usual manner. The quantity of sugar originally present in the sample must be previously determined, and this amount deducted from the total amount found after treatment with starch, and the remainder calculated as maltose.

CHAPTER LIV.

URINE.

Normal Urine when fresh is clear and transparent. Its color is yellowish, reddish, or colorless. It has a peculiar odor, a distinctly acid reaction, and its average specific gravity is from 1018 to 1022.

On standing it generally gives a slight cloud of mucus, which slowly sinks to the bottom; and after heavy exercise or a hearty meal of nitrogenous food, a sediment of urates.

If the urine be very dilute and the temperature is above the mean, decomposition rapidly takes place, and the urine becomes turbid, acquires an alkaline reaction, and develops a nauseous ammoniacal odor.

Reaction.—The acid reaction of fresh urine is probably due to the presence of acid phosphate of sodium. If it has an alkaline reaction when first voided it is probably due to the conversion of urea into ammonium carbonate within the bladder; it is then generally turbid, and indicates an abnormal condition.

The reaction is best tested by dropping a small piece of a red and a blue litmus-paper into it. If both are found red in a few minutes the reaction is acid, if both are blue it is alkaline, if both remain unchanged it is neutral.

Composition.—The average composition of healthy urine is as follows:

	Per Cent.	Grains per diem.
Water	96.00	50 fl. ozs.
Solids as tabulated below	4.00	1000 grs.
Urea	2.50	500 "
Uric acid	0.04	9.5 grs.
Hippuric acid	0.075	15.0 "
Creatinine	0.075	15.0 "
Pigment, mucus, xanthine, and other extractives	0.50	170.0 "
Chlorides of potassium and sodium	0.50	170.0 "
Sulphates of potassium and calcium	0.11	40.0 "
Phosphates of potassium and sodium	0.12	45.0 "
Phosphates of magnesium and calcium	0.80	35.5 "

Beside these there have been found traces of indican, diastase, glucose, oxalic acid, lactic acid, carbolic acid, and unoxidized sulphur and phosphorus. (From "The Urine;" Holland.)

The composition of urine is not constant: it is influenced by the amount of water and other fluids taken, by the temperature of the skin, by the emotions, the blood-pressure, the amount of work done, the time of day, age, sex, and medicine.

The Quantity passed in 24 hours varies considerably. The average quantity passed daily by a healthy adult is 1400 to 1600 cc.—about 50 fl. ozs. The quantity of total solids contained in this is, as seen in the table, about 60 gms., or 1000 grains. About one half of these solids is composed of urea.

In making an analysis of urine the analyst looks for the presence of abnormal constituents, and determines the excess or deficiency of the normal constituents; and therefore, since the composition of urine is not the same at all hours of the day, it is important when accurate results are desired to examine a portion of the total quantity of the urine passed in twenty-four hours. If

this cannot easily be obtained, or only a casual examination is to be made, the first urine passed in the morning may be used.

Specific Gravity.—This varies from 1015 to 1028, according to the degree of dilution or concentration. But pathological urine may vary from almost that of water to 1050. The urine of Bright's disease is, as a rule, of low specific gravity, and in diabetes of high specific gravity.

The specific gravity may be taken by any of the usual methods, but the urinometer (a special hydrometer; see Fig. 48) is generally used for this purpose. This instrument is usually graduated so that only the last two figures of the specific gravity appear upon the stem, and so as to read correctly at 60° F. If the temperature is above 60° F. it will be sufficiently accurate for ordinary clinical purposes to add one degree in specific gravity for every 10 degrees of temperature; that is, if it read 1018 at 80° F., it would read 1020 at 60° F., or for every 1° F. above 60° add 0.0001 to the observed specific gravity. The urinometer is used as follows: Sufficient urine is placed in the upright jar or cylinder to float the urinometer, which is carefully

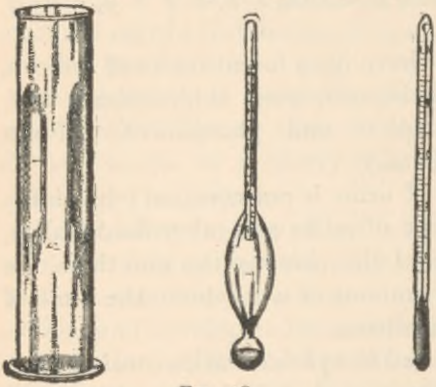

FIG. 48.

introduced. When it has come to rest bring the eye on a level with the surface of the liquid in the jar, and take the reading at the lower edge of the meniscus formed by the upper surface of the urine.

The mark on the instrument which is cut by this line, and which can be distinctly seen, is taken as the correct reading.

If the urine be turbid this method cannot be employed.

After taking the specific gravity, reaction, etc., set a portion of the urine aside in a conical glass so as to allow a deposit to form, which must be examined microscopically and chemically, as described later on.

Total Solids.—The total solids in urine may be roughly estimated as follows:

The last two figures of the specific gravity when multiplied by the factor 2.33 will give the number of grammes of solid matter in 1000 cc. of the urine.

From this it is easy to calculate the quantity of solids passed in twenty-four hours.

If, for example, 1500 cc. of urine were passed in twenty-four hours, and the specific gravity of this was 1020, the total solids would be $20 \times 2.33 = 46.6$ gms. in 1000 cc. In 1500 cc. there will be $\frac{46.6 \times 15}{10} = 69.9$ gms. If it be desired to use the English measures, we may determine the total solids by multiplying the last two figures of the specific gravity by the number of fluid ounces of urine passed, for these last two figures represent approximately the grains of solid matter in a fluid ounce. Thus if 50 fluid ounces were passed and the specific gravity is 1020, the total solids will be $50 \times 20 = 1000$ grs. in twenty-four hours.

A more exact method of determining the total solids is to evaporate 10 cc. in a white porcelain dish and dry in a water-oven to a constant weight. The difference between the weight of the dish, and of the dish with the solids will be the weight of the solids in 10 cc. of urine. Even by this method there is some loss through volatilization.

Chlorides.—For the detection of chlorides a few drops of nitric acid are added to the urine in a test-tube, and then silver-nitrate test solution. A white, curdy precipitate of silver chloride forms, which should occupy not more than one fourth the volume of the urine taken. If it occupies more, the chlorides are said to be increased; if it occupies less space than one fourth, the chlorides are diminished. It is always advisable to compare the specimen under examination with normal urine, subjected to the same test. In most cases such an approximate result is all that is required in a clinical examination.

The Volumetric Estimation.—It is sometimes necessary to make a more accurate determination. For this purpose a decinormal solution of silver nitrate is used. 10 cc. of the urine are diluted with about 50 cc. of water; a few drops of potassium chromate T. S. are added, and then the decinormal silver nitrate V. S. run in from a burette until a permanent reddish color is produced. Note the number of cc. of the V. S. used, and multiply this number by the factor for chlorine, 0.00354 gm., the factor for sodium chloride, or 0.00584 gm. This will give the quantity of chlorine or sodium chloride in 10 cc. of urine. This when multiplied by 10 gives the percentage. In highly colored urines this method is sometimes inapplicable, because the change of color is

hidden by the color of the urine. In such cases Volhard's method (see page 128) may be employed.

Phosphates.—Phosphoric acid exists in the urine combined with the alkalies and with the alkaline earths. These phosphates are, therefore, generally distinguished by the terms *alkaline* and *earthy* phosphates. By adding an alkali to normal urine the earthy phosphates (calcium and magnesium) are precipitated.

The earthy phosphates may be approximately estimated by adding a few drops of ammonia-water to the urine and observing the amount of turbidity produced after boiling. By comparing this with the amount obtained by the same treatment of normal urine the excess or deficiency is determined. The ppt. is $Ca_3(PO_4)_2$ and $MgNH_4PO_4$.

The alkaline phosphates may be detected in the filtrate from the earthy phosphates by the addition of a few drops of magnesium-sulphate solution and some ammonium chloride. The precipitate will be much more voluminous than that produced by the earthy phosphates, and the excess or deficiency may be determined by comparison with normal urine. The precipitate has the composition $MgNH_4PO_4$.

The quantitative estimation of the phosphate is rarely required, but may be made by the volumetric process with uranium nitrate (see page 243).

Total Phosphates.—50 cc. of the urine are poured into a beaker and 5 cc. of the sodium acetate solution are added. The mixture is warmed over a water-bath to near boiling, and then titrated with the uranium solution, which is added drop by drop as long as a precipitate falls or until a drop of the hot solution brought in contact, on a white porcelain plate, with a

drop of freshly prepared potassium ferrocyanide solution produces a brown color due to the formation of uranic ferrocyanide.

The quantity of uranic solution used is next read off and the phosphoric acid calculated.

Each cc. of uranic solution represents

0.005 gm. of P_2O_5;
0.0069 " " H_3PO_4.

A second and even a third titration should always be made, and all the above-named conditions should in every case be strictly adhered to.

The Earthy Phosphates are found by adding to 200 cc. of the urine a sufficient quantity of ammonia-water to render it strongly alkaline. This causes the earthy phosphates to precipitate. After the mixture has stood for twelve hours, the precipitate is collected on a filter and thoroughly washed with dilute ammonia-water (1–3). A hole is then made in the bottom of the filter and the precipitate washed through it into a beaker and dissolved in the smallest possible quantity of hot acetic acid. To this solution are added 5 cc. of the sodium acetate solution and water sufficient to make 50 cc , and then treated as for total phosphates. The amount of earthy phosphates thus found subtracted from the total phosphates gives the alkaline phosphates.

Sulphates.—About 30 grains or 2 grammes of sulphates are daily discharged in the urine.

Test.—A few drops of hydrochloric acid are added to the urine in a test-tube to prevent the formation of barium phosphate. Barium chloride T. S. is now added, which causes a white precipitate in the presence of sulphates. This should be compared with results

obtained from equal quantities of healthy urine treated in the same way.

Volumetric Estimation.—This is done by the use of a standard solution of barium chloride.

The Gravimetric Method.—Take 100 cc. of urine, add 5 cc. HCl and heat to near boiling, then add barium chloride T. S. in slight excess; place the beaker containing the mixture on a water-bath until the precipitate has subsided, decant the clear liquid carefully from the precipitate, add hot water, and when the precipitate has again settled decant again; continue this until the decanted liquid no longer gives a cloudiness with sulphuric acid. Then dry the precipitate and weigh carefully. This gives the quantity of $BaSO_4$ which is precipitated out of the urine by barium chloride.

207.7 parts of barium sulphate represent 98 parts of sulphuric acid. Therefore by multiplying the weight obtained by 98 and dividing by 207.7 the number of grammes of sulphuric acid in the 100 cc. of urine taken is obtained. From these we can easily calculate the quantity eliminated in twenty-four hours.

Total Acidity.—Place 50 cc. of the urine in a beaker, add 3 or 4 drops of phenolphthalein, and then run into the beaker carefully from a burette decinormal sodium hydroxide V. S. until a faint permanent red color appears. The number of cc. of the decinormal alkali used multiplied by 0.0063 gives the acidity of 50 cc. of the urine, expressed in grammes of oxalic acid. From this the total acidity is determined by multiplying by the quantity of urine passed in twenty-four hours, and dividing by 50.

If the urine is highly colored the end reaction is

sometimes difficult to see. In such a case the color may be removed by shaking up a portion of the urine with coarsely powdered animal charcoal, then filtering. The urine is thus decolorized, and the pink color produced by the indicator at the completion of the reaction is easily seen.

Urea, $CO(NH_2)_2$.—This is the most important constituent of the urine, as it is the chief condition in which the nitrogen leaves the body. It may be detected by evaporating a few drops of urine on a glass slide, moistening with nitric acid, allowing it to crystallize, and examining the crystals of urea nitrate under a microscope of low power. As urea is generally looked upon as an index of the retrograde changes going on in the body, or of the eliminating power of the kidneys, its quantitative estimation is a matter of great importance.

The quantity of urea eliminated in twenty-four hours has been put as being 30 to 33 gms., or from 430 to 550 grains.

The Quantitive Estimation of Urea is effected by treating it with alkaline hypochlorites or hypobromites which decompose the urea into CO_2, N, and H_2O.

Uric Acid, $C_5H_4N_4O_3$, occurs in urine, sometimes in a free state, but oftener in combination with potassium, sodium, or ammonium, and occasionally with calcium and magnesium. These are called *urates*. It is detected microscopically, and varies in quantity from 0.4 to 0.8 gm. (6 to 12 grs.) in twenty-four hours. The crystals are sometimes large enough to be seen by the naked eye. It deposits, upon standing, in the form of a brick-colored precipitate, commonly called brick-dust.

Qualitative Chemical Tests.—The Murexid Test.—A portion of the urine is evaporated to dryness in a porcelain dish upon a water-bath. The residue is then moistened with nitric acid, and after evaporating off the nitric acid the residue is moistened with ammonium hydroxide. If uric acid is present the residue assumes a beautiful purple-red color, due to the formation of murexid.

The Silver-carbonate Test.—Make the urine alkaline with Na_2CO_3 or K_2CO_3, and moisten a filter paper with the liquid. Now touch the moistened paper with a solution of $AgNO_3$. In the presence of uric acid a distinct gray stain is produced.

Quantitative Estimation of Uric Acid.—Acidulate a portion of the urine with HCl, and set aside for twenty-four hours. The uric acid is thus set free, and, being insoluble, precipitates and adheres to the bottom and sides of the vessel. It is collected on a weighed filter, washed thoroughly, dried, and weighed. The heat used should not be over 100° C. (212° F.). The weight of the filter and its contents minus the weight of the filter alone gives the weight of uric acid in the volume of urine taken. The quantity eliminated in 24 hours can then be calculated.

ABNORMAL CONSTITUENTS.

Albumen.—In all cases the urine should be clear before applying the tests for albumen. If not clear, it should be filtered.

(*a*) *Boiling Test.*—About 10 cc. of the clear urine are placed in a narrow test-tube, one drop of acetic or nitric acid is added, and the tube heated over a small

flame in such a way that the upper portion of the liquid only will be heated. In the presence of albumen the urine will become turbid, more or less so in proportion to the amount of albumen present.

If the acetic or nitric acid is not added before heating, a turbidity will be produced by the phosphates; this, however, will again disappear upon adding the acid.

(*b*) *The Nitric-acid Test.*—About 2 cc. of pure nitric acid are placed in a test-tube, and the tube being inclined to one side, the urine is carefully run down the side of the tube so that it will float upon and not mix with the acid. An *opaque-white* zone will appear at the line of contact of the two liquids, if albumen is present.

A mixture of nitric acid one volume, and saturated solution of magnesium sulphate five volumes, is sometimes used instead of pure nitric acid in the above test, and is used in the same way.

(*c*) *Ferrocyanide-of-potassium Test.*—A small portion of the urine is acidulated with acetic acid, and filtered if much of a precipitate forms. This acidulated urine is then floated on a solution of potassium ferrocyanide. A white precipitate appears if albumen is present. This is a very delicate and reliable test; peptone, mucin, or alkaloids are not precipitated by it. This is known as Bödeker's Test.

(*d*) *Picric-acid Test.*—A cold saturated solution of picric acid may be used in the same way as the nitric acid—by contact. A white zone appears at the line of contact. Alkaloids, mucin, peptones, and urates are, however, precipitated as well as albumen in this

test, and the solution should be heated to redissolve these.

(*e*) *Sodium-tungstate Test.*—The reagent is made by mixing equal parts of a cold saturated solution of sodium-tungstate and citric-acid solution. This is a very delicate test, and is applied in the same way as the nitric acid and the above. Peptones, alkaloids, mucin, and urates are also precipitated by this reagent, but these are redissolved upon boiling.

(*f*) *Potassio-mercuric-iodide Test, or Tanret's Test.*—The reagent is prepared as follows: Mercuric chloride, 1.35 gms.; potassium iodide, 3.32 gms.; acetic acid, 20 cc.; distilled water, 80 cc. The two salts are separately dissolved in water, and then the solutions mixed and the acetic acid added. This solution is also used by the contact method. It is very delicate, detecting 1 part of albumen in 20,000 parts of urine. It is necessary to heat in order to dissolve the alkaloids, mucin, and peptone, which are precipitated together with the albumen.

(*g*) *Acidulated-brine Test.*—The reagent is made by adding one fluid ounce of hydrochloric acid to a pint of a saturated solution of common salt and filtering.

It is used as follows: The solution is heated to boiling, and the urine added by the contact method. A white zone appears at the line of contact if albumen is present. Peptone, alkaloids, etc., are not precipitated by this reagent.

The Quantitative Estimation of albumen is of great importance, but comparative tests are, as a rule, sufficient. An easy comparative test is to heat a given quantity of urine in a test-tube, add a few drops of

nitric acid, and set aside for about twelve hours, and then note the volume occupied by the precipitated albumen. This is generally spoken of as *volume per cent. and has no relation to actual percentage.*

FIG. 49.

More accurate results are obtained with Esbach's Albuminometer. This is a graduated glass tube (Fig. 49). Fill the tube to *U* with the urine, then to *R* with the reagent. Close the tube with a rubber stopper, shake, and set aside for 24 hours. Then note the height of the precipitate, as indicated by the graduations. Each of the numbered divisions represents a gramme of albumen in 1000 cc. of urine. The reading should be taken at the middle of the albuminous surface. The reagent: Picric acid, 10 gms.; citric acid, 20 gms.; water, 1000 gms.

Blood.—A small quantity of the urine is mixed in a test-tube with an equal volume of a mixture of freshly prepared tincture of guaiac and spirit of turpentine, which has been exposed to the air for some time. If blood-coloring matter is present the mixture assumes an indigo-blue color, the rapidity of formation of which depends upon the amount of blood-coloring matter present. Pus, saliva, and salts of iodine also give a blue color with this test; but it appears only after a considerable lapse of time, and is seldom likely to mislead. Instead of the spirit of turpentine, peroxide of hydrogen may be used.

Pus.—The presence of pus is easily revealed by the microscope.

Urine containing pus is always turbid to the naked eye, and deposits a white or greenish-white sediment,

which resembles urates or earthy phosphates. If heated the sediment does not disappear—difference from urates, neither is it dissolved by dilute acids—difference from earthy phosphates. It dissolves, however, in strongly alkaline solutions, giving a gelatinous, ropy liquid. Pus effervesces with hydrogen peroxide.

Sugar.—(*a*) *Bismuth Test.*—A few cc. of urine are placed in a test-tube, and an equal volume of sodium-hydroxide solution and a little bismuth subnitrate; mix well, and boil for a few minutes. A black precipitate is produced if sugar is present.

If albumen is present it must be removed before applying the test, as it is decomposed by boiling with the alkali, forming a black sulphide of bismuth.

(*b*) *Nylander's Test* is a modification of the above. A solution is made of bismuth subnitrate 2 gms., Rochelle salt 4 gm., sodium hydroxide 8 gms., and distilled water 100 cc.

Heat the urine to boiling, and add a few drops of this alkaline solution of bismuth, continuing the boiling. If sugar is present, the mixture turns black.

This is a very delicate test, but as in the previous one, any albumen must be removed.

(*c*) *Moore's Test.*—Add one part of liquor soda to two parts of urine, and boil. If sugar is present the urine will become blackish brown. Albumen must be removed before applying the test.

(*d*) *Picric-acid Test.*—About 5 cc. of the urine are mixed with half as much of picric-acid solution and about 2 cc. of liquor potassa, and boiled. A dark mahogany-red color is developed in the presence of sugar. Albumen will cause turbidity, but will not interfere with the test.

(*e*) *Trommer's Test.*—5 cc. of urine are mixed in a test-tube with one half of its volume of liquor soda, and one or two drops of a solution of $CuSO_4$ (1–10). In the presence of sugar a clear, deep-blue color is obtained. Heat the solution now almost, though not quite, to boiling. At first a greenish then a yellow turbidity forms, which rapidly changes to a reddish-yellow color, and precipitates red cuprous oxide. An excess of the copper solution should not be used.

(*f*) *Haines' Test.*—The reagent used is a solution of copper sulphate in a mixture of equal parts of glycerine and water.

To about 5 cc. of urine add a few drops of this reagent, and then add sodium-hydroxide solution until the liquid assumes a deep-blue color. The mixture is then gradually heated to boiling. If sugar is present the color changes to yellow, and finally brick-red.

(*g*) *Indigo-carmine Test.*—The reagent is made by mixing 1 part of dried commercial extract of indigo with 30 parts of pure dry sodium carbonate.

The test: Add enough of this powder to 5 cc. of the urine to give it a transparent-blue color, and heat to boiling. If sugar is present, the color changes to violet, cherry-red, and finally yellow. On gently agitating the tube the colors appear in the reversed order.

(*h*) *Molisch's Test.*—Put 1 cc. of the urine in a test-tube, add 2 cc. of a saturated solution of alpha-naphthol, mix well, and then add an excess of sulphuric acid. A deep violet color is produced if sugar is present. On dilution with water a blue ppt. occurs.

Thymol or menthol may be used instead of naphthol. The color then produced is deep red.

Quantitative Estimation.—This is generally effected

by the use of Fehling's solution. The process is described on page 351.

By Fermentation.—This is performed by adding a small quantity of yeast to a certain volume of urine and setting aside for about 24 hours. As the sugar is decomposed the specific gravity of the urine becomes less. Therefore by taking the specific gravity of the urine before and after fermentation a fairly accurate estimation of the sugar present may be made, provided the quantity be not less than 0.5 per cent. Each degree of the urinometer indicates 0.219 per cent. of sugar. If the specific gravity of a sample of urine is found to be 1032, and after subjecting it to fermentation it is 1022, the quantity of sugar present in the sample is 10 times $0.219 = 2.19\%$.

Estimation of Sugar by Dr. Einhorn's Fermentation Saccharometer.—Take one gramme of commercial compressed yeast (or $\frac{1}{16}$ of a cake of Fleischmann's yeast), shake thoroughly in the graduated test-tube with 10 cc. of the urine to be examined. Then pour the mixture into the bulb of the saccharometer (Fig. 50). By inclining the apparatus the mixture will easily flow into the cylinder, thereby forcing out the air. Owing to the atmospheric pressure the fluid does not flow back, but remains there.

The apparatus is to be left undisturbed for twenty to twenty-four hours in a room of ordinary temperature.

If the urine contains sugar, the alcoholic fermentation begins in about twenty to thirty minutes. The evolved carbonic-acid gas gathers at the top of the cylinder, forcing the fluid back into the bulb.

On the following day the upper part of the cylinder is filled with carbonic-acid gas. The changed level of

the fluid in the cylinder shows that the reaction has taken place, and indicates by the numbers—to which it corresponds—the approximate quantity of sugar present.

If the urine contains more than one per cent of

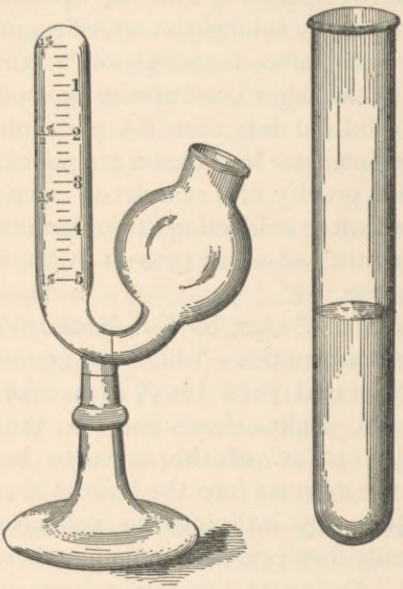

FIG. 50.

sugar, then it must be diluted with water before being tested.

Diabetic urines of straw color and a specific gravity of 1018–1022 may be diluted twice; of 1022–1028, five times; 1028–1038, ten times.

The original (not diluted) urine contains in proportion to the dilution two, five, or ten times more sugar than the diluted urine.

In carrying out the fermentation test it is always recommendable to take, besides the urine to be tested, a normal one, and to make the same fermentation with it.

The mixture of the normal urine with yeast will have on the following day only a small bubble on the top of the cylinder. That proves at once the efficacy and purity of the yeast.

If there is likewise in the suspected urine a small bubble on the top of the cylinder, then *no* sugar is present; but if there is a much larger gas volume, then we are *sure* that the urine contains sugar.

Test for Bile.—(*a*) *Oliver's Test.*—Dissolve 2 gms. of fresh peptone (Savory & Moore's Pulverized), 0.25 gm. salicylic acid, and 2 cc. of 33% acetic acid in water to make 200 cc. The solution should be rendered perfectly clear by filtration.

The urine should also be clarified by filtration, and diluted to a specific gravity of 1008. One cc. of this urine is added to 3 cc. of the above reagent. If biliary salts are present a distinct opalescence at once appears, which becomes more intense in about five minutes. This opalescence will be more or less distinct in proportion to the quantity of bile present.

(*b*) *Gmelin's Test.*—2 or 3 cc. of partially decomposed yellow nitric acid are placed in a test-tube, and an equal volume of the urine is cautiously poured on top. In the presence of bile pigments a play of colors will appear, beginning with green, then passing through blue, violet, red, and yellow.

The nitric acid may be prepared for this test by adding a fragment of zinc to ordinary nitric acid.

(*c*) *Pettenkofer's Test.*—Mix equal parts of urine and

sulphuric acid, add one drop of simple syrup, and apply a gentle heat. The color will change from cherry-red to purple if biliary acids are present.

(*d*) *Ultzmann's Test.*—5 cc. of urine are mixed with 2 cc of a strong solution of KOH (1–3) and then an excess of pure HCl added. The mixture will become emerald-green if biliary pigments are present.

(*e*) *Tincture-of-iodine Test.*—A few drops of iodine tincture are floated upon the surface of the urine. If biliary pigments are present, there will appear at the line of contact of the two liquids, after a few minutes, a beautiful emerald-green zone.

URINARY DEPOSITS.

Chemical Examination.—Draw off a portion of the sediment with a pipette or glass tube, and transfer to a watch-glass or small test-tube.

- White Deposit.
  - Dissolves on heating urine ..... *Ammonium urate.*
  - Insoluble on heating.
    - Sol. in NH_4OH ..... *Cystine.*
    - Insol. in NH_4OH,
      - Soluble in acetic acid, *Earthy Phosphates.*
      - Insoluble in acetic acid, *Calcium oxalate* or *oxalurate.*
    - Gelatinizes in NH_4OH... *Pus* (see above).
- Colored Deposit.
  - Visibly crystalline (red) ..... *Uric acid.*
  - Amorphous.
    - Pale, easily soluble by heat ..... *Urates.*
    - Deep colored, slowly soluble by heat, *Acid urates with uroerythrin.*
    - Red, insoluble by heat, alkalies or acids. *Blood.*

Microscopical Examination.—With a clean pipette draw off a small portion of the sediment, transfer to a clean glass slide, and examine with a $\frac{1}{2}$-in. or $\frac{1}{4}$-in. objective.

- **Deposit is Amorphous.**
  - Small granules with spicules on larger granules.....
    - light = *Sodium urate.*
    - dark = *Ammonium urate.*
  - Vanishes on adding KOH or NaOH.....
  - Permanent, adding KOH or NaOH..... *Calcium phosphate* (rare).
  - Globules, strongly refracting light..... *Fat.*
- **Deposit is Crystalline.**
  - **Urine Acid.**
    - Reddish, cross, or whetstone shape, or in groups..... *Uric acid.*
    - Regular octahedra, envelope-shaped, *Calcium oxalate.*
    - Hexagonal plates, soluble in NH_4OH (white)..... *Cystine.*
    - Bundles of needles crossing each other..... *Tyrosin.*
  - **Alkaline Urine.**
    - Large prisms, soluble in acetic acid (coffin-lid shape), *Ammon. magnesium phosphate.*
    - Brown, double spheres, spiculated, *Urate of ammonium.*
    - Club-shaped crystals, single or in groups, *Calcium phosphate.*
    - Double spheres, radiated structure, soluble in acetic acid, with effervescence, *Calcium carbonate* (rare).
    - Double spheres, insoluble in acetic acid, *Calcium oxalurate* (rare).
- **Cellular Elements.**
  - Double spheres, yellow or red, radiated..... *Uric acid.*
  - Red or yellow disks, biconcave; sometimes irregular in outline, *Blood cells.*
  - Granulated corpuscles. With dilute acetic acid show 3 to 5 nuclei.
    - Albumen present..... *Pus.*
    - " absent, *Mucus corpuscles.*
  - Round, conical, or flat cells with one nucleus, *Epithelium from urinary tract.*
  - Tadpole-shape, with long tail..... *Spermatozoa.*
  - Cylinders, parallel margins, clear, granular, or containing epithelial cells as blood cells... *Casts of uriniferous tubules.*
  - Fungi, yeast, hairs, threads, etc., etc.... *Extraneous matters.*

—*From Bartley's Medical Chemistry.*

A little experience in the microscopical examination of urinary sediments will usually enable one to readily recognize the various forms, and thus obviate the necessity for a chemical examination.

CHAPTER LV.

DETERMINATION OF THE MELTING-POINT OF FATS.

THE melting-point of a fat can be quickly found by immersing the bulb of a thermometer in the melted fat, then suspending the bulb which is coated with congealed fat in the middle of a beaker of water to which heat is gradually applied, and noting the temperature at which the fatty coat melts from the bulb.

Another Way.—Draw out a long capillary tube, Fig. 51. Melt the fat, and draw a small portion of it up into the tube. The melted fat will rise in the tube by capillary attraction. This tube is bound or held against the bulb of a thermometer, and immersed in a beaker of cold water to which heat is applied. The fat is congealed upon immersion in water and becomes opaque. When the temperature of the water is raised to the proper degree, the opaque cylinder of fat melts and becomes transparent. At this point the temperature must be noted. The congealing-point may be found by removing the source of heat and allowing the water to cool gradually, and noting the point at which the fat in the tube again congeals and becomes opaque. The congealing may be hastened by adding cautiously cold water to that in the beaker. The congealing-point will be identical with, or close to the melting-point.

FIG. 51.

CHAPTER LVI.

ESTIMATION OF OIL OR FAT IN EMULSIONS AND OINTMENTS.

Apparatus.—A test-tube of about eight inches in length, fitted with two good corks, one of which is provided with a wash-bottle arrangement, Fig. 52.

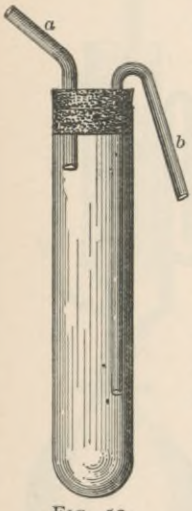

FIG. 52.

The Process.—A weighed quantity of the emulsion (2 to 5 gms.) or ointment (1 to 2 gms.) is put into the test-tube, the latter half filled with ether, corked and shaken for about 5 minutes, and set aside so as to allow the liquids to separate. The ethereal solution of the fat or oil, which forms the upper layer, is carefully drawn off into a tared vessel. This is done by inserting the stopper having the wash-bottle arrangement, and gently blowing in the tube *a*. The tube *b* is raised or lowered so that its lower end is slightly above the surface of the lower layer in the tube.

This process is repeated until the fat is completely extracted, which is shown by there being no residue left, when a few drops of the last portion drawn off are evaporated on a watch-glass.

The mixed ethereal solutions are now subjected to evaporation, thus leaving the oil behind. The tared evaporating-dish containing the oil is dried in a water-bath and weighed.

By deducting the weight of the dish when empty from the above weight, the weight of the fat or oil is obtained.

In this way the fat in powdered drugs, in chocolate, in milk, etc., may be estimated. The estimation is more rapid than though not as accurate as, when made by the Soxhlet's extraction apparatus which is illustrated in Fig. 53. Into the tarred flask *A* the ether or other solvent is put. The substance *B*, inclosed in a cartridge of filtering-paper, is introduced into the tube *C*. The latter in turn is connected with an upright condenser *D*. The flask is now heated by a water-bath, and the vapor of the ether rises through *E*, condenses and drops onto the powdered substance in the cartridge. When the instrument has become filled by the solvent to the level of the top of *F*, it runs back into the flask charged with part of the soluble matter. This process repeats itself until the whole of the soluble matter of the substance has been extracted.

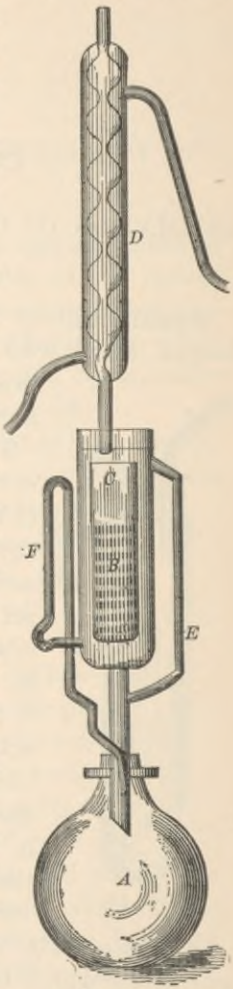

FIG. 53.

The flask is then detached, and the ether evaporated or distilled off; the soluble matter of the original powder being left in the flask. Resinous or sticky substances should be mixed with a little clean sand, in order to facilitate the extraction and prevent clogging up of the apparatus.

CHAPTER LVII.

ESTIMATION OF FATTY ACIDS.

Estimation of Oleic Acid.—Oleic acid may be estimated volumetrically by standard solution of potassa or soda, using phenolphthalein as an indicator.

The reaction is expressed by the following equation:

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + KOH = KC_{18}H_{33}O_2 + H_2O.$$

282 gms. 56 gms. or 1000 cc. $\frac{N}{1}$ KOH.

Thus each cc. of the normal alkali solution consumed represents 0.282 gm. of oleic acid.

Free Fatty Acids in Lard may be estimated as follows: 10 gms. of lard are dissolved in 10 cc. of chloroform, and 10 cc. of alcohol and one drop of phenolphthalein T. S. are added. The mixture is then titrated with normal potassium hydroxide V. S. until a pink tint is produced, which remains after violently shaking the mixture. Not more than 0.2 cc. should be required.

Formic Acid.—5 cc. of formic acid are titrated with $\frac{N}{1}$ potassium hydroxide V. S. in the presence of phenolphthalein. 28 or 29 cc. should be required.

Each cc. = 0.046 gm. of formic acid.

CHAPTER LVIII.

ESTIMATION OF TANNIN.

G. FLEURY (Jour. Phar. Chim., 1892, 499) proposes to use egg-albumen for estimating tannin in wine and in the petals of red roses.

The hard-boiled egg-albumen is dried at a moderate temperature, and powdered. This is washed with dilute alcohol (10 per cent), very slightly acidulated with tartaric acid, to saturate the alkali. The albumen is again dried, and kept in a well-stoppered bottle.

The method of operation is as follows:

Albumen powder, equal to seven or eight times the quantity of tannin, which is supposed to be present, is added to the liquid in a flat dish. The dish is then set aside for forty-eight hours, stirring occasionally; the liquid must during this time be acid, not alkaline.

The end of the reaction is attained when the liquid ceases to give a color with ferric chloride T. S.

The powder is then collected on a filter, washed with very dilute alcohol, and then dried at 100° C. At the same time a sample of the original powder is dried and weighed, to determine the amount of water it contains.

The increase in weight of the albumen which was in contact with the tannin, minus the loss of weight of the albumen in the check experiment, gives the weight of tannin present.

This method is not available for determining the

tannin in nutgalls, because the absorption by the albumen is incomplete and too slow. In testing, it must be borne in mind that gallic acid is not absorbed by the albumen, and consequently still gives its reaction with ferric chloride.

ESTIMATION OF TANNIN IN BARKS, ETC. (LÖWENTHAL'S METHOD.)

The principle of this method depends upon the oxidation of the tannic acid, together with other easily oxidizable substances, by titrating with potassium permanganate.

The total amount of such substances is thus found, and expressed by a known volume of permanganate. The actual available tannin is then removed by gelatine or glue, and another titration made, to determine the amount of oxidizable matters other than tannin.

The difference between the amounts of permanganate solution used in the two titrations gives the amount of tannin present which is available for tanning purposes, expressed in terms of permanganate.

Solutions Required.—1. $\frac{N}{30}$ *Potassium Permanganate V.S.* (1.05 gm. per litre).

2. *Indigo Solution.*—6 gms. of pure precipitated indigo and 50 cc. of concentrated sulphuric acid are dissolved in sufficient water to make one litre.

3. *Glue and Salt Solution.*—25 gms. of good transparent glue are macerated in cold water, and then heated to dissolve; the solution is then made up to one litre, and saturated with common salt. The solution should be filtered clear when used.

4. *Acidified Solution of Common Salt.*—This is a saturated solution of common salt, containing in one litre 25 cc. of sulphuric acid.

The Analysis.—20 gms. of the bark or 10 gms. of sumach are boiled with several portions of water until exhausted, and the solution when cold is made up to one litre.

10 cc. of this solution are diluted to 1000 cc.; 25 cc. of the indigo solution are added, and the permanganate solution then run in, drop by drop, from a burette, stirring constantly, until the blue color changes to yellow, and the number of cc. of permanganate solution consumed noted.

25 cc. of the indigo solution are now taken and diluted to 1000 cc., titrated with permanganate, and the number of cc. again noted. By deducting this number from the number of cc. used in the first titration, the quantity of permanganate required by the tannin and the other oxidizable substances in the 10cc. of solution taken is found.

The next step is to deprive a portion of the tannin solution of its tannin, and again titrate.

100 cc. of the tannin solution are treated with 50 cc. of the glue and salt solution, and, after stirring, 100 cc. of the acidulated salt solution are added, the mix ture stirred again, and set aside for several hours. The glue absorbs the tannin out of solution. The solution is then filtered. The filtrate should be perfectly clear.

Of this filtrate take 50 cc. (containing 20 cc. of the tannin solution), mix with 25 cc. of the indigo solution, and titrate with the permanganate solution as before, noting the number of cc. consumed.

Another 25 cc. of the indigo solution are now taken,

diluted as in the other trial, and again titrated with permanganate. By deducting the number of cc. so obtained from the number required by the 50 cc. of filtrate, the quantity required by the oxidizable matter other than tannic acid in the 20 cc. of tannin solution is obtained. Therefore one half of this quantity, when deducted from the quantity of permanganate solution representing the total oxidizable matter in 10 cc. of the tannin solution, gives the quantity of permanganate which was effected by the tannin above.

Duplicate titrations should always be made, and should agree within 0.1 or 0.2 cc. of the permanganate solution.

Thus far we have only the tannin value (expressed in terms of permanganate), of 10 cc. of the original solution, representing $\frac{1}{100}$ of the material under examination.

The permanganate solution may be compared with a standard solution of the purest gallo-tannic acid obtainable, or with any tannin of known value, and thus a coefficient obtained.

According to the experiments of Neubauer, 63 gms. of pure crystallized oxalic acid (equivalent to 31.4 gms. potassium permanganate) correspond to 41.57 gms. of purified gallo-tannic acid (nutgall tannin). And Oser found that 63 gms. of oxalic acid correspond to 62.355 gms. of querci-tannic acid (oak-bark tannin). These coefficients are now largely used.

Based upon these figures each cc. of $\frac{N}{30}$ permanganate solution represents .0013856 gm. of gallo-tannin, or .0020785 gm. of querci tannin. In most analyses, however, especially when the composition of the tannin is not exactly known, it is expressed as oxalic acid.

CHAPTER LIX.

ESTIMATION OF GLYCERIN.

Glycerin (Glycerol) $C_3H_5(OH)_3 = \left\{ {}^{91.79}_{*92} \right.$—The estimation of glycerin, of fats, etc., may be made by the method of Benedikt and Zsigmondy. This method consists in saponifying the fat and oxidizing the resultant glycerin by permanganate in alkaline solution; thus oxalic acid, carbon dioxide, and water are formed The excess of permanganate is then destroyed by sulphurous acid or a sulphite, the liquid filtered to separate the manganese dioxide, and the oxalic acid then precipitated by a soluble calcium salt in the presence of acetic acid, and the precipitated calcium oxalate then titrated with permanganate, or after ignition and conversion into carbonate titrated with standard acid solution in the usual way.

Aqueous solutions of glycerin may of course be submitted to the method very easily.

The reactions are as follows:

$$\underset{92}{C_3H_5(OH)_3} + 2KMnO_4 = \underset{\substack{\text{(Potassium}\\ \text{oxalate)}\\ 166}}{K_2C_2O_4} + K_2CO_3 + 4MnO_2 + 4H_2O;$$

then

$$\underset{166}{K_2C_2O_4} + CaCl_2 = 2KCl + \underset{\substack{\text{(Calcium oxalate)}\\ 128}}{CaC_2O_4};$$

then

$$\underset{\substack{100)640\\ 6.40\text{ gms.}}}{5CaC_2O_4} + 8H_2SO_4 + \underset{\substack{100)315\\ 3.15\text{ gms. or 1000 cc. }\frac{N}{10}\text{ V. S.}}}{2KMnO_4} = 5CaSO_4$$

$$+ 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2.$$

Thus 1000 cc. $\frac{N}{10}$ permanganate solution represents 6.4 gms. of calcium oxalate, which is equivalent to 8.3 gms. of potassium oxalate, which is equivalent to 4.6 gms. of glycerin.

Thus each cc. of the permanganate solution of decinormal strength used up by the calcium oxalate represents .0046 gm. of glycerin.

If the precipitated calcium oxalate is ignited and converted into carbonate, and the carbonate then titrated with decinormal sulphuric or hydrochloric acid, the reactions are as follows:

$$\underset{\substack{4)256\\ 10)\ 64\\ 6.4\text{ gms.}}}{2CaC_2O_4} + O_2 = \underset{\substack{4)200\\ 10)\ 50\\ 5.0\text{ gms.}}}{2CaCO_3} + 2CO_2;$$

$$\underset{\substack{4)200\\ 10)\ 50\\ 5.0\text{ gms.}}}{2CaCO_3} + \underset{\substack{4)196\\ 10)\ 49\\ 4.9\text{ gms. or 1000 cc. }\frac{N}{10}\text{ V. S.}}}{2H_2SO_4} = 2CaSO_4 + 2H_2O + 2CO_2.$$

Thus each cc. of decinormal acid represents 0.005 gm. of $CaCO_3$, or 0.0064 gm. of calcium oxalate, or .0046 gm. of glycerin.

If experimenting with pure glycerin, operate upon 10 cc. of a 2% solution. This is diluted with cold water

to about 400 cc., about 10 gms. of caustic potash are added to this, and then a saturated solution of potassium permanganate until the liquid is no longer green, but blue or blackish. An excess does no harm.

The liquid is then boiled for about one hour, and a strong solution of sodium sulphite is added to the boiling liquid until the violet or green color is destroyed; the liquid is then filtered while yet hot, to separate the precipitated manganese dioxide. When cool, it is acidified with acetic acid, and calcium chloride added to precipitate the oxalic acid as calcium oxalate. When the deposition of calcium oxalate is complete it is separated by filtration, and titrated either with permanganate or after ignition with standard sulphuric acid.

The former method is preferable. For this purpose the filter is pierced, and the precipitate rinsed into a porcelain basin; about 10 cc. of dilute sulphuric acid are then added through the funnel slowly, so that it comes into contact with and washes through any of the precipitate that may still cling to it.

The liquid is now diluted to about 200 cc., brought to 60° C., and the decinormal permanganate run in from a burette, slowly, until a faint but distinct pink color appears and remains permanent after stirring; each cc. of the permanganate thus used represents 0.0046 gm. of glycerin.

The process for *estimating the glycerin of fats* is as follows:

Ten grammes of the fat or oil are placed in a strong small bottle together with 4 gms. of pure potassium hydroxide, dissolved in 25 cc. of water; the bottle is then closed with a solid rubber stopper and tied down

firmly with wire; it is then placed in boiling water and heated, with occasional shaking, from six to ten hours, or until the fat or oil is completely saponified. The contents of the bottle are then poured into a beaker and diluted with hot water; this should give a clear solution.

A dilute acid is then added to separate the fatty acids, which are filtered out and the filtrate made up to a given volume.

This solution, which will usually contain 0.2 to 0.5 gm. of glycerin, according to its origin, is transferred to a porcelain basin, diluted with cold water to about 400 cc., and the glycerin estimated as described under the experiment with pure glycerin.

ESTIMATION OF GLYCERIN IN FLUID EXTRACTS.

Take 10 gms. of the fluid extract, evaporate it at a low temperature to 5 gms. It is important that a low temperature be employed in order that the alcohol, but not the glycerin, be volatilized.

Dissolve the residue in 50 cc. of water, and add solution of lead subacetate drop by drop until precipitation is complete. Allow the precipitate to subside, filter the clear liquid through a wet filter, wash the precipitate thoroughly with water, add to the filtrate and washings a few drops of dilute sulphuric acid, then 10 gms. of solid potassium hydroxide, and an excess of potassium permanganate solution. Bring the liquid to the boiling-point and keep there for about one hour, then add sufficient of a strong solution of sodium sulphite to destroy the violet color due to the excess of permanganate.

Filter while still hot to separate the precipitated MnO_2, and when cool acidify with acetic acid and add calcium chloride solution to precipitate the oxalic acid as calcium oxalate.

When precipitation is complete filter and titrate (after the addition of sulphuric acid) with $\frac{N}{10}$ potassium permanganate.

Each cc. = 0.0046 gm. glycerin.

CHAPTER LX.

ESTIMATION OF PHENOL.

Decinormal Bromine, V. S. (Koppeschaar's Solution), $Br = \left\{ \frac{79.76}{*80} \right.$. $\left. \frac{7.976}{*8} \right\}$ gms. in 1 litre.—

$KBr = 118.79$ $NaBr = 102.76$
$KBrO_3 = 166.67$ $NaBrO_3 = 150.64$

This solution does not contain free bromine, but it contains two salts, a bromide and a bromate, which when treated with hydrochloric acid, liberate a definite quantity of bromine.

It is made as follows:

Dissolve 3 gms. of sodium bromate and 50 gms. of sodium bromide (or 3.2 gms. of potassium bromate and 50 gms. of potassium bromide) in sufficient water to make 900 cc.

Transfer 20 cc. of this solution 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, then 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, then

add from a burette decinormal sodium thiosulphate V. S. until the color of the free iodine is nearly all discharged, then add a few drops of starch T. S., and continue the titration with $\frac{N}{10}$ thiosulphate V. S. until the blue color disappears.

Note the number of cc. of the $\frac{N}{10}$ sodium thiosulphate V. S. thus used, and dilute the bromine solution so that equal volumes of it and the $\frac{N}{10}$ sodium thiosulphate V. S. will exactly correspond to each other under the above-mentioned conditions.

Example.—Assuming that the 20 cc. of bromine solution required 25.2 cc. of the $\frac{N}{10}$ thiosulphate to completely absorb the iodine, the bromine solution must be diluted in the proportion of 20 to 25.2; that is, each 20 cc. must be diluted to make 25.2 cc.

Thus if 850 cc. are left, they must be diluted to make 1071 cc., and the solution is decinormal.

A new trial should always be made after diluting, and the bromine solution should correspond, volume for volume, with the decinormal sodium thiosulphate V. S.

The first step in the preparation of this solution is to dissolve the salts; then hydrochloric acid is added, which liberates a definite quantity of bromine, as the equation illustrates:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

The stopper should be inserted into the bottle as soon as the hydrochloric acid has been added, in order

that no bromine vapor escape, and the bottle rotated so as to mix the acid thoroughly with the liquid.

The next step is to determine the quantity of bromine which a definite volume of solution will liberate. The bromine solution should be of such strength that 1000 cc. of it will contain 7.976 gms. of available bromine. Bromine, like chlorine, liberates iodine from potassium iodide, and is estimated in the same manner.

One atomic weight of iodine is liberated by one atomic weight of bromine:

$$Br_2 + 2KI = 2KBr + I_2.$$

Thus by determining the quantity of iodine liberated the quantity of bromine is found.

The iodine is determined by the $\frac{N}{10}$ sodium thiosulphate V. S., one litre of which represents 12.65 gms. of iodine, which is equivalent to 7.976 gms. of bromine, as is shown by the following equation:

$$\underset{20)159.52}{(Br_2)} = \underset{20)253}{I_2} + 2(\underset{20)496}{Na_2S_2O_3} + 5H_2O)$$

7.976 gms. 12.65 gms. 24.8 gms. or 1000 cc. $\frac{N}{10}$ V. S.

$$= 2NaI + Na_2S_4O_6 + 10H_2O.$$

Carbolic Acid, $C_6H_5(OH) = \left\{ \begin{matrix} 93.78 \\ *94 \end{matrix} \right.$ (Phenol, Phenylhydrate, Hydroxylbenzene, Phenylalcohol).—This is regarded as benzene (C_6H_6) in which one atom of hydrogen has been replaced by hydroxyl (OH).

The Valuation of Carbolic Acid according to the U. S. P. is as follows:

1.563 gm. of the carbolic acid are dissolved in suffi-

cient water to make 1000 cc. 25 cc. of this solution, containing 0.039 gm. of the acid, are transferred to a glass-stoppered bottle having a capacity of about 200 cc.

To this 30 cc. of decinormal bromine V. S., followed by 5 cc. of hydrochloric acid, are added, and the bottle immediately stoppered, and shaken repeatedly during half an hour.

Then the stopper is removed just sufficiently to introduce 5 cc. of a 20-per-cent. aqueous solution of potassium iodide, being careful that no bromine escape.

The bottle is then thoroughly shaken and the neck rinsed with a little water, the washings being allowed to flow into the bottle.

The solution is now ready for titration, and the decinormal sodium thiosulphate is delivered in from a burette, until the iodine is almost completely absorbed; then add a few drops of starch T. S., and continue the titration until the blue color is just discharged.

Note the number of cc. of $\frac{N}{10}$ thiosulphate V. S. used; deduct this number from 30 cc. (the quantity of $\frac{N}{10}$ bromine V. S. originally added), and the quantity of $\frac{N}{10}$ bromine V. S. which went into combination with the phenol is obtained.

Each cc. of $\frac{N}{10}$ bromine V. S. represents 0.001563 gm. of pure phenol.

Example.—Assuming that 6 cc. of $\frac{N}{10}$ sodium thio-

sulphate were required to discharge the color of the starch iodide, this deducted from 30 cc. leaves 24 cc., the quantity which combined with the phenol.

$$0.001563 \times 24 = .037512 \text{ gm.}$$

$$\frac{0.037512 \times 100}{0.039} = 96.1\% \text{ of pure phenol.}$$

The above method originated with Koppeschaar, and is the only volumetric method by which accurate results may be obtained.

It is based upon the fact that bromine reacts with phenol, producing an insoluble precipitate of tribromphenol.

The titration is not made directly; but the phenol solution is treated with an excess of standard bromine solution in the presence of some hydrochloric acid. The hydrochloric acid liberates the bromine, and the freed bromine then reacts with the phenol, as shown by the equations:

(a) $5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3H_2O + 3Br_2$;

(b) $C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$

$6)93.78$ $\quad$ $6)478.56$

$10)15.63$ $\quad$ $10)79.76$

1.563 gms. $\quad$ 7.976 gms. or 1000 cc. $\frac{N}{10}$ bromine V. S.

Thus each cc. of the $\frac{N}{10}$ bromine V. S. represents 0.001563 gm. of pure phenol.

The bromine solution which was added in excess, and the liberated bromine of which, is not fixed by phenol, is then found by residual titration with $\frac{N}{10}$

sodium thiosulphate V. S. after the addition of some potassium iodide.

The decinormal bromine solution and the decinormal sodium thiosulphate solution being equivalent, each cc. of the latter consumed represents one cc. of the former. Then by subtracting the number of cc. of the sodium thiosulphate solution used from the number of cc. of bromine solution originally added, the quantity of the latter which was actually consumed by the phenol present is found. This number when multiplied by the factor for phenol then gives the quantity of pure phenol present.

The hydrochloric acid used in the above estimation must contain no free chlorine. The potassium iodide must be free from iodate. The starch T.S. should not be added until most of the free iodine has been taken up, and the color of the solution has diminished to light yellow.

The carbolic acid should be diluted with water before titration, and should never be stronger than 0.1 gm. in 25 cc.

Mr. H. Bechurts reports that the precipitate obtained from phenol and bromine is not pure tribromphenol, but a mixture of tribromphenol ($C_6H_2Br_3OH$) and tribromphenol bromide ($C_6H_2Br_3OBr$).

Thus the results obtained by direct titration are often too high, since in the formation of tribromphenol only 6 atoms of bromine are required, while for the production of tribromphenol bromide 8 atoms of bromine are taken up by one molecule of phenol.

The correct results obtained by Koppeschaar's method are attributable to the use of potassium iodide,

which decomposes the tribromphenol bromide, liberating iodine, thus:

$$C_6H_2Br_3OBr + 2KI = C_6H_2Br_3OK + KBr + I_2.$$

The free iodine is then estimated by residual titration, together with that liberated by the excess of bromine added.

Thus the nature of the original precipitate does not affect the final results.

ESTIMATION OF PHENOL BY DR. WALLER'S METHOD.

Solutions Required.—1. A standard solution of phenol containing 10 gms. of pure phenol in 1 litre.

2. Diluted sulphuric acid of 15% or 20% strength, saturated with alum. This is needed to facilitate the settling of the precipitate.

3. A solution of bromine in water.

The Estimation.—Of the sample 10 gms. are introduced into a litre flask, and made up with water to one litre. This solution is filtered through a dry filter, and 10 cc. of the clear filtrate taken for analysis. It is placed into an 8-oz. glass-stoppered bottle, and about 30 cc. of the acid-alum solution added. Into another bottle of the same kind 10 cc. of the standard phenol solution is put, and to this also 30 cc. of the acid-alum solution are added.

The bromine solution is now added from a burette to the bottle containing the standard phenol solution till no more precipitate forms, the bottle being stoppered and well shaken after each addition. The end reaction is further indicated by the appearance of a

yellow color when a slight excess of bromine is reached. Near the end the precipitate forms slowly.

The other solution containing the sample under analysis is titrated in the same way. Then the calculation is made as follows:

The number of cc. of bromine solution consumed by the sample is multiplied by 100, and then divided by the number of cc. of bromine solution used by the standard phenol solution. The answer is the per cent. of pure phenol contained in the sample analyzed.

The Amount of Water contained in a solution of carbolic acid may be determined by agitating the solution with an equal volume of chloroform in a graduated cylinder. After standing, the upper layer consists of the water contained in the mixture.

Crude or Impure Carbolic Acid.—Phenol in crude carbolic acid is estimated after separating the tarry matters. 20 cc. of the crude carbolic acid are placed in a beaker with 20 cc. of a strong solution of potassium hydrate (sp. gr. about 1.30). The mixture is well shaken and allowed to stand for half an hour; it is then diluted to ¼ litre with water. The tarry matters and other foreign impurities are thus set free, and may be removed by filtration, the filter and contents being washed with lukewarm water till the washings are no longer alkaline. The filtrate and washings are then slightly acidulated with hydrochloric acid, and made up to 3 litres with water.

The small quantity of tarry matters which is left in the filtrate does not interfere in the titration which follows. 50 cc. of this solution are now taken, and 120 cc. of the decinormal bromine V. S. are added, followed by 5 cc. of hydrochloric acid, and the mixture

shaken frequently during half an hour. 10 cc. of potassium iodide T. S. are then added, shaken, allowed to rest (not longer than 5 minutes), and finally titrated with decinormal sodium thiosulphate, using starch T. S. as an indicator.

The number of cc. of the thiosulphate solution used are deducted from 120 cc., the quantity of $\frac{N}{10}$ bromine V. S. originally added, and the quantity of the latter which was actually taken up by the phenol is obtained. This figure when multiplied by the factor for phenol, 0.001563 gm., gives the quantity of phenol present in the sample operated upon. It must be remembered that the 50 cc. of the diluted carbolic acid used in this assay represent $\frac{1}{5}$ of one cc. of the original sample.

Example.—Let us assume that 80 cc. of decinormal sodium thiosulphate were required in the residual titration. Deducting this from 120 leaves 40 cc. of bromine V. S. which actually went into combination with the phenol; then $40 \times .001563 = 0.06252$ gm. of phenol present in 0.33 cc. of the solution analyzed.

CHAPTER LXI.

ESTIMATION OF ALKALOIDS (VOLUMETRICALLY).

In making alkaloidal assays of drugs it has long been the custom to evaporate the final ethereal or chloroformic extract, and to weigh the residue as alkaloid. This residue seldom if ever consists of the pure alkaloid, and the amount of impurity is very variable; consequently gravimetric results were in many cases very wide of the truth, and hence unreliable.

The volumetric methods are in most cases much more satisfactory.

While the results of the titration of the *total alkaloids* of drugs cannot be called absolutely accurate, nevertheless experience has shown that they are nearer the truth than those obtained by the gravimetric method.

In estimating an alkaloid by titration, it is essential to know the formula and molecular weight of the alkaloid, as well as the equivalent of acid with which it will combine.

In the case of drugs where two or more alkaloids are present, accurate results can only be obtained by determining how much of each alkaloid is present by a separate assay. But as a rule it is assumed that the alkaloids are present in equal quantities, and the mean of their molecular weights is taken as the basis for the calculation.

If the alkaloid be from a recent extraction and is in the form of a free alkaloid, it is dissolved in a measured excess of $\frac{N}{10}$ acid solution and the excess of acid solution then determined by residual titration with $\frac{N}{100}$ alkali solution.

In this the $\frac{N}{10}$ sulphuric acid solution is preferred, except in the case of quinine or cinchonine, in which $\frac{N}{10}$ hydrochloric acid gives better results.

The process in detail is as follows: Place 2 gms. of the alkaloid into a beaker, add 75 cc. of $\frac{N}{10}$ sulphuric acid solution, and warm on a water-bath until the alkaloid is completely dissolved. The solution is then allowed to cool and diluted to 100 cc.

10 cc. of the solution (containing 0.2 gm. of the alkaloid and 7.5 cc. of $\frac{N}{10}$ sulphuric acid solution) are removed by means of a pipette and retitrated with $\frac{N}{100}$ potassium hydroxide solution. One tenth of the quantity of the $\frac{N}{100}$ alkali used is deducted from the 7.5 cc. of the $\frac{N}{10}$ acid solution, and the remainder is the quantity of the latter which combined with, and hence represents, the alkaloid present.

Either hæmatoxylin solution or Brazil-wood T. S. may be employed as the indicator.

The quantity of alkaloid present is easily calculated when we know that a molecular weight of a monobasic acid or half a molecular weight of a dibasic acid will combine with and neutralize a molecular weight of an alkaloid, provided the alkaloid is a monacid base. If the alkaloid is a diacid base, one molecular weight will combine with two molecules of a monobasic acid or one molecular weight of a dibasic acid.

Sparteine and emetine are diacid alkaloids; most of the others are monacid bases.

Thus 1000 cc. of $\frac{N}{10}$ hydrochloric acid will combine with $\frac{1}{10}$ of the molecular weight of a monacid alkaloid or $\frac{1}{20}$ of the molecular weight of a diacid alkaloid, as the following equations show:

(Quinine.)

$$C_{20}H_{24}N_2O_2 + HCl = C_{20}H_{24}N_2O_2HCl.$$

10)324 grms. 10)36.4 grms. or 1000 cc. $\frac{N}{1}$ acid.

32.4 grms.

3.62 grms. or 1000 cc. $\frac{N}{10}$ acid.

(Sparteine.)

$$C_{15}H_{26}N_2 + 2HCl = C_{15}H_{26}N_2(HCl)_2$$

2)114 2)72.8

10) 57 10)36.4

5.7 grms. 3.64 grms. or 1000 cc. $\frac{N}{10}$ acid.

Prof. Plugge made a number of experiments with a view to determine the possibility of estimating volumetrically the amount of acid contained in alkaloidal salts, and from this determining the amount of alkaloid. He found—

(1) That in the salts of the weak opium bases narcotine, papaverine, and narceine the amount of acid can

be volumetrically estimated with either litmus or phenolphthalein, the reaction being as precise and well defined as if no alkaloid were present.

(2) That in the salts of alkaloids in general, the acid can be readily determined by the use of phenolphthalein, the volatile alkaloids coniine and nicotine being exceptions; and that in the case of morphine, brucine, codeine, and thebaine, phenolphthalein may be used with certain restrictions.

(3) That the *free* acid in solutions of alkaloidal salts can be determined by the use of litmus, but in solutions of weak opium bases litmus cannot be used. The entire quantity of acid, both free and combined, may be determined by the use of phenolphthalein. The difference between the two titrations gives the quantity of acid united to the base.

Thus he estimates the alkaloid by titrating the acid of the salt of the alkaloid with standard alkali, and from the result calculates the quantity of alkaloid present. He first determines the uncombined (free) acid by titrating with standard alkali in the presence of litmus.

He then titrates another portion of the solution in the presence of phenolphthalein to determine the total quantity of acid (both free and combined) present, and from this, indirectly, the quantity of alkaloid is calculated.

For the *estimation* of the *alkaloid* in a *commercial salt*, such as quinine sulphate, strychnine sulphate, etc.:

Dissolve the salt in hot water, and titrate with $\frac{N}{10}$ sodium-hydroxide solution, using phenolphthalein, methyl-orange, or some other suitable indicator.

The acid in combination with the alkaloid acts as though it were a free acid, and may be readily estimated by this method.

Phenolphthalein should be used with caution, as an indicator, in titrating morphine, as this alkaloid has a faint acid reaction with it.

It is generally preferable to titrate the solution of the salt of an alkaloid with $\frac{N}{10}$ potassium hydroxide to *exact neutrality*, using phenolphthalein as indicator. The alkaloid which is thus set free and in a neutral liquid may be titrated in the same by means of $\frac{N}{10}$ hydrochloric acid, using Brazil-wood T. S. as indicator. This gives very good results, and the two titrations are a check upon each other.

A. H. Allen states: "In titrating an alkaloid with methyl-orange as indicator it is rarely convenient to employ an aqueous solution of the base.

"A solution in proof-spirit can be employed, but the indicator is much less sensitive under such conditions.

"I have found it preferable, especially when an alkaloid is much colored, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkaloid in a little chloroform, ether, amylic alcohol, or other suitable *immiscible solvent.*

"The solution is placed in a small stoppered cylinder, together with a few cc. of water colored with a drop or two of methyl-orange. Then on gradually running in the standard acid from a burette, and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the coloring matter remains in

the immiscible layer, and presents a marked contrast to the red color of the aqueous liquid."

Allen has obtained satisfactory results with aconitine and its allies, even when working on as little as 0.030 gm., by using ether as a solvent, and titrating with $\frac{N}{50}$ hydrochloric acid.

In the titration of cinchona alkaloids such anomalous results are obtained that there is some doubt as to whether the relation of these alkaloids to acids is thoroughly understood. When quinine is titrated with an acid, almost twice as much of the latter is used, when methyl-orange is the indicator, as when Brazil-wood is employed as indicator. This is probably due to the fact that ordinary quinine sulphate is slightly alkaline to methyl-orange, and the end reaction with this indicator is not reached until the acid sulphate is formed, while with Brazil-wood as indicator the end reaction is reached sooner, that is, when the normal sulphate is formed, which is practically neutral to this indicator.

Quinine sulphate is also neutral to cochineal, but distinctly alkaline to litmus; hence the latter, like methyl-orange, is inapplicable in the titration of quinine. These anomalies should be had in mind when working upon the cinchona bases.

In titrating alkaloids, the personal equation plays an important part. It is generally correct to titrate to the point where a change of color is developed, though there is no agreement among authorities as to the proper end-reaction tints, and each operator relies upon his own judgment.

Lyman F. Kebler says: "In order to obtain

standard end reaction tints for alkaloids, it will be necessary to prepare some absolutely pure alkaloid. Treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid color-reaction."

"For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared."

The color changes produced by the principal indicators used in alkaloidal titrations are as follows:

	Acid.	Alkali.
Hæmatoxylin	Yellow.	Orange.
Brazil-wood	Yellow.	Red.
Cochineal	Yellow.	Purplish.
Phenolphthalein	Colorless.	Red.
Litmus	Red.	Bluish.
Methyl Orange	Red.	Straw Yellow.

TABLE SHOWING BEHAVIOR OF SOME OF THE ALKALOIDS WITH INDICATORS.

Name.	Formula.	Methyl-orange.	Phenolphthalein	Litmus.
Aconitine	$C_{33}H_{45}NO_{12}$	Alkaline	Neutral	Alkaline
Atropine	$C_{17}H_{23}NO_3$	"	Alkaline	"
Brucine	$C_{23}H_{26}N_2O_4$	"	Neutral	"
Cinchona bases		"	"	"
Cocaine	$C_{17}H_{21}NO_4$	"	"	"
Codeine	$C_{18}H_{21}NO_3$	"	Alkaline	"
Coniine	$C_8H_{15}N$	"	"	"
Morphine	$C_{17}H_{19}NO_3$	"	Faintly acid	"
Nicotine	C_5H_7N	"	Alkaline	"
Quinine	$C_{20}H_{24}N_2O_2$	"	Neutral	"
Strychnine	$C_{21}H_{22}N_2O_2$	"	"	"

Urea is neutral to methyl-orange, phenolphthalein, and litmus. Caffeine is neutral to phenolphthalein and litmus. Antipyrine is neutral to phenolphthalein and litmus. Pyridine is neutral to phenolphthalein and alkaline to litmus.

TABLE SHOWING THE FACTOR FOR VARIOUS ALKALOIDS WHEN TITRATING WITH $\frac{N}{10}$ ACID OR ALKALI.

Name.	Formula.	Molecular Weight.*	Factor.
Aconitine	$C_{33}H_{45}NO_{12}$	647	0.0647
Atropine	$C_{17}H_{23}NO_3$	289	0.0289
Brucine	$C_{23}H_{26}N_2O_4$	394	0.0394
Cinchonine	$C_{19}H_{22}N_2O$	294	0.0294
Cinchonidine	$C_{19}H_{22}N_2O$	294	0.0294
Cocaine	$C_{17}H_{21}NO_4$	303	0.0303
Codeine	$C_{18}H_{21}NO_3$	299	0.0299
Coniine	$C_8H_{15}N$	125	0.0125
Emetine	$C_{30}H_{44}N_2O_4$ (Glenard)	496	0.0248
	$C_{30}H_{40}N_2O_5$ (Kunz)	508	0.0254
Hyoscine	$C_{17}H_{21}NO_4$	303	0.0303
Hyoscyamine	$C_{18}H_{23}NO_3$	265	0.0265
Morphine	$C_{17}H_{19}NO_3$	285	0.0285
Nicotine	C_5H_7N	81	0.0081
Pilocarpine	$C_{11}H_{16}N_2O_2$	208	0.0208
Quinine	$C_{20}H_{24}N_2O_2$	324	0.0324
Sparteine	$C_{15}H_{26}N_2$	114	0.0114
Strychnine	$C_{21}H_{22}N_2O_2$	334	0.0334

ESTIMATION OF ALKALOIDS BY MAYER'S REAGENT.

The results of titrating with Mayer's solution have only an approximate value, being influenced to a large extent by various conditions, such as degree of dilution, mode of conducting the operation, and the length of time allowed for precipitation after each addition of the reagent.

The Mayer's solution is added from a burette, and the precipitate allowed to subside after each addition until no further precipitation takes place, which can be seen by bringing a drop of the clear supernatant liquid in contact on a watch-glass, with two or three drops of the reagent.

A more common practice is to filter the solution after each addition of the reagent, using the same filter.

When 10 cc. of the filtered liquid are no longer affected by two drops of the reagent, the titration is complete.

If a considerable length of time is allowed to elapse after each addition of reagent, it is found that the results of a titration will coincide more nearly with what theory requires; but the principal advantage which volumetric analysis has over gravimetric, namely, rapidity of execution, is thereby forfeited.

The presence of alcohol, free acetic acid, or ammonia vitiates the result; but gum, albumen, glucose, or extractives in moderate quantities have no effect upon the reaction.

In all comparative titrations with this reagent the dilution of the alkaloidal solution should be the same. The solution should be slightly acid, and its strength about 1–200.

In titrations where the end reaction can only be ascertained by the cessation of the formation of a precipitate, it is often necessary to filter a portion of the turbid solution at intervals during the titration, and test it to see whether the process is completed. In such cases Beale's filter, Fig. 54, may be used. Over the lower end of this instrument a piece of filter-paper is tied, and over that a piece of thin muslin to keep the paper from being broken. When dipped into a turbid mixture the clear liquid rises, and may be poured out of the little spout for testing. If the process is shown to be unfinished, the contents are washed back to the bulk of the liquid, and small portions filtered out at intervals until the process is found to be completed.

FIG. 54.

The Decinormal Mayer's Solution is made as follows:

$\frac{N}{10}$ *Mercuric Potassium Iodide V. S., U. S. P.*—$HgI_2 + 2KI = 783.98$. 39.2 gms. in a litre.

Dissolve 13.546 gms. of pure mercuric chloride in 600 cc. of water, and 49.8 gms. of potassium iodide in 100 cc. of water.

Mix the two solutions, and then add enough water to make the mixture measure at or near 15° C. (59° F.) exactly 1000 cc.

The reaction which takes place when these two solutions are mixed is

$$HgCl_2 + 4KI = HgI_2 + 2KI + KCl.$$

A. B. Lyons and many others prefer to use a solution of half the above strength.

Each cc. of the *decinormal solution*, according to Dr. Mayer, precipitates of—

	gm.		gm.		gm.
Aconitine...	0.0267	Coniine. ..	0.00416	Quinidine...	0.0120
Atropine....	0.0145	Morphine..	0.0200	Quinine ...	0.0108
Brucine	0.0233	Narcotine..	0.0213	Strychnine..	0.0167
Cinchonine .	0.0102	Nicotine...	0.00405	Veratrine...	0.0269

The precipitates are hydriodates of the alkaloids, respectively, with iodide of mercury; but Lyons finds that they are not of definite composition, though the variation is very slight. This reagent will give similar precipitates with all of the alkaloids, except perhaps colchicine, caffeine, and digitaline.

ESTIMATION OF ALKALOIDS BY WAGNER'S REAGENT.

Recently Wagner's reagent has been again brought into notice as a volumetric reagent for alkaloids.

This reagent is a solution of iodine in potassium iodide (see decinormal iodine V. S., page 179). Wagner's reagent has long been known to have the power of completely precipitating most alkaloids, even from very dilute solutions. Its use in volumetric analysis depends upon precipitating the alkaloids in the form of definite periodides.

The alkaloid in acidulated solution is treated with Wagner's reagent, added in excess. The precipitate is allowed to settle, and an aliquot portion of the clear liquid decanted, and titrated with thiosulphate solution, to determine the excess of iodine. This deducted from the quantity of iodine added gives the quantity of the latter which combined with the alkaloid.

The difficulty that presents itself is that different alkaloids when treated under apparently the same conditions give periodides of entirely different composition. Thus morphine is said to give with Wagner's reagent, Alkaloid $HI.I_3$; codeine gives, Alkaloid $HI.I_4$; caffeine gives, Alkaloid $HI.I_4$.

Thus in the first case one equivalent of morphine equals three of iodine, in the case of codeine and caffeine one equivalent of the alkaloid equals in each case four of iodine; therefore we must ascertain exactly the composition of the precipitate in a particular case before we can make use of the reagent for volumetric analysis. And when the composition of the different periodides, as produced under the condition of titrations, is exactly known, this method may be placed upon a sound basis. Caffeine may be accurately estimated by this method, as described on the following page.

ESTIMATION OF CAFFEINE BY WAGNER'S REAGENT.

Caffeine may be titrated as follows: 0.1 gm. of caffeine is dissolved in 30 cc. of water and acidulated with 5 or 6 drops of hydrochloric acid. $\frac{N}{10}$ iodine solution is then run in from a burette, a few cc. at a time until 30 cc. have been used; this is a little over one and one-third the quantity required theoretically to precipitate 0.1 gm. of caffeine. The precipitated caffeine periodide is separated by filtration through a dry asbestos filter after five minutes standing and an aliquot portion of the filtrate then titrated with $\frac{N}{10}$ sodium thiosulphate solution, in order to determine the excess of iodine. The difference between the quantity of thiosulphate used for the whole filtrate and the quantity of iodine solution originally added, gives the quantity of the latter which reacted with the caffeine.

Each cc. of the $\frac{N}{10}$ iodine solution = 0.00485 gm. of caffeine.

The calculation in detail is as follows:

Caffeine solution ..... 30 cc.

$\frac{N}{10}$ iodine " ..... 30 cc.

Total..... ... 60 cc.

30 cc. of filtrate required 5.8 cc. $\frac{N}{10}$ thiosulphate;

whole " " " 11.6 cc. " "

30 cc. $\frac{N}{10}$ iodine — 11.6 cc. " "

= 18.4 cc. of $\frac{N}{10}$ iodine consumed by caffeine;

$18.4 \times 0.00485 = 0.08924$ gm. caffeine.

CHAPTER LXII.

VOLUMETRIC ASSAYING OF VEGETABLE DRUGS.

EXTRACTION OF THE ALKALOIDS.

Selection of the Sample.—Care must be taken to secure a fairly representative sample

If the drug is in small pieces or consists of seeds or leaves, mix it well, take a portion, pulverize it and of the powder take a sufficient quantity for the assay. If the drug be in large lumps, which vary in quality, select a few representative lumps and cut from each a fairly representative section; pulverize these, mix well and weigh off a sufficient quantity for the assay.

If drying is necessary, the loss of weight in drying must be made note of.

The Exhaustion of the Drug is usually effected by maceration in a suitable menstruum, although percolation, boiling and hot repercolation must be employed in some cases.

The Choice of Solvent depends upon the nature of the drug. Water dissolves besides the alkaloids so much inert matter that the subsequent steps in the assay are liable to be interfered with. Alcohol dissolves too much of the resinous matter, and besides does not penetrate the drug very well. Acidulated water has been much used, but chloroform and ether, separately and in various combinations are now most generally employed for exhausting drugs, in conjunction with alcohol and ammonia. Petroleum benzene has of late been recommended.

Prollius' fluid or some modification of it is very satisfactory.

Prollius' Fluid consists of ether 325 cc., alcohol 25 cc., and concentrated ammonia water 10 cc.

Modified Prollius' Fluid consists of ether 250 cc., chloroform 80 to 100 cc., alcohol 25 cc., concentrated ammonia water 10 cc.

General Method of Extracting Alkaloids from Drugs (Kebler, *J. A. C. S.*, XVII. 828).—Treat 10 gms. of the dry powdered drug in a 250-cc. flask with 25 gms. of chloroform and 75 gms. of ether; stopper the flask securely, agitate well for a few minutes and add 10 gms. of ammonia-water U. S. P., and shake frequently during one hour. Then on adding 5 gms. more of the ammonia-water and shaking, the suspended powder agglutinates into a lump and leaves the solution clear after a few minutes' standing. Then proceed by A or B.

A. When the mixture has completely separated, 50 gms. (representing 5 gms. of the drug) are poured off into a beaker and heated on a water-bath until the solvent is evaporated. 10 cc. of ether are then added and again evaporated. The varnish-like residue is then dissolved in 15 cc. of warm alcohol and water added to slight permanent turbidity, then the indicator is added, followed by an excess of standard acid solution and the mixture retitrated with standard alkali.

B. When the mixture has completely separated pour off 50 gms. into a separatory funnel, and add 20 cc. of acidulated water, agitate and when the liquids have separated draw off the aqueous solution into a second separatory funnel. Repeat this operation with two more portions of 15 cc. of acidulated

water. Now render the contents of the separatory funnel alkaline by adding ammonia water. This liberates the alkaloids, which are then separated by treatment with a mixture of chloroform 3 parts (by volume) and ether 1 part, using three successive portions, first 20 cc., then twice 15 cc.

The chloroform-ether solution is heated on a water-bath until the solvent is evaporated, and then the varnish-like residue treated twice with 8 cc. of ether and again evaporated.

The residue is then dissolved in 15 cc. of alcohol, water added to slight permanent turbidity, and then the indicator. Titrate in usual way with decinormal acid and centinormal alkali.

ALKALOIDAL ASSAY BY IMMISCIBLE SOLVENTS.

Many alkaloids are soluble in certain liquids in which their salts are insoluble, while in other liquids the case is reversed. When such liquids are not miscible the separation may be effected by the so-called "shaking-out process."

In many cases the extraction or separation may be effected by adding to the concentrated aqueous extract, a suitable alkaline precipitant, such as ammonia water or sodium-carbonate solution, which liberates the alkaloid, then shaking up with some solvent, such as chloroform, ether, benzine, benzol, or amylic alcohol. The liberated alkaloid is thus dissolved or washed out of the aqueous solution.

The alkaloid may be again abstracted from this solution by the addition of a dilute acid, which forms again a salt of the alkaloid.

In the U. S. P. chloroform is exclusively used as a solvent for alkaloids.

The extraction is directed to be performed in a glass separator or separatory funnel, which consists of an elongated (globular, cylindrical, or conical) glass vessel, provided with a well-fitting stopper and an outlet-tube containing a well-ground glass stop-cock. (See Fig. 55.)

FIG. 55.

When the alkaloidal solution, suitably prepared, is introduced into the separator, and the chloroform subsequently added, the latter, owing to its higher specific gravity, will form the lower layer.

If the two are violently shaken together there will often result an emulsion, which will separate slowly, and often imperfectly. This is particularly liable to happen if the aqueous liquid containing the alkaloid, either in solution or suspension, is strongly alkaline, or has a high specific gravity. To avoid this formation of an emulsion it is better to frequently invert the separator or to rotate it rapidly than to shake it violently.

The emulsion may sometimes be destroyed by the addition of more of the solvent, and, if necessary, aided by the application of gentle heat, or by the introduction of a small quantity of alcohol or hot water.

On withdrawing the chloroform solution of an alkaloid from the separator, a small amount of the solution will generally be retained in the outlet-tube by capillary attraction. If this were lost the results of the assay would be seriously vitiated. To avoid this loss, several successive small portions of chloroform should be poured into the separator without agitation, and

drawn off through the stop-cock to wash out the outlet-tube.

Another source of loss is due to the pressure generated in the separator by the rise of temperature caused when an alkaline and an acid liquid are shaken together. Some of the liquid adheres to the juncture of the stopper and neck, and when the stopper is loosened some of the liquid is ejected.

When an alkaline carbonate is used instead of caustic alkali for liberating the alkaloid, the liquids should be cautiously and gradually mixed by rotation, and the separator left unstoppered until gas is no longer given off.

GENERAL METHOD FOR THE ESTIMATION OF THE ALKALOIDAL STRENGTH OF EXTRACTS.

One gm. of the extract is dissolved in 20 cc. of water, heating gently if necessary. 20 cc. of a solution containing 6 gms. of sodium carbonate are added, followed by 20 cc. of chloroform. Agitate, warm gently, and separate the chloroform. Add to this 20 cc. of dilute sulphuric acid with an equal bulk of water, again agitate, warm, and separate the acid liquor from the chloroform. To this acid liquor add an excess of ammonia, and agitate with 20 cc. of chloroform. When the liquors have separated, transfer the chloroform to a weighed dish, and evaporate over a water-bath. Dry the residue for one hour at 100° C. (212° F.), and weigh. This process may be extended to almost any extract containing alkaloids, except opium. If the residue consists of only one alkaloid, the formula and molecular weight of which are known, it may be titrated instead of weighed.

Assay of Aconite Root (C. C. Keller).—Place 12 gms. of the root (in No. 80 powder) in a 250-cc. flask, add 30 gms. of chloroform and 90 gms. of ether; stopper securely, and shake the flask for 5 or 10 minutes; then add 10 gms. of ammonia-water U. S. P. and shake frequently during half an hour, and introduce 20 gms. of water and again shake; this causes the drug to gather in lumps and permit the chloroform-ether mixture to separate so that it can be easily poured off.

When the mixture has completely separated, pour off 100 gms. of the chloroform-ether solution (representing 10 gms. of the drug) into a separatory funnel and treat at once with 25 cc. of a 1 per cent solution of hydrochloric acid. Agitate, and when the liquids have separated draw off the aqueous solution into a second separatory funnel, and repeat the operation with two more portions of the hydrochloric acid solution, using first 15 and then 10 cc.

The acidulated solution is then rendered alkaline by adding ammonia-water and the reprecipitated alkaloid removed by treatment with successive portions of a mixture of chloroform 3 parts and ether 2 parts (by weight), using in all about 100 gms. of the mixed solvent. It is best to add a portion of the solvent before the ammonia.

The chloroform-ether solution is collected in a beaker or flask and the solvent distilled off. The residuum is treated with two or three small portions of ether and the latter removed by heating on a water-bath. The alkaloids are then dissolved in 10 cc. of absolute alcohol and water added to slight permanent turbidity. The solution is then titrated with $\frac{N}{10}$ hydro-

chloric acid in the presence of hæmatoxylin as indicator.

1 cc. of $\frac{N}{10}$ acid equals 0.0647 gms. of aconitine, the principal alkaloid.

Assay of Aconite Leaves.—This assay is the same as that of the root. Use the following quantities: aconite leaves (No. 80 powder) 25 gms., ether 100 gms., chloroform 25 gms., ammonia water U. S. P. 10 gms. Pour off 105 cc. of the chloroform-ether solution and after it has stood for a few minutes to settle, transfer 100 gms. of it into a separatory funnel and proceed as above. In this way a clearer solution is obtained.

Assay of Belladonna Leaves (Lyman F. Kebler, *J. A. C. S.*, XVII. 828).—Place 10 gms. of the powder in a 250-cc. flask, add 25 gms. of chloroform and 75 gms. of ether; stopper the flask securely, agitate well for several minutes, add 10 gms. of 10 per cent ammonia water, then agitate frequently and during one hour. On adding 5 gms. more of the ammonia-water and shaking well, the suspended powder agglutinates into a lump, and the liquid becomes clear after standing a few minutes and can be poured off almost completely.

When the mixture has completely separated pour 50 gms. into a separatory funnel, and treat at once with 20 cc. of acidulated water. After thorough agitation and complete separation remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with 15 cc. of slightly acidulated water.

The acidulated aqueous solution in the second

separatory funnel is then rendered alkaline with ammonia water and the reprecipitated alkaloid removed by adding successively 20 cc., 15 cc., and 15 cc. of a mixture of 3 parts (by volume) of chloroform and 1 part of ether. Collect the chloroform-ether mixture in a beaker and distil off the solvent. The varnish-like residue is next dissolved in 15 cc. of alcohol with heat, water is added to slight permanent turbidity, a few drops of hæmatoxylin solution added, then a slight excess of $\frac{N}{20}$ sulphuric acid, and retitrate with $\frac{N}{20}$ alkali solution.

Each cc. of $\frac{N}{20}$ acid = 0.01445 gm. of alkaloid as atropine.

The use of decinormal sulphuric acid and of centinormal alkali solution is preferred by many; one tenth the number of cc.'s of the alkali used is then deducted from the quantity of decinormal acid added and the remainder multiplied by 0.0289 gm.

Belladonna Root may be assayed by exactly the same process.

Assay of Cinchona, U. S. P.—(*a*) *For Total Alkaloids.*—Cinchona, in No. 80 (or finer) powder and completely dried at 100° C., 20 gms.; alcohol, ammonia-water, chloroform, ether, normal sulphuric acid V. S., potassium hydroxide V. S., each a sufficient quantity. 20 gms. of the cinchona in very fine powder is introduced into a bottle provided with an accurately fitting glass stopper, and to this is added 200 cc. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia-

water; the bottle is stoppered, and thoroughly and frequently shaken during four hours. The liquid is then passed through a plug of cotton in a funnel into another bottle, being careful that there occurs no loss by evaporation.

100 cc. of the clear filtrate (representing 10 gms. of cinchona) are transferred to a beaker and evaporated to dryness. The crude alkaloids thus obtained are dissolved in 10 cc. of water and 4 cc. of normal sulphuric acid with the aid of gentle heat. The cooled solution is then filtered into a separator, and the beaker and filter washed with water until the washings no longer have an alkaline reaction, using as little water as possible.

Now add 5 cc. of potassium hydroxide V. S., or sufficient to render the liquid alkaline. The alkaloids are thereby reliberated, and may be shaken out by chloroform. 20 cc. of chloroform are first added, and the extraction repeated, using 10 cc. at a time, until a drop of the last chloroform extraction leaves no residue when evaporated on a watch-glass.

The chloroformic extracts are then mixed, evaporated in a tared beaker, the residue dried at 100° C. (212° F.), and weighed.

The weight multiplied by 10 will give the percentage of total alkaloids in the specimen tested.

The volumetric method cannot very well be employed here, as the alkaloids exist in varying proportions and are very numerous, thus making it difficult to find a factor which will answer for all cases.

However, some experimenters dissolve the weighed alkaloids in 10 or 15 gms. of alcohol, adding water until slight permanent turbidity appears, and then

titrate with $\frac{N}{10}$ hydrochloric acid, using hæmatoxylin as indicator. 1 cc. of the $\frac{N}{10}$ acid is assumed to be equivalent to 0.0315 gm. of calisaya alkaloids and of 0.0304 gm. of succirubra alkaloids.

(*b*) *For Quinine.*—Transfer 50 cc. of the clear filtrate remaining over from the preceding process (and representing 5 gms. of cinchona) to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only half the amounts of volumetric acid and alkali there directed.

Add the united chloroformic extracts containing the alkaloids in solution, gradually and in small portions at a time, to about 5 gms. of powdered glass contained in a porcelain capsule placed over a water-bath, so that when the contents of the capsule are dry all or nearly all of the dry alkaloids shall be in intimate admixture with the powdered glass, and the chloroform completely expelled. Now moisten the residue with ether, and having placed a funnel containing a filter (7 cm. in diameter) and well wetted with ether over a small graduated tube (*A*), transfer to the filter the ether-moistened residue from the capsule. Rinse the latter, several times if necessary, with fresh ether, so as to transfer the whole of the residue to the filter; then percolate with ether, drop by drop, until exactly 10 cc. of percolate are obtained. Then collect another 10 cc. by similar slow percolation with ether in a second graduated tube (*B*). Transfer the contents of the tubes to two small tared capsules, properly marked (*A* and *B*), and evaporate to a constant weight at 100° C. (212° F.) and weigh them. (The residue in (*A*) will con-

tain practically all of the quinine, together with a portion of the alkaloid less soluble in ether; the residue in (*B*) will consist almost entirely of these alkaloids.)

From the amount of residue obtained in (*A*) deduct that contained in (*B*). This will give approximately the amount of quinine present in the 5 gms. of sample. Multiply this by 20 and the percentage of quinine containing one molecule of water is obtained.

Cinchona calisaya should contain not less than 5 per cent, of total alkaloids, and at least 2.5 per cent, of quinine.

Cinchona succirubra should contain not less than 5 per cent, of its peculiar alkaloids.

Assay of Fluid Extract of Cinchona.—6 cc. of the fluid extract are diluted with 15 gms. of water; 90 gms. of ether are then added and 5 gms. of ammonia water, and the mixture agitated repeatedly during half an hour.

75 gms. of the clear ethereal solution (representing 5 cc. of the fluid extract) are then decanted, the ether distilled off, and the residual alkaloid weighed, or dissolved in 10 gms. of alcohol, the solution then diluted with 40 gms. of water, a few drops of hæmatoxylin solution added, and then titrated with $\frac{N}{10}$ hydrochloric acid.

Assay of Coca Leaves.—Place 10 gms. of the drug in fine powder into a 250-cc. flask and proceed as directed for belladonna leaves. Use hæmatoxylin as the indicator, and the decinormal factor 0.0303 gm.

Assay of Fluid Extract of Coca.—10 cc. of the fluid extract are diluted with 10 gms. of distilled water in a 250-cc. flask. Add 25 gms. of chloroform

and 75 gms. of ether, stopper the flask securely and shake well for several minutes, then add 5 gms. of ammonia water U. S. P., and shake frequently during half an hour and proceed as directed for belladonna.

The decinormal factor for cocaine is 0.0303 gm.

Aconite, conium, hyoscyamus, stramonium, and many other alkaloidal drugs may be assayed in the same manner as belladonna leaves, or by means of the process of Keller. (See assay of aconite root.)

Assay of Fluid Extract of Ipecac.—8 gms. of the fluid extact are diluted with 8 gms. of water in an ordinary vial, 32 gms. of chloroform and 48 gms. of ether are added and shaken up; 4 gms. of ammonia water are now introduced, and the mixture frequently agitated during half an hour.

Fifty gms. of the chloroform-ether solution (representing 5 gms. of the fluid extract) are separated, poured into a tared flask, and the solvent distilled or evaporated off; the varnish-like residue is twice treated with 5 to 10 cc. of ether, and evaporated by forcing a current of air into the flask by means of a rubber bulb; the residue is then dried in a water-bath and weighed. For the titration, the residue may be dissolved in a known quantity of decinormal hydrochloric acid; the solution may be assisted by a gentle heat, or the addition of a small quantity of alcohol; 10 or 12 drops of Brazil-wood T. S. are then added and the excess of acid determined by means of decinormal alkali, the latter being added until the liquid becomes cardinal to purplish red in color.

The quantity of decinormal alkali used is then subtracted from the quantity of decinormal acid first added. This gives the quantity of the decinormal acid which was used to neutralize the alkaloids present.

Emetine, according to Kunz, is diacid, and has the formula $C_{30}H_{40}N_2O_5$, molecular weight 508. Therefore one molecule of emetine will neutralize two molecules of hydrochloric, or, half a molecular weight, 254 in grammes, will neutralize 1 litre of normal hydrochloric, acid, while 25.4 gms. will neutralize 1000 of decinormal acid.

Thus each cc. of decinormal acid represents 0.0254 gm. of emetine. If $\frac{N}{20}$ acid is used, each cc. represents 0.0127 gm. of emetine.

$$C_{30}H_{40}N_2O_5 + 2HCl = C_{30}H_{40}N_2O_5(HCl)_2.$$

Emetine (Kunz).

2)508 2)72.79

10)254 gms. 10)36.37 gms. or 1000 cc. $\frac{N}{1}$ V. S.

2) 25.4 gms. 2) 3.637 gms. or 1000 cc. $\frac{N}{10}$ V. S.

12.7 gms. 1.818 gms. or 1000 cc. $\frac{N}{20}$ V. S.

Thus if decinormal acid is employed, the number of cc. which were neutralized by the alkaloid when multiplied by .0254 gm. gives the quantity of emetine present in 5 gms. of the fluid extract; and when this is multiplied by 20 the percentage is obtained.

Assay of Ipecac Root.—10 gms. of the finely powdered and dried root are placed in a bottle having a capacity of about 150 cc.; 40 gms. of chloroform and 60 gms. of ether are added, and shaken well for several minutes; 10 gms. of ammonia-water are now added; this liberates the emetine, which immediately dissolves in the chloroform and ether, while the suspended powder settles to the bottom of the bottle. The bottle is frequently shaken during one hour, and 5 gms. more of ammonia-water added; the powder then agglu-

tinates in a lump, and the liquid becomes perfectly clear. 50 gms. of the chloroform-ether solution are now taken (representing 5 gms. of the root) and transferred to a tared flask, and the process completed as described under the assay of the fluid extract.

The titration is in this case a little more difficult because of the presence of fat from the root. It is advisable to extract the fat from the root before subjecting it to this assay.

Assay of Nux Vomica.—Proceed as directed under *General Method for Extracting Alkaloids* (process B). Hæmatoxylin or Brazil-wood solutions may be used as indicator. The $\frac{N}{10}$ factor for total alkaloids is 0.0364 gm.

Assay of Extract of Nux Vomica.—Extract of nux vomica dried at 100° C., 2 gms.; alcohol; ammonia-water sp. gr. 0.960, water, chloroform, decinormal sulphuric acid V. S., centinormal potassium hydroxide V. S., of each q. s.

Put 2 gms. of the dried extract of nux vomica into a glass separator. Add to it 20 cc. of a previously prepared mixture of 2 volumes of alcohol, 1 volume of ammonia-water, and 1 volume of water. Shake the separator until the extract is dissolved.

Then add 20 cc. of chloroform and agitate during five minutes. The chloroform dissolves the alkaloids which the ammonia liberated. Allow the chloroformic solution to separate, remove it as far as possible, pour a few cc. more of chloroform into the separator, and without shaking draw this off through the stop-cock to wash the outlet-tube. Repeat the extraction with two further portions of chloroform of 15 cc. each, washing the outlet-tube each time as just directed.

Collect all the chloroformic solutions in a wide beaker; expose the latter to a gentle heat on a water-bath until the chloroform and ammonia are completely dissipated. Add to the residue 10 cc. of decinormal sulphuric acid measured accurately from a burette, stir gently, and then add 20 cc. of hot water. When solution has taken place add 2 cc. of Brazil-wood T. S. (The sulphuric acid combines with the alkaloids, and forms sulphates of the alkaloids.)

Now carefully run into this solution centinormal potassium hydroxide V. S. until a permanent pinkish color is produced, showing a slight excess of the alkali. Divide the number of cc. of centinormal potassium hydroxide used by 10. Subtract the number found from 10 (the 10 cc. of $\frac{N}{10}$ acid first used), and the number of cc. of the $\frac{N}{10}$ acid which went into combination with the alkaloids is found.

The two principal alkaloids of nux vomica are strychnine and brucine, and it is assumed that they are present in equal proportions; and thus the factor for total alkaloids is found by taking the mean of their respective molecular weights:

Strychnine,	334	2)728
Brucine,	394	364
	728	

364 gms. of the total alkaloids of nux vomica will neutralize 1000 cc. of normal sulphuric acid. 36.4 gms. will neutralize 1000 cc. of decinormal sulphuric acid.

Hence each cc. of decinormal sulphuric acid used in the above assay represents 0.0364 gm. of an equal mixture of strychnine and brucine. And by multi-

plying the number of cc. used by this factor, the quantity of these alkaloids in the 2 gms. of extract taken is obtained, and this quantity multiplied by 50 will give the percentage.

The extract should contain 15 per cent of total alkaloids by the above assay.

Fluid Extract of Nux Vomica is evaporated to a solid extract, and then assayed by the above process.

Tincture of Nux Vomica is assayed by evaporating 100 cc. to dryness, and the residue then tested by the above process. It should contain 0.3 gm. of alkaloids.

Assay of Extract of Opium.—Extract of opium dried at 100° C., 4 gms.; ammonia-water, 2.2 cc.; alcohol, ether, water, of each a sufficient quantity.

Dissolve the extract of opium in 30 cc. of water, filter the solution through a small filter, and wash the filter and residue with water until all soluble matters are extracted, collecting the washings separately. Evaporate in a tared porcelain capsule first the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 10 gms. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved. Pour the liquid into a tared flask, and rinse the capsule with a few drops of water at a time until the entire solution weighs 15 gms.

Then add 8.5 cc. of alcohol, shake well, add 20 cc. of ether, and shake again.

Now add the ammonia-water, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and set it aside in a moderately cool place for at least six hours, or overnight.

At the expiration of this time remove the stopper carefully, and brush into the flask any crystals which may adhere to the cork. Place two rapidly acting, plainly folded filters, one within the other, in a small funnel, wet them well with ether, and decant upon the inner one, the ethereal solution, as completely as possible.

Add 10 cc. of ether to the contents of the flask, rotate, and again decant upon the filter; repeat this operation with another 10 cc. of ether. Then pour the liquid in the bottle upon the filter in small portions at a time, in such a way as to transfer the greater portion of the crystals to the filter. When the liquid has passed through transfer the remaining crystals to the filter by rinsing the flask with several small portions of water, using not more than 10 cc. in all.

Apply water to the crystals drop by drop, until they are practically free from mother-liquor, and afterwards wash them with a saturated alcoholic solution of morphine, added drop by drop. When this has all passed through displace the remaining alcohol by ether, using about 10 cc. or more if necessary.

Dry to a constant weight at a temperature not exceeding 60° C., and carefully transfer the crystals to a tared watch-glass and weigh them. The weight multiplied by 25 gives the percentage of crystallized morphine present in the extract.

Instead of drying and transferring the crystals to a watch-glass as above directed, the filter containing them may be immersed in some boiling water in a beaker, and an excess of decinormal sulphuric acid added to dissolve the crystals (the quantity being noted); a few drops of methyl-orange are then added,

and the mixture titrated with decinormal potassium hydroxide. Deduct the quantity of the latter used from the quantity of decinormal acid first added, and the quantity of decinormal acid which combined with the morphine is found.

1000 cc. of normal acid represents one molecular weight of the alkaloid.

1000 cc. of decinormal acid represents one tenth of a molecular weight of the alkaloid (30.3 gms.); thus each cc. of $\frac{N}{10}$ acid represents 0.0303 gm. of crystallized morphine.

The number of cc. used, multiplied by this factor gives the quantity of morphine present in the 4 gms. of extract taken.

This multiplied by 25 gives the per cent. of crystallized morphine; it should contain 18 per cent.

Assay of Tincture of Opium (Laudanum).—Tincture of opium, 100 cc.; ammonia-water, 3.5 cc.; alcohol, ether, water, each a sufficient quantity. Evaporate the tincture to about 20 cc., add 40 cc. of water, mix thoroughly, and set the liquid aside for an hour, stirring occasionally and disintegrating the resinous flakes adhering to the capsule; then filter, and wash the filter and residue with water, collecting the washings separately. Evaporate first the washings to a small volume, then add the first filtrate and evaporate to 14 gms. Pour the liquid into a tared flask; rinse the capsule, and add the rinsings until the entire solution weighs 20 gms. Then add 12.2 cc. of alcohol; shake well; add 25 cc. of ether; shake again. Now add the ammonia-water, cork well, shake for ten minutes, and

set aside for at least six hours or overnight, so that the crystals may form.

At the expiration of this time decant the ethereal layer upon a double, plain, rapidly acting filter previously wet with ether; add 10 cc. of ether to the contents of the flask, rotate, and again decant. Repeat this operation with another 10 cc. of ether. Then pour the liquid in the bottle upon the filter, in small portions at a time, so as to transfer the greater portion of the crystals to the filter, and wash the remaining crystals on to the filter with the aid of a small quantity of water, using not more than 10 cc. Then wash the crystals, first with a few drops of water, then with an alcoholic solution of morphine, and finally with ether to displace the alcohol. Dry the crystals to a constant weight and weigh on a tared watch-glass.

If 100 gms. of tincture have been operated upon, the weight of the crystals is at once the per-cent. of crystallized morphine. The yield should be 1.3 to 1.5 gms. of morphine from 100 cc. of tincture.

Assay of Opium.—Opium, in any condition to be valued, 10 gms.; ammonia-water, 3.5 cc.; alcohol, ether, water, each a sufficient quantity. Introduce the opium (which, if fresh, should be in very small pieces, and if dry, in very fine powder) into a bottle having a capacity of 300 cc.; add 100 cc. of water; cork well. Agitate the bottle frequently during twelve hours; then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 cm., and when the liquid has drained off wash the residue with water carefully dropped upon the edges of the filter and contents until 150 cc. of filtrate are obtained. Then carefully transfer the moist opium back to the bottle by means of a

spatula, add 50 cc. of water, agitate thoroughly and repeatedly during fifteen minutes, and return the whole to the filter.

When the liquid has drained off, wash the residue as before until the second filtrate measures 150 cc., and finally collect about 20 cc. more of a third filtrate.

Evaporate in a tared capsule, first the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 gms. From this point proceed exactly as in the assay of tincture of opium.

The weight of the crystals obtained, when multiplied by 10, represents the percentage of crystallized morphine present in the sample of gum. Opium should contain 9%; the powdered not less than 13% nor more than 15%.

Assay of Wild Cherry Bark.—A. B. Stevens (*Proceedings A. Ph. A.*, 1896, 215).—10 gm. of the ground bark are macerated in 100 cc. of water for 24 hours, then distilled and the distillate containing the hydrocyanic acid is passed into a decinormal solution of potassium hydroxide.

The alkaline solution of potassium cyanide is then titrated with decinormal silver nitrate in the usual manner.

Dr. A. R. L. Dohme (*Pharm. Rundsch.*, XIII. 260) distils the hydrocyanic acid by passing live steam into the flask containing the bark and water, instead of using direct flame; otherwise the process is the same as the above, except that he adds 0.1 gm. of NaCl to the distillate before titrating. This is deducted from the final result.

Another method consists in distilling by means of live steam, and receiving the distillate in $\frac{N}{10}$ silver nitrate solution. The distillation is known to be complete when, upon agitating the receiver, the distillate no longer produces a precipitate in the silver solution. The excess of silver nitrate is then estimated by Volhard's method (see page 129).

Estimation of Caffeine in Crude Drugs (Gomberg, *Journ. Am. Chem. Soc.*, XVIII. 331).—The drug is thoroughly digested with water for some time, with the aid of heat, cooled and made up to a definite volume and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle and filtered. It is then treated with H_2S to precipitate the lead, filtered and boiled to drive off the H_2S. The solution is then divided into two equal parts and each treated with a measured excess of standard iodine solution, one portion without the addition of a mineral acid and the other with hydrochloric or sulphuric acid (about 1 cc. in 50) of the solution. After 5 or 10 minutes' standing, the excess of iodine is estimated in each of the two solutions by means of standard sodium thiosulphate solution.

The first portion, containing no other acid but acetic, serves to indicate whether the filtrate from the lead precipitate contains any other materials besides caffeine that are likely to be precipitated by the iodine solution. Caffeine is not precipitated in the presence of even strong acetic acid.

If any absorption of iodine be found in the first portion, that quantity is to be subtracted from the

quantity taken up by the second portion. The difference represents the iodine used up in the formation of caffeine periodide. The calculation is then made on the basis that the periodide has the composition $C_8H_{10}N_4O_2.HI.I_4$, and the quantity of alkaloid present is found by calculating upon the amount of iodine used up:

$$I_4 : C_8H_{10}N_4O_2 :: 506 : 194.$$

Thus 1 gm. of iodine represents 0.3834 gm. of caffeine. Or, each cc. of $\frac{N}{10}$ iodine solution = 0.00485 gm. of caffeine.

In carrying out the above process the iodine solution should be added in excess, to the extent at least of one and one-third the theoretical quantity. The caffeine solution must be free from other alkaloids and other substances which absorb iodine and must be acidulated. Precipitation does not take place in neutral solutions.

An excess of acid, however, must be avoided, as this will interfere with the reaction. Either hydrochloric or sulphuric acid may be employed, but the best results are obtained with the former.

The standard iodine solution should be added, a few cc. at a time, shaking after each addition and allowing to stand a few moments so that the color of the supernatant liquid may be observed: when this becomes wine-red, the iodine solution is in sufficient excess.

Estimation of the Strength of Resinous Drugs.—Take 5 to 10 gms. of the drug in powder and place it in a strong glass flask with 100 cc. of pure alcohol (U. S. P. and free from resin). Close the flask with

a good cork, and digest it in a warm place at about 49° C. (120° F.) for 12 hours, shaking from time to time. Pour or filter off 80 cc. (representing $\frac{8}{10}$ of the total drug taken), place it in a weighed beaker, and evaporate to 25 cc. on the top of the water-bath. Now add 50 cc. of distilled water, and boil gently over a low gas flame till all the alcohol is driven off. Let it cool and perfectly settle, pour off the supernatant liquor, wash the deposited resin by decantation with hot distilled water, and then dry the beaker and its contents in the air-bath at 105° C. (220° F.) and weigh, deducting the tare of the beaker. Thus treated, jalap, for example, should show 12 per cent of resin, of which not over 10 per cent should be soluble in ether. Scammony should show 75 per cent resin, which is entirely soluble in ether and in solution of potassa. From the latter it is not reprecipitated by dilute hydrochloric acid in excess. For other resinous drugs no official standard has yet been laid down.

Estimation of the Alkaloidal Strength of Scale Salts.—Four gms. of the scales are dissolved in 30 cc. of water in a capsule with the aid of gentle heat. The solution is cooled and transferred to a glass separator; an aqueous solution of 0.5 gm. of tartaric acid is then added, followed by an excess of solution of sodium hydroxide. The tartaric acid prevents the precipitation of $Fe_2(OH)_6$, and the NaOH sets free the alkaloid. The alkaloid is then extracted by shaking up the mixture with successive portions of chloroform, 15 cc. each time. The chloroformic layers are separated each time and mixed and evaporated in a tared capsule on a water-bath, and the residue dried 100° C. (212° F.), and weighed. Or the residue may

be titrated by adding sufficient decinormal sulphuric or hydrochloric acid to dissolve the salts and still remain in excess, then titrating residually with decinormal NaOH or KOH to determine the excess of acid.

CHAPTER LXIII.

GLUCOSIDES.

GLUCOSIDES are proximate vegetable principles, which when boiled with a dilute acid, or subjected to some other method of decomposition, take up the elements of water, and yield *glucose* and some other substance, this other substance differing in each case according to the particular glucoside operated upon.

Upon this property of these bodies is based a method for their estimation.

This method depends upon converting the glucoside into glucose, and then estimating the glucose by Fehling's solution in the usual way, and from the amount of glucose formed calculating the quantity of the glucoside.

The conversion of glucosides into glucose is shown by the following equations:

$$\underset{\text{Salicin, 286.}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Saligenol.}}{C_6H_4(OH)CH_2} + \underset{\text{Glucose, 180.}}{C_6H_{12}O_6}.$$

Thus it is seen that 180 gms. of glucose are derived from 286 gms. of salicin.

$$\underset{\text{Digitalin.}}{C_{27}H_{45}O_{15}} + 2H_2O = \underset{\text{Digitaliretin.}}{C_{15}H_{25}O_5} + 2\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

$$\underset{\text{Jalapin.}}{C_{31}H_{50}O_{16}} + 5H_2O = \underset{\text{Jalapinol.}}{C_{13}H_{24}O_3} + 3\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

$$\underset{\text{Glycyrrhizin.}}{C_{24}H_{36}O_9} + H_2O = \underset{\text{Glycyrrhetin.}}{C_{18}H_{26}O_4} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

CHAPTER LXIV.

ASSAYING SURGICAL DRESSINGS.

THE assaying of surgical dressings, especially those most frequently employed, may be readily done by volumetric methods. Since the medicinal content of such dressings is usually very small, a sufficiently large quantity of the material must be taken for the assay.

The smallest quantity of medicinal substance is contained in the sublimate dressings, while salicylic, boric, and carbolic dressings contain larger proportions of the respective antiseptics, and as high as 30 per cent is contained in some iodoform dressings. Hence in assaying sublimate dressings a larger quantity of the material must be taken, while a comparatively small quantity is needed of iodoform dressing.

In taking a sample for analysis it is important that it be so selected from different parts of the package that it will fairly represent the average strength of the whole. S. W. Williams suggested that, as gauzes are sold by the yard, it is evident that the strength of the medication, even if expressed in terms per cent by weight, should have some definite relation to the measurement.

In the case of an expensive medication like iodoform it would seem far more equitable to give the strength in grains per square yard or grammes per square metre. Thus the claims of the manufacturers might be compared on a common basis. This method would

obviate the confusion attendant upon the allowance in the computation for water in the "moist dressings."

The weight of the water present in the so-called "moist dressings" is so varying a quantity that it must be excluded from the computation, in order to fairly compare the strength of moist dressings with the dry kind.

Carbolic Acid Dressings.—If the dressing is of a low per cent, 10 gms. are taken, if of a high per cent 5 gms This is put into a litre flask, some water added and the whole warmed to and kept at about 80° C. for some time, rotating the flask occasionally. Then allow to cool, dilute to the 1000-cc. mark, and filter. The paraffin, resin, or oil, etc., rises to the surface of the aqueous solution and is easily separated by the filtration. The carbolic acid is then estimated by means of bromine solution, as described on page 402, 25 or 50 cc. of the carbolic acid solution being taken.

Meissinger and Wortmann's Process (*Pharm. Zeit. f. Russland*, XXIX. 759).—Transfer 25 cc. of the carbolic acid solution prepared as above to a 150-cc. flask, and add 20 cc. of a 1 per cent solution sodium hydroxide (free from nitrite). Warm the mixture to 60° C. and add $\frac{N}{10}$ iodine solution from a burette, until the brown color of the iodine solution is no longer decolorized and the mixture in the flask assumes a permanent brownish-yellow color, and upon shaking deposits a red-colored precipitate if much carbolic acid is present. A light-colored precipitate indicates deficiency of alkali. Cool the contents of

the flask, acidulate with dilute sulphuric acid, and dilute to 150 cc. with distilled water and mix.

Remove 10 cc. of this solution by means of a pipette, and titrate it with $\frac{N}{10}$ sodium thiosulphate, with starch as indicator. The number of cc. thus found multiplied by 15 gives the cc. of $\frac{N}{10}$ iodine solution which were added in excess to the carbolic acid solution. This deducted from the amount of iodine added gives the number of cc. of the latter which reacted with the carbolic acid.

One cc. of $\frac{N}{10}$ iodine solution is equivalent to 0.001563 gm. of carbolic acid. Therefore, by multiplying this by the cc. of $\frac{N}{10}$ iodine solution which reacted with the carbolic acid, the quantity of the latter in the 25 cc. of solution taken for analysis is ascertained.

If the carbolic acid solution is made from 10 gms. of the dressing in a litre, 25 cc. of it represents 0.25 of the dressing. Hence to find the percentage by weight of the carbolic acid in the dressing, multiply the amount found by 100 and divide by 0.25.

Example.—25 cc. of the carbolic acid solution, representing 0.25 gm. of the dressing, were heated with 20 cc. of a 1 per cent solution of NaOH, and 55 cc. of $\frac{N}{10}$ iodine V. S. added and the mixture made up to 150 cc. 10 cc. of this titrated with $\frac{N}{10}$ thiosulphate V. S. required 3.47 cc.

$$3.47 \times 15 = 52.05 \text{ cc.};$$
$$55 - 52.05 = 2.95 \text{ cc.};$$
$$2.95 \times 0.001563 = 0.00461085 \text{ gm.};$$

then $$\frac{0.00461085 \times 100}{0.25} = 1.84 + \text{ per cent.}$$

In the above process the iodine reacts with the carbolic acid in proportion of one molecular weight of the latter and six atomic weights of iodine; the greater part of the iodine added is, however, taken up by the NaOH to form sodium iodide and iodate. Upon the addition of dilute sulphuric acid these two salts give up their iodine, but the iodine combined with the phenol is not liberated by the acid.

Salicylic Acid Dressings.—5 or 10 gms. of the material, according to the claimed strength, are placed in a beaker or porcelain dish and heated with 500 cc. of distilled water. A few drops of phenolphthalein T. S. are then added and the solution titrated with $\frac{N}{10}$ sodium hydroxide.

In case resinous or fatty matters are present they must be removed by filtration and the gauze or cotton thoroughly washed and pressed before the titration.

Each cc. of $\frac{N}{10}$ alkali = 0.0138 gm. salicylic acid.

Benzoic acid in surgical dressings may be estimated in the same manner as the foregoing.

Each cc. $\frac{N}{10}$ alkali = 0.0122 gm. benzoic acid.

Boric Acid Gauze.—Beckurts and Danert give (*Apoth. Zeit.*) the following process for determining volumetrically the quantity of boric acid present in

gauze: Cut 5 gms. of the gauze into fine shreds and shake with 400 cc. of a mixture of 1 part of glycerin with 19 parts of water in a 500-cc. flask, adding later enough solvent to make up to 500 cc. Draw off 100 cc. of the clear fluid, and with the addition of phenolphthalein and some glycerin titrate with $\frac{N}{10}$ sodium hydrate solution. The number of cc. of the solution required, when multiplied by 0.0062, gives the quantity of boric acid found in 1 gm. of the gauze; when multiplied by 100 the percentage content is obtained. The quantity of glycerin added during titration is regulated by the appearance of alkalinity, for as soon as the solution shows an alkaline reaction glycerin is added; this is followed usually at first by disappearance of the red color until actual neutralization has taken place. If sufficient glycerin is added, the color reactions are rendered sharp.

Sublimate Dressings.—In the estimation of mercuric chloride in surgical dressings the available bichloride only should be computed.

The mercury which is present in any other form but bichloride must be excluded from consideration. It is to be remembered that corrosive sublimate reacts and forms with many organic substances, compounds which are insoluble or which have no germicidal power.

Moreover, sublimated dressings contain such minute proportions of the bichloride that even traces of impurities, such as wood gum, oil, fatty acids, etc., may be capable of destroying all of the bichloride present. Even the cotton of which the dressing is made has a reducing influence upon the bichloride.

Therefore, in assaying a sublimate dressing, the mercuric chloride and not the mercury should be estimated. Hence the dressing should not be exhausted for the assay with acidulated water, which would tend to dissolve some of the bichloride combined with the cellulose.

The available sublimate may best be extracted by means of sodium chloride solution.

Denner's Process, Modified by Link and Vaswinkel. —Macerate a weighed portion of the dressing, say 20 gms., in a 20-ounce glass-stoppered bottle with 500 cc. of distilled water, shaking frequently for one hour. Decant an aliquot portion, say 250 cc., into an evaporating-dish. Add 100 cc. of chlorine-water and a few drops of hydrochloric acid and evaporate to expel the chlorine and reduce to small bulk. Treat with sulphuretted hydrogen, filter and wash the precipitate very thoroughly. Transfer with the filter-paper to a small glass-stoppered bottle; add 1 or 2 cc. of carbon bisulphide and 50 cc. of $\frac{N}{50}$ iodine solution. Stopper tightly and let stand, with frequent shaking, until the black precipitate of mercuric sulphide is dissolved. The carbon bisulphide prevents the separated sulphur from interfering with the reaction by coating the particles of sulphide. Open carefully to avoid loss by spurting, and add 50 cc. of $\frac{N}{50}$ sodium thiosulphate and starch-paste indicator. Stopper the bottle, and shake vigorously until there remains no color indicative of free iodine. Open carefully again, and titrate the excess of thiosulphate with $\frac{N}{50}$ iodine.

This last result represents the amount of iodine bound by the mercuric sulphide, according to the equation

$$HgS + 2KI + I_2 = (HgI_2.2KI) + S,$$

and each cc. corresponds to 0.00271 gm. of mercury bichloride in the 250 cc. of solution used for assay.

Beckurt's Process.—Weigh about 20 gms. of the gauze or cotton to be assayed. Macerate in a litre cylinder with 250 cc. of warm distilled water containing 0.5 gm. of sodium chloride. When cool dilute with distilled water to 1 litre, taking care that no air-bubbles are enmeshed in the material. Shake well and filter off 500 cc. (more accurately 493 cc., allowing for the volume of 20 gms. of cellulose) into a boiling-flask with 0.2 gm. of ferrous sulphate in solution. Mix; add excess of sodium hydrate, and then dilute sulphuric acid in slight excess. The subiimate present is thus reduced to calomel, and may be estimated by adding from a burette $\frac{N}{50}$ iodine until the color indicates a slight excess. Then titrate back the excess with $\frac{N}{50}$ sodium thiosulphate and starch indicator. The difference between the $\frac{N}{50}$ iodine and $\frac{N}{50}$ thiosulphate used represents the iodine reacting with the mercury present (in the absence of other reducing agents), according to the equation

$$Hg_2Cl_2 + 6KI + 2I = 2(HgI_2.2KI) + 2KCl,$$

and each cc. of $\frac{N}{50}$ iodine so used corresponds to

0.00542 gm. of sublimate in the 500 cc. of solution used for assay.

Iodoform Dressings.—10 gms. of the dressing are digested with alcohol until thoroughly exhausted. The alcoholic solution of iodoform is then placed upon a water-bath, acidulated with a few drops of nitric acid, and titrated with a $\frac{N}{10}$ alcoholic solution of silver nitrate. The end point is known when a drop of the solution brought in contact with a drop of sodium chloride solution produces a turbidity. It can be told approximately by the disappearance of the greenish-yellow color of the solution. It becomes colorless when the reaction is complete.

The reaction is as follows:

$$CHI_3 + 3AgNO_3 + H_2O = 3AgI + 3HNO_3 + CO.$$

Each cc. of the $\frac{N}{10}$ $AgNO_3$ V. S. = 0.01313 gm. of iodoform.

The following process (Huss') may be applied to all dressings containing iodine, iodoform, iodol, sozoiodol, aristol, etc. It is based upon the fact that such compounds when heated with metallic zinc yield all their iodine with formation of zinc iodide.

5 gms. of the dressing are placed in a dry test-tube, 20 gms. of zinc dust added, and shaken down, leaving a layer of the zinc 2 cm. thick about the dressing. The whole is heated some time in a water-bath. The zinc is then washed out and transferred to a 500-cc. volume flask, which also bears a mark at 503 cc. The flask is filled with water to the 503-cc. mark (compensating for the volume of 20 gms. of zinc dust sp.

gr. 7.17). 250 cc. of the mixture is boiled with sodium carbonate, diluted to 500 cc., and 250 cc. filtered off. In this solution the iodine as sodium iodine is titrated with $\frac{N}{10}$ silver nitrate V. S., each cc. of which represents 0.0127 gm. iodine.

Commercial zinc dust usually contains zinc oxide; it is purified by treatment with dilute hydrochloric acid, washing with water till the chlorine reaction disappears, and subsequently with alcohol, and drying.

Other methods depend upon digesting the iodoform dressing with an alcoholic solution of sodium hydroxide, thus forming sodium iodide, which is estimated by titrating with $\frac{N}{10}$ $AgNO_3$ V. S.

Styptic Cotton—C. E. Parker (*Drug. Circ.*, 1895, 231).—The iron in styptic cotton is determined by macerating 3 to 5 gms. in 50 cc. of water. The ferric salt is reduced by adding stannous chloride in hydrochloric acid solution until the brown color disappears, then removing the excess of stannous chloride by the addition of mercuric chloride as long as a precipitate is produced, and finally titrating with $\frac{N}{10}$ potassium dichromate solution until a drop tested on a white plate no longer gives a blue color with a drop of freshly prepared potassium ferricyanide solution, but only a bluish-gray color.

Each cc. of $\frac{N}{10}$ $K_2Cr_2O_7$ = 0.0056 gm. of metallic iron or 0.027 gm. of ferric chloride U. S. P.

CHAPTER LXV.

ESTIMATION OF FORMALDEHYDE.

THIS may be done, according to Dr. E. J. Lederle, as follows: 2 cc. of the solution are placed in a glass-stoppered bottle, and 50 cc. of $\frac{N}{2}$ ammonia solution added; let stand 12 hours, shaking occasionally. Then determine the excess of ammonia by titrating with $\frac{N}{2}$ sulphuric acid solution, using rosalic acid as indicator. The excess of ammonia subtracted from the quantity added gives the quantity which combined with the formaldehyde, and thus the amount of the latter is ascertained.

The reaction is represented as follows:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

$4)\overline{180}$ $\quad$ $4)\overline{68}$ $\quad$ Hexamethylenetetramine

$2)\overline{45}$ $\quad$ $2)\overline{17}$

22.5 gm. $\quad$ 8.5 gm. or 1000 cc. $\frac{N}{2}$ V. S.

0.0225 gm. $\quad$ 0.0085 gm. or 1 cc. " "

Assuming that 22 cc. of $\frac{N}{2}$ sulphuric acid were employed in the titration, 22 cc. of the $\frac{N}{2}$ ammonia solution must have been in excess; hence 28 cc. of the latter went into combination with the formaldehyde. Thus the 2 cc. of formaldehyde solution contained 28×0.0225 gm. $= 0.63$ gm.

CHAPTER LXVI.

ESTIMATION OF CHLOROFORM AND CHLORAL HYDRATE.

Chloroform, $CHCl_3$.—The volumetric estimation of chloroform is based upon the fact that when chloroform is heated with an alkaline hydroxide a formate and a chloride of the alkali are formed. The reaction between the chloroform and the alkali takes place in definite proportions. An alcoholic solution of potassium gives best results.

The process is carried out as follows: A weighed quantity of chloroform, which should be perfectly neutral in reaction, is introduced into a strong glass flask provided with a well-fitting glass stopper. To this is added an excess of normal alcoholic KOH V. S., the stopper securely tied down, and the flask warmed on a water-bath to 50° or 60° C. When reaction is complete the contents of the flask is cooled and titrated with normal acid V. S. to find the excess of KOH.

Each cc. of normal KOH represents 0.02977 gm. of chloroform.

$$CHCl_3 + 4KOH = 3KCl + HCOOK + 2H_2O.$$

$$\frac{4)119.08}{29.77 \text{ gm.}} \qquad \frac{4)224}{56} = 1000 \text{ cc. } \frac{N}{1} \text{. V. S.}$$

$$0.02977 \text{ gm.} \quad = \quad 1 \text{ cc. } \text{“} \quad \text{“}$$

Chloral Hydrate, $C_2HCl_3O + H_2O$.—When chloral hydrate is treated with an alkali it is decomposed and

chloroform and an alkali formate are formed. The reaction must take place in the cold, or at least at the ordinary temperature, otherwise the alkali will attack and decompose the chloroform which is formed and hence the result would indicate too high a quantity of chloral hydrate.

The process is conducted as follows: A weighed quantity of chloral hydrate is dissolved in water, neutralized if it is acid, as is frequently the case, and then a measured excess of normal alkali is added. The excess is determined by residual titration with normal hydrochloric acid, and thus the quantity of the alkali which reacted with the chloral hydrate is found, each cc. of which represents 0.16497 gm. of chloral hydrate.

The reaction is thus expressed:

$$\underbrace{C_2HCl_3O}_{164.97} + H_2O + NaOH = CHCl_3 + HCOONa + H_2O.$$

$$164.97 \qquad 40 \quad = 1000 \text{ cc. } \frac{N}{1} \text{ V. S.}$$

$$0.16497 \text{ gm.} \quad .040 = 1 \text{ cc. } \text{“} \quad \text{“}$$

The use of barium hydroxide is preferred by many to the sodium hydroxide.

CHAPTER LXVII.

ESTIMATION OF COMPOUND ETHERS.

COMPOUND ETHERS, also called esters, correspond in structure to the salts of the metals, in which the metal is replaced by a hydrocarbon radical.

All compound ethers when treated with a strong alkali give up their acids to the alkali, and set free the hydroxide of the hydrocarbon radical. Thus ethyl sulphate, $(C_2H_5)_2SO_4$, when treated with 2KOH reacts as follows:

$$(C_2H_5)_2SO_4 + 2KOH = 2C_2H_5OH + K_2SO_4.$$

This decomposition is termed saponification and upon it is based a method for the estimation of compound ethers. In the process a measured quantity of normal alkali in decided excess is brought in contact with a weighed quantity of the compound ether, and when saponification is complete the excess of alkali is determined by retitration with normal acid solution and thus the quantity of normal alkali which went into combination with the ester is obtained, each cc. of which represents of

ethyl sulphate, $(C_2H_5)_2SO_4$, 0.077 gm.;
ethyl acetate, $C_2H_5C_2H_3O_2$, 0.088 gm.;
ethyl chloride, C_2H_5Cl, 0.06437 gm.;
ethyl nitrite, $C_2H_5NO_2$, 0.075 gm.

In this process certain precautions must be taken. The decomposition does not occur immediately, but takes place slowly; it may be hastened by the application of heat, but since most esters are volatile, great care must be exercised so as not to dissipate it.

A quantity of the ether is weighed in a weighing-flask, which can be well closed with a tightly fitting stopper. A measured excess of the alkali solution is then run in from a burette, the solution diluted with some water, for the decomposition is effected more readily in dilute than in concentrated solutions, the stopper inserted, and the flask placed upon a water-bath and heated to 50° or 60° C. It is kept at this temperature for two hours and frequently shaken. The flask and contents are then cooled and the stopper withdrawn. If the saponification is complete, the characteristic odor of the ether is no longer noticeable.

The retitration with normal acid is now in order. If barium hydroxide was used for the saponification, normal oxalic acid solution is indicated.

Spirit of Nitrous Ether.—The following method for determining the amount of ethyl nitrite in spirit of nitrous ether is given in the *Süddeutsche Apotheker-Zeitung*, 1897, 306. 10 gms. of the spirit are treated with 20 gms. of a 5 per cent solution of potassium chlorate and 5 gms. of nitric acid sp. gr. 1.153, and allowed to stand for an hour in a closed flask, shaking occasionally. The ethyl nitrite is thus oxidized to ethyl nitrate, and the potassium chlorate reduced to chloride.

The reaction is probably as follows:

$$3C_2H_5NO_2 + KClO_3 = KCl + 3C_2H_5NO_3.$$

The chloride so formed is then estimated by means of $\frac{N}{10}$ silver nitrate solution.

To the above mixture 25 cc. of $\frac{N}{10}$ silver nitrate solution are added, together with a few drops of a saturated solution of ammonio-ferric sulphate, and then the excess of silver nitrate solution determined by retitration with $\frac{N}{10}$ ammonium sulphocyanate or potassium sulphocyanate. By deducting the quantity of sulphocyanate solution used from the 25 cc. of $\frac{N}{10}$ silver nitrate added, the quantity of the latter which combined with the potassium chloride is found. This multiplied by 0.0225 gives the weight of ethyl nitrite in the 10 gms. taken.

$$3C_2H_5NO_2 = KCl = AgNO_3.$$

225 74.4 169

22.5 7.44 16.9 = 1000 cc. $\frac{N}{10}$ V. S.

0.0225 gm. = 0.00744 gm. = 1 cc. " "

See also Chapter LXIX.

PART IV.

GASOMETRIC ANALYSIS.

CHAPTER LXVIII.

THE NITROMETER.

FOR general gas analysis, and for the rapid estimation of such substances as ethyl nitrite, hydrogen peroxide, urea, bleaching-powder, manganese peroxide, etc., an instrument called the *nitrometer* is used.

The apparatus in its simplest form is shown in Fig. 56. It consists of a measuring-tube (*A*) graduated in cc., and fitted at the top with a three-way stop-cock (*D*) and a glass cup or funnel (*C*). The stop-cock is so arranged that according to the way in which it is turned it will discharge the contents of the cup either into the tube below or out in the waste-opening (*E*); or it will discharge the contents of the graduated tube into the waste-opening.

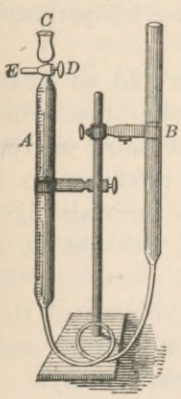

FIG. 56.

The graduated tube generally has a capacity of 50 cc., and is graduated in $\frac{1}{10}$ cc., the graduation beginning at the top. This measuring-tube is connected by means of a strong

flexible india-rubber tube with an ungraduated tube (*B*) called the control-tube, pressure-tube, or level-tube. Both tubes are held in clamps upon a stand.

With this apparatus gases can be rapidly and accurately measured at definite temperature and pressure.

In measuring the gas the instrument is filled with some liquid in which the gas is insoluble—generally mercury. In many cases a saturated solution of salt may be used.

Suppose we fill the instrument with mercury in such quantity that when the stop-cock is opened and the control-tube raised, the mercury will rise as far as the top, and about two inches in the control-tube.

The top is now closed, the control-tube lowered, and a little carbonic-acid gas admitted through (*E*). The top is then again closed, and the instrument allowed to stand until its contents have acquired the temperature of the room. A centigrade thermometer suspended to the stand will then give the temperature of the gas.

The control-tube is now raised or lowered so as to make the level of the liquid in both tubes the same. This makes the pressure in the tube the same as the atmospheric pressure outside, and by referring to a barometer standing near this pressure is ascertained.

We now have a definite volume of the gas at a known temperature and pressure.

It now only remains to read off the volume of the gas, and correct it to the normal temperature and pressure by Charles' and Boyle's laws, respectively.

The normal temperature and pressure is 0° C. and 760 mm. pressure.

The weight of the gas in grammes may then be cal-

culated from its volume by multiplying the number of cc. at the normal temperature and pressure, by the weight of one cc. of the gas in grammes.

This weight may be found as follows:

1000 cc. of hydrogen at normal temperature and pressure weigh 0.0896 gm. One cc. of H then weighs 0.0000896 gm.

One cc. of oxygen weighs 16 times as much, and one cc. of nitrogen weighs 14 times as much. Therefore, by multiplying the weight of one cc. of H by the atomic weight of an elementary gas, or half the molecular weight of a compound gas, the weight of one cc. of that gas is obtained.

According to the law of Charles, *the volume of a gas under constant pressure varies directly with the absolute temperature.*

All gases expand or contract by $\frac{1}{273}$ of their volume for each centigrade degree of temperature, increased or decreased.

We may regard a gas at 0° C. as having passed through 273° C. In other words, 273° below zero must be regarded as the absolute zero, and 0° C. as 273° absolute temperature.

Thus the absolute temperature centigrade is the observed temperature + 273°.

Example.—A given volume of oxygen gas at 15° C. measures 20 cc. What will it measure at 0° C.?

$$\frac{0° + 273° \times 20}{15° + 273°} \quad \text{or} \quad \frac{273° \times 20}{288°} = 18.95 \text{ cc.} \quad \textit{Ans.}$$

Boyle's Law.—The volume of a confined gas is inversely proportional to the pressure brought to bear upon it. That is, the less the pressure the greater the volume, and *vice versa.*

Rule.—Multiply the observed volume by the observed pressure, and divide by the normal pressure.

Example.—A given volume of gas at 750 mm. pressure measures 20 cc. What will it measure at 760 mm. (the normal pressure)?

$$\frac{750 \times 20 \text{ cc.}}{760} = 19.73 \text{ cc.} \quad \textit{Ans.}$$

Now let us take an example in which both laws are involved.

A given volume of oxygen at 15° C. subjected to a pressure of 750 mm. measures 20 cc. What will it measure at the normal temperature and pressure?—i.e., 0° C. and 760 mm.

In the first example we find that 20 cc. of oxygen at 15° C. will measure at 0° C. 18.95 cc. Then

$$\frac{750 \times 18.95 \text{ cc.}}{760} = 18.70 \text{ cc.} \quad \textit{Ans.}$$

Now to find the weight of this volume of oxygen we proceed as follows:

1 cc. of H weighs 0.0000896 gm.;

1 cc. of O weighs $16 \times .0000896 = 0.0014336$ gm.;

18.70 cc. of O = 18.70×0.0014336 gm., or 0.02680832 gm.

CHAPTER LXIX.

ASSAY OF SPIRITUS ÆTHERIS NITROSI.

Spirit of Nitrous Ether.—This is an alcoholic solution of ethyl nitrite ($C_2H_5NO_2 = 74.97$), yielding when freshly prepared and tested in the nitrometer not less than 11 times its own volume of nitrogen dioxide ($NO = 29.97$), U. S. P.

When nitrites are mixed with an excess of KI and acidulated with H_2SO_4, iodine is liberated, and all the nitrogen of the nitrite is evolved in the form of NO, as shown in the equation

$$\underset{149.74}{2C_2H_5NO_2} + 2KI + 2H_2SO_4 = 2C_2H_5OH + 2KHSO_4 + I_2 + \underset{59.94}{2NO}.$$

The process of the U. S. P. is conducted as follows:

Open the stop-cock of the measuring-tube, raise the control-tube, and pour into the latter a saturated solution of NaCl until the measuring-tube, including the bore of the stop-cock, is completely filled. Then close the stop-cock and fix the control-tube at a lower level. Now introduce into the funnel at the top of the measuring-tube 5 cc. of recently prepared spirit of nitrous ether, open the stop-cock, and allow the spirit to run into the nitrometer, being careful that no air enters at

the same time. 10 cc. of potassium iodide T. S. are now added in the same manner, and followed by 10 cc. of normal sulphuric acid V. S. Effervescence takes place immediately, and if the tube be vigorously shaken at intervals the reaction will complete itself in ten minutes. The control-tube is now lowered so as to make the level of the liquid in both tubes the same, and the volume of the gas in the graduated tube read off.

According to the U. S. P., the volume of NO generated at the ordinary indoor temperature (assumed to be at or near 25° C., 77° F.) should not be less than 55 cc. if 5 cc. of the spirit are taken, corresponding to about 4 per cent. of pure ethyl nitrite.

Sodium-chloride solution is used in the above assay, because owing to its density the spirit will float on top, and the gas evolved will not dissolve in it. At the same time the expense of using mercury is saved. It is important that no air be allowed to get into the measuring-tube, because this would convert the NO into a higher oxide of nitrogen, which would dissolve in the salt solution, and thus vitiate the result.

If it is desired to ascertain the percentage of ethyl nitrite present in a sample of spirit of nitrous ether which is either above or below the U. S. P. standard, it is necessary to find how much ethyl nitrite each cc. of NO represents, under a definite degree of temperature and pressure.

It is generally convenient to correct the volume of gas evolved at higher temperatures to its corresponding volume at 0° C.

The calculations involved are fully explained below.

Example.—5 cc. of spirit of nitrous ether (sp. gr. 0.840)

are treated in a nitrometer, and the NO evolved measures 55 cc.

The temperature at which the operation is conducted is 25° C., and the atmospheric pressure normal.

What per-cent. of ethyl nitrite is present in the sample?

By consulting the equation given above, it will be seen that one molecular weight of NO = 29.97 is evolved from one molecular weight of ethyl nitrite, 74.87.

Now reduce the volume of the gas liberated at 25° C. to its corresponding volume at 0° C. Thus

$$273° + 25° : 55 :: 273° + 0° : x. \quad x = 50.4 \text{ cc.}$$

Thus the gas evolved from 5 cc. of the spiritus ætheris nitrosi, measured at 0° C., is 50.4 cc.

The next step in the calculation is to find how much ethyl nitrite each cc. of the evolved NO represents. One litre of hydrogen at 0° C. and normal pressure weighs 0.0896 gm.

By multiplying this weight by half the molecular weight of NO, the weight of 1000 cc. of the latter gas is obtained; this will be found to be 1.3423. Now if 1.3423 gm. of NO measures 1000 cc., 29.97 gms. will measure 22328.24 cc.

$$1.3423 : 1000 :: 29.97 : x. \quad x = 22328.24.$$

Then if 22328.24 cc. of NO are evolved by, and consequently represent, 74.87 gms. of ethyl nitrite, as the equation shows, 1 cc. of NO will represent 0.0033529 gm. of pure ethyl nitrite.

Now, since in the above example 50.4 cc. of gas were

evolved at 0° C., the 5 cc. of spirit of nitrous ether examined must contain

$$50.4 \times 0.0033529 \text{ gm.} = 0.1689912 \text{ gm.}$$

of pure ethyl nitrite.

In order to determine the percentage strength, the weight of the spirit taken must be known. This may be found by multiplying the measure by the specific gravity, 5 cc. × 0.840 = 4.2 gms. Then

$$4.2 \text{ gms.} : 0.1689912 \text{ gm.} :: 100 : x. \quad x = 4\%.$$

1 litre of NO { at 0° C., and 760 mm. = 1.3423 gms., at 25° C., and 760 mm. = 1.2297 gms.

1 cc. of NO is the equivalent of—

	At 0° C.	At 25° C.
Amyl nitrite, $C_5H_{11}NO_2$	0.0052305	0.0047923 gm.
Ethyl nitrite, $C_2H_5NO_2$	0.0033529	0.0030716 "
Sodium nitrite, $NaNO_2$	0.0030873	0.0028283 "

Amyl Nitrite is a liquid containing about 80 per cent. of amyl nitrite (principally iso-amyl nitrite), $C_5H_{11}NO_2 = 116.78$, together with variable quantities of undetermined compounds.

The U. S. P. assay is as follows: 0.26 gm. of amyl nitrite are diluted with 5 cc. of alcohol, introduced into the nitrometer as directed for spiritus ætheris nitrosi; 10 cc. of potassium iodide T. S. and 10 cc. of $\frac{N}{1}$ H_2SO_4 V. S. are then added; and the volume of NO generated, measured at the ordinary indoor temperature (assumed to be at or near 25° C. or 77° F.), should be about 40 cc. Each cc. at this temperature represents 0.004792 gm. of pure amyl nitrite, or about 2 per cent.

Sodium Nitrite, $NaNO_2 = \left\{ \begin{matrix} 68.93 \\ *69 \end{matrix} \right.$.—This, like the other nitrites mentioned, when treated with potassium iodide and sulphuric acid, is decomposed, and NO is given off.

The reaction is here illustrated:

$$2NaNO_2 + 2KI + 2H_2SO_4 = K_2SO_4 + Na_2SO_4 + 2H_2O + 2NO + I_2.$$

A molecule of $NaNO_2$ (68.93) evolves, when properly treated, one molecule of NO (29.97).

The U. S. P. assay process is as follows: Weigh out 0.15 gm. of $NaNO_2$, dissolve it in about 5 cc. of water, and introduce the solution into a nitrometer. This is followed by a solution of 1 gm. of KI in 6 cc. of water and 15 cc. of $\frac{N}{1}$ H_2SO_4. The gas which is liberated should measure not less than 50 cc. at 15° C. (59° F.) or 51.7 cc. at 25° C. (77° F.), corresponding to not less than 97.6 per cent of the pure salt. Each cc. at 25° C. represents 0.0028283 gm. and at 0° C. 0.0030873 gm., of pure $NaNO_2$.

ESTIMATION OF NITRIC ACID IN NITRATES.

This may also be effected by the use of the nitrometer.

When a nitrate is shaken up with an excess of sulphuric acid and mercury, the nitrate is decomposed and NO is evolved, as seen in the following equation:

$$\underset{\underset{101}{2)202}}{2KNO_3} + 4H_2SO_4 + 3Hg = 3HgSO_4 + K_2SO_4 + \underset{\underset{29.97}{2)59.94}}{2NO} + 4H_2O.$$

Thus each molecule of the nitrate radical NO_3 gives off a molecule of NO.

Not more than 0.2 gm. of nitrate should be taken for analysis, since, if this quantity is exceeded, the volume of gas evolved will be greater than the instrument can conveniently hold. In this estimation the nitrometer is filled with mercury instead of brine; the nitrate is dissolved in 5 cc. of water, introduced into the nitrometer, and followed by excess of strong sulphuric acid. The instrument is well shaken for some time, and when action has ceased and the contents have cooled down to the temperature of the room, the level is adjusted and the volume of NO read off and calculated in the usual way.

CHAPTER LXX.

ESTIMATION OF SOLUBLE CARBONATES BY THE USE OF THE NITROMETER.

THE nitrometer may be used for estimating ammonium carbonate in aromatic spirit of ammonia.

The nitrometer in this case must be charged with mercury, as the liberated CO_2 is soluble in aqueous liquids.

A given volume of the spirit is introduced into the nitrometer, followed by an excess of dilute HCl, and the evolved gas then read off; and from its quantity the proportion of ammonium carbonate may be calculated by applying the equation

$$\underset{*96}{(NH_4)_2CO_3} + 2HCl = 2NH_4Cl + H_2O + \underset{*44}{CO_2}.$$

The volume of gas liberated must first be reduced to its corresponding volume at 0° C.

Each cc. of CO_2 at 0° C. weighs 0.001966 gm. Now if 44 gms. of CO_2 represent 96 gms. of normal ammonium carbonate, how much ammonium carbonate does 0.001966 gm. of CO_2 represent?

$$44 : 96 :: 0.001966 : x. \quad x = 0.004289 \text{ gm.}$$

Thus each cc. of CO_2 at normal pressure and 0° C. represents 0.004289 gm. of $(NH_4)_2CO_3$, approximately.

CHAPTER LXXI.

ESTIMATION OF UREA IN URINE.

THIS determination is based upon the fact that when urea is decomposed by an alkaline hypochlorite or hypobromite, carbon dioxide and nitrogen are given off, as the equation shows:

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + CO_2 + N_2 + 2H_2O.$$

The liberated N may be measured, and from its quantity the quantity of urea calculated; the other products of the decomposition go into solution.

The hypobromite solution is prepared as follows: 100 gms. NaOH are dissolved in 250 cc. of water, and when this solution has become cold 25 cc. of bromine are added, and the solution kept cold. This solution contains sodium hypobromite, bromate, and hydroxide; it readily undergoes decomposition, and should therefore always be freshly prepared when wanted for use.

The solution of sodium hypochlorite is generally preferred to the hypobromite, because it is more stable, just as efficacious, and the disagreeable handling of bromine is obviated.

Various forms of apparatus have been devised for the quantitative estimation of urea.

The simplest of these is probably the one devised by Dr. Chas. A. Doremus. (See Fig. 57.)

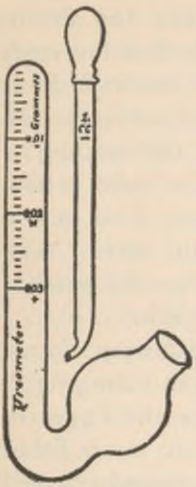

FIG. 57.

The long arm of the *ureometer* is filled with the hypobromite solution, and then 1 cc. of the urine is introduced by the aid of the pipette. The pipette is introduced through the bulb as far as it will go in the bend, and the nipple is then gently but steadily compressed, being careful that no air is admitted.

The volume of the liberated gas is read off after the froth has subsided.

The ureometer indicates, according to its graduation, either milligrammes of urea in 1 cc. or grains of urea per fluid ounce of urine.

It also indicates by the signs +, N, and − whether the urea is present in an increased, normal, or decreased quantity.

Another Convenient Form of Apparatus is a tube closed at one end, and graduated so that each division indicates a grain of urea in a fluid ounce of urine, when 1 cc. of urine is taken for the estimation. (See Fig. 58.)

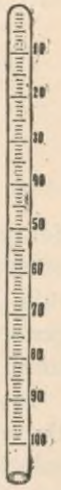

FIG. 58.

The process is conducted as follows: A 25-per-cent. solution of KBr is introduced to the fifth division. The chlorinated-soda solution is then added to the fifteenth or twentieth division. The tube is now inclined, and pure water carefully poured upon the liquid so that it will float on top; 1 cc. of urine is then added carefully, so that it will not mix with the reagents below, but remain in the water at the surface of the fluid. The open end of the tube is then

quickly closed with the thumb, and the top firmly grasped in the right hand. The tube is then inverted, and the contents well mixed. The decomposition which takes place is usually ended in five minutes. As soon as the effervescence has ceased, the reading is taken at the surface of the liquid. The tube is now opened under water, when the column of fluid in the tube will fall; the reading is then again taken. The difference between the two readings gives the number of grains of urea in a fluid ounce of the urine.

Squibb's Urea Apparatus (Fig. 59) is a very simple apparatus, and can be easily improvised in a drug-store. It consists of two wide-mouthed bottles, the larger of which (*C*), capable of holding about 250 cc., is fitted with a rubber stopper, through which is passed a curved

FIG. 59.

delivery-tube and a short straight tube, the latter connected by a piece of rubber tubing to the short glass tube in the rubber stopper of the smaller bottle or generating-bottle (*B*). In the generating-bottle is a small test-tube (*A*).

Into the test-tube *A* is placed 5 cc. of urine, and into the smaller bottle *B* is put 20 cc. of the hypobromite solution, or strong liquor sodæ chlorinatæ. The test-tube is then placed in the generating-bottle *B*, being careful that the urine and the reagent do not come in contact. The larger bottle *C* is now filled with water

and the two bottles connected by the rubber tube, the larger bottle being placed on its side upon a block, and when all connections are tight, the generating-bottle is shaken so that the urine will mix with the reagent.

Decomposition takes place, and the generated gas passes into the bottle *C*, displacing water, which is caught in a graduated cylinder or other measuring vessel. The volume of water displaced is equivalent to the volume of gas evolved.

Each cc. of nitrogen gas evolved at 0° C. and normal pressure represents 0.0027 gm. of urea. Then by multiplying the number of cc. evolved by this number the quantity of urea in the 5 cc. of urine taken is ascertained.

The volume of gas obtained when the operation is conducted at ordinary temperatures should always be reduced to its corresponding volume at 0° C. and 760 mm.

The factor 0.0027 is found in the following manner:

1000 cc. of H at 0° C. weigh 0.0896 gm.;
1000 cc. of N at 0° C. weigh 1.2544 gms.

By the equation it is seen that 60 gms. of urea evolve when decomposed 28 gms. of N.

$$\underset{60\text{ gms.}}{CO(NH_2)_2} + 3NaBrO = 3NaBr + CO_2 + \underset{28\text{ gms.}}{N_2} + 2H_2O.$$

Now we will find the volume occupied by 28 gms. of N at 0° C.

1.2544 gms. of N = 1000 cc.

gms. cc. gms. cc.
1.2544 : 1000 :: 28 : x. $x = 22321.43$ cc.

Thus 60 gms. of urea evolve 22321.43 cc. of N; 1 cc. of N thus represents 0.0027 gm. of urea.

CHAPTER LXXII.

HYDROGEN DIOXIDE

As stated in a previous chapter, hydrogen dioxide when acted upon by an acidulated solution of potassium permanganate, is decomposed and oxygen is evolved. One half of this oxygen comes from the dioxide and the other half from the permanganate.

Therefore if 1 cc. of the dioxide be treated in this way and 20 cc. of oxygen are evolved, the strength of the solution is 10 volumes.

The nitrometer may be used for this estimation.

This instrument is charged with a concentrated solution of sodium sulphate (which in this case is better than brine), and 1 cc. of the dioxide introduced from the funnel, followed by excess of solution of permanganate acidulated with sulphuric acid.

This latter solution should be of such strength that when the reaction is completed, the solution should still have a purple color.

The reaction is thus illustrated:

$$5H_2O_2 + 3H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

By the use of *Squibb's Urea Apparatus* the estimation may be easily and rapidly made.

Into the generating-bottle is put about 30 cc. of a

strong, acidulated solution of potassium permanganate, and a small test-tube containing 1 cc. of H_2O_2 is carefully introduced. The two liquids must not be allowed to come in contact.

The larger flask is filled with water or, better, a solution of sodium sulphate, the connection is then made by means of the rubber tube, and the generating-bottle tipped over and agitated so that the liquids will mix and the reaction take place.

The liberated oxygen then passes into the larger bottle, displacing an equal volume of water, which is collected and measured. Half of this volume represents the volume strength of the H_2O_2.

An Improvised Nitrometer may be used. The author has found the following instrument convenient:

To the bottom of an ordinary 50-cc. burette is attached a suitable length of rubber tubing, to the other end of which is attached another burette or *ungraduated* tube, which serves as a control-tube.

Into the top of the burette is fitted a rubber stopper, through which passes a short glass tube, which is connected by means of a rubber tube to a generating-bottle similar to that used with *Squibb's Urea Apparatus.* Into the control-tube is poured the solution of sodium sulphate, sufficient to fill the burette to the zero-mark and have the surface of the liquid in both tubes on a level.

About 30 cc. of strong permanganate solution acidulated with sulphuric acid are now placed in the generating-bottle, and then the small test-tube or homopathic vial, containing exactly 1 cc. of hydrogen dioxide, is placed in. The generating-bottle is then stoppered and agitated, the evolved gas passes over, and

forces the liquid in the burette, down. The control-tube is then lowered so as to bring the surfaces of the liquid in both tubes on a level.

The reading is then taken.

Each cc. of gas represents $\frac{1}{2}$ volume of oxygen evolved from the peroxide if 1 cc. of the latter is used. Each cc. of oxygen evolved from 1 cc. of the peroxide represents also 0.001696 gm. of absolute H_2O_2, or 0.0008 gm. of available oxygen.

Thus if from 1 cc. of the solution of hydrogen peroxide, 20 cc. of gas are evolved, it is a so-called 10-volume solution, and contains $.001696 \times 20 = 0.03392$ gm. of absolute H_2O_2, or $0.0008 \times 20 = 0.016$ gm. of available oxygen.

APPENDIX.

INDICATORS.

ACCORDING to R. A. Cripps, the requirements of a good indicator are :

I. The end reaction should be marked by a prominent change of color.

II. The smallest possible quantity of the reagent should be required to effect this change.

III. High tinctorial power, which of itself assists in the fulfilment of the second requirement, less of the indicator being required.

IV. The change of color should not be effected by the impurities commonly present in the substance under examination, nor by the products of the reaction.

In addition to these requirements it is a distinct advantage if the color reaction is equally decided in alcoholic as in aqueous liquids.

Litmus.—The coloring principles of litmus are azolitmin, erythrolitmin, and erythrolein. The first, which is the most important, is soluble in water, but insoluble in alcohol. The other two are readily soluble in alcohol, but only sparingly soluble in water.

The U. S. P. process for making litmus test-solution, consists in exhausting coarsely powdered litmus with boiling alcohol.

The residue is then digested with about an equal

weight of cold water so as to dissolve the excess of alkali present.

The blue solution thus obtained, after being acidulated may be used to make *red litmus-paper*. Finally, the residue is extracted with about five times its weight of boiling water, and the solution filtered.

The filtrate is preserved as *test solution*, in wide-mouthed bottles, stoppered with loose plugs of cotton to exclude dust, but to admit air.

When kept in closed vessels litmus solution gradually loses color, but this returns upon exposure to air and consequent absorption of oxygen.

The fermentation to which the loss of color is due may be prevented by saturating the solution with NaCl.

The British Pharmacopœia recommends to boil the litmus in powder with three successive portions of rectified spirit, and then to digest the residue in distilled water, and filter, the object of these steps in the process being to get rid of the greater portion of erythrolitmin and erythrolein, which are soluble in alcohol. Then by treating the residue with water a larger proportion of azolitmin is dissolved, and the solution is contaminated with very little of the other two principles.

Litmus may be used in a very large number of titrations. It is of value in the titration of most mineral acids and of a few organic acids, e. g., benzoic and oxalic. It is also useful in the titration of alkaline hydroxides when the latter are free from carbonates.

But for carbonates, bicarbonates, etc., a reliable end reaction can only be obtained by boiling the solution during the titration, in order to dispel the liberated CO_2.

Free CO_2 has an acid reaction with litmus, and interferes very much with the finding of the end reaction.

Litmus may be used for ammonia and for borax. It is of no use for phosphoric or arsenic acid, nor for phosphates or arsenates, because the change of tint is too gradual.

It is unsatisfactory in titrating many organic acids, e.g., tartaric and citric.

Sometimes it is required to perform a titration with litmus at night. Gas or lamp light is not adapted for showing the reaction satisfactorily, but by using a monochromatic light, such as the sodium flame, a very sharp line of demarcation may be found.

The operation should be conducted in a dark room; using a piece of platinum-foil sprinkled with salt or a piece of pumice-stone saturated with a solution of salt, heated in a Bunsen flame.

The red color then appears perfectly colorless, while the blue appears like a mixture of ink and water.

Phenolphthalein.—*Preparation.*—5 parts of phthalic anhydride ($C_8H_4O_3$), 10 parts of phenol (C_6H_5OH), and 4 parts of H_2SO_4 are heated together at 120° to 130° C. for several hours. The product is then boiled with water, and the residue, which consists of impure phenolphthalein, is dissolved in dilute soda solution and filtered. By neutralizing this solution the phenolphthalein is precipitated, and may be purified by crystallization from alcohol; or the alcoholic solution may be boiled with animal charcoal, filtered, and the phenolphthalein reprecipitated by boiling water.

Uses.—Phenolphthalein is a very valuable indicator; it is extremely sensitive, and exhibits a well-marked and prompt change from colorless to pink, and *vice versâ*.

A few drops of the solution of the indicator show no color in neutral or acid liquids, but the faintest excess of alkali produces a sudden change to red.

It may be employed in the titration of mineral and organic acids and most alkalies, but it is not suited for the titration of ammonia or its salts. It is very sensitive to CO_2, and therefore in estimating carbonates the liquid must be boiled, as with litmus. It is inapplicable for borax, because the color gradually fades away as the acid is added. One great advantage which phenolphthalein possesses is that its indications may be clearly read in many colored liquids; another is that it may be used in alcoholic liquids or in mixtures of alcohol and ether, and therefore many organic acids which are insoluble in water may be accurately titrated by its help.

Phenolphthalein T. S. is prepared as follows: Dissolve 1 gm. of phenolphthalein ($C_{20}H_{14}O_4$) in 100 cc. of diluted alcohol U. S. P.

Methyl-orange.—Porrier's Orange III, Tropæolin D, Helianthin, Mandarin-orange, para-sulpho-benzene-azo-dimethylaniline.

This is prepared by the action of diazo-sulphanilic acid upon dimethylaniline; the acid so formed is converted into a sodium or ammonium salt, purified by reprecipitation with HCl, and again converted into a sodium or ammonium salt. If prepared carefully and from the purest materials, it is a bright orange-red powder, perfectly soluble in water and slightly soluble in alcohol; but it is often found in commerce as a dull orange-brown powder, often not completely soluble in water. Many conflicting statements have been made by operators as to the value of methyl-orange as an

indicator, which have tended to bring this indicator into disrepute.

Sutton has examined many specimens, but has not found any in which the impurities sensibly affected its delicate action. He claims that the common error is the use of too much indicator, and that some eyes are more sensitive to a change of tint than others.

Methyl-orange is no doubt a very good indicator, but practice with it must be had, in order to obtain good results. The author has found one sample which had a beautiful orange color, but which was absolutely useless as an indicator.

A. H. Allen describes as follows the characters and tests of a good article:

1. Aqueous solution, not precipitated by alkalies. (Orange I becomes red-brown; orange II brownish red.)

2. Hot concentrated aqueous solution yields with HCl microscopic acicular crystals of the free sulphonic acid, soon changing to small lustrous plates or prisms having a violet reflection. (Orange I gives yellow-brown color or flocculent precipitate; orange II brown-yellow precipitate.)

3. Dissolves in concentrated H_2SO_4 with a reddish or yellowish-brown color, which on dilution becomes fine red.

4. $BaCl_2$ yields a precipitate.

5. $CaCl_2$ yields no precipitate. Orange I gives a red precipitate.)

6. $Pb(C_2H_3O_2)_2$ yields an orange-yellow precipitate.

7. $MgSO_4$ in dilute solutions precipitates the coloring matter in microscopic crystals.

Methyl-orange T. S. is made by dissolving 1 gm.

of methyl-orange in 1000 cc. of water. Add to it carefully diluted sulphuric acid in drops, until the liquid turns red and just ceases to be transparent. Then filter.

The great value of this indicator consists in the fact that it is not affected by carbonic-acid gas, sulphuretted hydrogen, or boric, silicic, arsenous, oleic, stearic, and many other acids.

It answers well for ammonia, but it is useless for most of the organic acids. Phosphoric and arsenic acids are rendered neutral to methyl-orange when only one third of the acid has combined with the base, the end reaction being well defined. (Phenolphthalein indicates neutrality when two thirds of acid are combined.)

Rosolic Acid, $C_{20}H_{14}O_3$.—This compound is also called Aurin and Corallin, and is prepared as follows:

A mixture of phenol and sulphuric acid is placed upon a water-bath, and oxalic acid gradually added, waiting each time till the evolution of gas ceases, and using less oxalic acid than is required to attack all the phenol.

In this process the oxalic acid is decomposed into CO, CO_2, and H_2O. The CO immediately reacts with the phenol and forms rosolic acid, as the following equation shows:

$$3C_6H_5OH + 2CO = C_{20}H_{14}O_3 + 2H_2O.$$

Rosolic acid is soluble in 50% alcohol. Its color is pale yellow, unaffected by acids, but turning violet-red with alkalies.

It is an excellent indicator for all the mineral acids, but is not reliable for the organic acids, excepting oxalic.

Rosolic-acid Test Solution, U. S. P.—Dissolve 1 gm. of commercial rosolic acid (chiefly methylaurin, $C_{20}H_{16}O_3$) in 10 cc. of diluted alcohol, and add enough water to make 100 cc. The solution turns violet-red with alkalies, yellow with acids. In place of rosolic acid, commercial pæonin (also known as aurin R) [chiefly $C_{19}H_{14}O_3$] may be employed.

Fluorescein or Resorcin Phthalein $C_{20}H_{12}O_5$, is prepared by heating resorcin with phthalic anhydride to 200° C. Dark-brown crystals are formed, which dissolve in ammonia, forming a red solution, with a splendid green fluorescence.

Fluorescein Test Solution, U. S. P.—Agitate 1 gm. of fluorescein with 100 cc. of diluted alcohol until the latter is saturated; then filter.

Eosin, or Tetra-bromo-resorcin-phthalein.—This is made by adding bromine to a solution of fluorescein in glacial acetic acid. Crystals gradually separate, which may be purified by conversion into a potassium salt and precipitated with an acid.

The composition of this substance is $K_2C_{20}H_6Br_4O_5$.

Eosin Test Solution, U. S. P.—Dissolve 1 gm. of commercial yellowish eosin in 30 cc. of water.

Corallin Test Solution, U. S. P.—Dissolve 1 gm. of corallin (a coloring matter derived from coal-tar, and containing rosolic and para-rosolic acids) in 10 cc. of alcohol and enough water to make 100 cc.

Gallein.—Anthracene violet or pyrogallo-phthalein was proposed by M. Dechan for use as an indicator.

It is prepared by heating a mixture of one part of phthalic anhydride and two parts of pyrogallol, and finally recrystallizing in a similar way to phenolphthalein.

It is described as a dark reddish crystalline solid, possessing a greenish lustre. It is nearly insoluble in water, but readily soluble in alcohol. In commerce it is frequently found as a paste, mixed with water.

It forms a violet-pink coloration with alkalies, which is changed to yellowish brown on addition of an acid in excess.

It is said to be more delicate towards alkalies than phenolphthalein, and may be used in its stead for titrating many of the alkaloids. It may be used in the presence of ammonia or its salts. It indicates sharply with the organic acids. A solution in rectified spirit 1–1000 is generally employed.

Lacmoid is somewhat allied to litmus, but differs from it in many respects. It is a product of resorcin, and may be prepared by heating gradually to 110° C. a mixture of 100 parts of resorcin, 5 parts of sodium nitrite, and 5 parts of water. After the violent reaction moderates it is heated to 120° C. until ammonia ceases to be evolved. The residue is then dissolved in warm water and the lacmoid precipitated therefrom by HCl; the free acid is then removed by washing and the residue dried.

Lacmoid is soluble in dilute alcohol. A solution containing 2 gms. in a litre is generally employed.

Lacmoid Paper.—This is prepared by dipping slips of calendered unsized paper into the blue or red solution and drying them.

Lacmoid is affected by carbonic-acid gas. It may be used cold for the alkaline and earthy hydroxides, arsenites, and borates, and the mineral acids. The carbonates and bicarbonates of the alkalies and alkaline earths are titrated hot with this indicator.

Many of the metallic salts, such as the sulphates and chlorides of iron, copper, and zinc, which are more or less acid to litmus, are neutral to lacmoid; therefore free acids in such solutions may be estimated by its aid.

Lacmoid paper reacts alkaline with the chromates of potassium or sodium, but neutral with the dichromates, so that a mixture of the two or of chromic acid and dichromate may be titrated by its aid.

Phenacetolin.—This may be prepared by boiling together for several hours equal molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is then well washed with water to remove excess of acid, and dried for use. It is soluble only in alcohol, and a convenient strength of solution is 2 gms. per litre. The solution is dark brown, which gives a scarcely perceptible yellow with caustic soda or potassa, when a few drops are used with the ordinary volumes of liquid. With the normal alkaline carbonates and with ammonia it gives a dark pink, with bicarbonate a much more intense pink, and with the mineral acids a golden yellow.

This indicator may be used for estimating the amount of caustic potash or soda in the presence of their normal carbonates. Practice is, however, required, so as to acquire knowledge of the exact shades of color.

Cochineal Test Solution, U. S. P.—Macerate 1 gm. of unbroken cochineal during four days with 20 cc. of alcohol and 60 cc. of water, then filter. The color of this test solution turns violet with alkalies and yellowish red with acids.

Brazil-wood Test Solution, U. S. P.—Boil 50 gms.

of finely cut Brazil-wood [the heart-wood of *Peltophorum dubium* (Sprengel) Britton, nat. ord. *Leguminosæ*] with 250 cc. of water during half an hour, replacing from time to time. Allow the mixture to cool; strain; wash the contents of the strainer with water until 100 cc. of strained liquid are obtained; add 25 cc. of alcohol and filter. This solution turns purplish red with alkalies and yellow with acids.

Turmeric Tincture, U. S. P.—Digest any convenient quantity of ground curcuma-root [from *Curcuma longa* Linné, nat. ord. *Scitamineæ*] repeatedly with small quantities of water, and throw this liquid away. Then digest the dried residue for several days with six times its weight of alcohol, and filter.

Turmeric Paper.—Impregnate white, unsized paper with the tincture and dry it.

Resazurin.—This is a new indicator for alkalimetry, proposed by Crismer. It is prepared as follows: Dissolve 4 gms. of resorcin in 300 cc. of anhydrous ether and add 40 to 45 drops of nitric acid (sp. gr. 1.25) saturated with nitrous anhydride. Allow the mixture to stand in a cold place for two days, whereupon a deposit of blackish crystals, having a reddish-brown reflection, will be formed in the bottom of the vessel. The supernatant clear red liquid is decanted and the crystals washed with ether until the washings show a blue color with ammonia-water.

Resazurin, $C_{12}H_7NO_4$, is slightly soluble in water, more so in alcohol, and freely soluble in acetic ether. It produces a blue solution with water, alkalies and alkaline carbonates, which are turned red upon the addition of a slight excess of acid. To use this indi-

cator in alkalimetry, Crismer recommends the following solution: Resazurin 0.2 gm. dissolved in 40 cc. of $\frac{N}{10}$ ammonia solution, and made up to 1000 cc. with distilled water.

This is deep blue in color and keeps well; two or three drops are sufficient to color 200 cc. of liquid.

This indicator is not suited for the titration of nitric acid or monobasic organic acids, and it is not very sensitive to carbonic acid. It is, however, extremely sensitive to alkalies. If the solution is acidulated to a rose-red color and heated in a white glass flask, the solution will turn blue through the alkaline reaction of the dissolved glass before the boiling-point is reached.

Hæmatoxylin.—A peculiar principle obtained from logwood, having the composition $C_{16}H_{14}O_6$, and crystallizing with one or three molecules of water. It is an efflorescent yellowish-rose colored substance, but when pure is said to be colorless, reddening on exposure to light.

It is soluble in hot water or alcohol. Its alcoholic solution is largely used as an indicator in the titration of alkaloids, for which it is considered the indicator par excellence. It gives a yellowish color in acid solution, and turns orange with alkalies.

The solution is prepared by dissolving one gramme of the well-crystallized material in 100 cc. of alcohol. In titrating use about three drops of this solution.

REAGENTS AND TEST SOLUTIONS.

Ammonium-carbonate Test Solution.—10 gms. of ammonium carbonate $NH_4HCO_3.NH_4NHC_2O_2$ are dissolved in a mixture of 10 cc. of ammonia-water and 40 cc. of water.

Ammonium-chloride Test Solution.—10 gms. of NH_4Cl are dissolved in sufficient water to make 100 cc.

Ammonium-molybdate Test Solution.—1 gm. of finely powdered ammonium molybdate $(NH_4)_2MoO_4$ is dissolved in 6.7 cc. of hot water, using a little ammonia-water, if necessary, to effect solution; the liquid is then poured gradually into a mixture of 3.3 cc. of nitric acid (sp. gr. 1.414) and 3.4 cc. of water.

The solution should be preserved in the dark, and if a sediment should form in it after some days, carefully decant the clear solution from it.

Ammonium-oxalate Test Solution.—1 gm. of pure crystallized ammonium oxalate in sufficient water to make 100 cc.

Barium-chloride T. S.—12.2 gms. of the pure salt in enough water to make 100 cc.

Cupric-sulphate T. S.—10 gms. of $CuSO_4 + 5H_2O$ in water to make 100 cc.

Ferric-ammonium Sulphate T. S.—10 gms. of ferric ammonium sulphate in water to make 100 cc.

Hydrochloric Acid, Pure, for Tests, HCl. See U. S. P.

Indigo T. S.—Place 6 gms. of fuming sulphuric acid into a beaker well cooled by immersion in water, and stir into it very gradually 1 gm. of finely powdered Bengal indigo. Set the mixture aside for two days, then pour it into 20 cc. of water, and decant. Or, dissolve 1 gm. of commercial indigo-carmine (the sodium or potassium salt of sulphindigotic acid) in 150 cc. of water.

Iodine T. S.—Iodine 1 gm., potassium iodide 3 gms., water 50 cc.

Iron (Metallic) Fe.—See U. S. P.

Magnesium Sulphate T. S.—10 gms. of $MgSO_4 + 7H_2O$ in water to make 100 cc.

Nitric Acid, Pure, for Tests, HNO_3.—See U. S. P.

Potassium Chromate T. S.—Dissolve 1 gm. of K_2CrO_4 in enough water to make 10 cc. On adding silver nitrate T. S. to a little of the solution a red precipitate is produced, which should be completely dissolved by nitric acid (absence of *chloride*). Another portion of the solution mixed with an equal volume of diluted hydrochloric acid should yield no precipitate with barium chloride T. S. (absence of *sulphate*).

Potassium Ferricyanide T. S.—1 part of $K_6Fe(CN)_{12}$ in about 10 parts of water. Should be freshly prepared when wanted.

Potassium Hydroxide T. S.—Use the official liquor potassæ.

Potassium Iodide T. S.—16.556 gms. of KI in enough water to make 100 cc. The solution should be kept in dark-amber colored, well-stoppered bottles to prevent the formation of iodate. It is well to renew it frequently or prepare it freshly when wanted.

Silver Nitrate T. S.—For ordinary purposes use the decinormal volumetric solution.

Sodium Hydroxide T. S.—Use the official liquor sodæ.

Starch T. S.—Mix 1 gm. of starch with 10 cc. of cold water, and then add enough boiling water, under constant stirring, to make 200 cc. of a thin, transparent jelly.

Sulphuric Acid, Pure, for Tests, H_2SO_4.—See U. S. P.

For other test solutions see the United States Pharmacopæia.

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