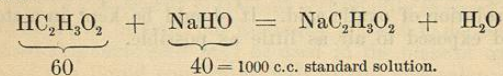


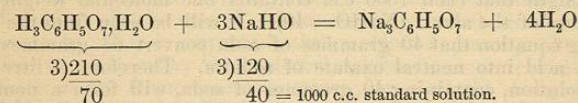
titration in all the estimations with this solution. Litmus is used throughout as an indicator of completion of the reaction. The following substances are officially estimated with this solution. The list admits of considerable extension (see Sutton's *Volumetric Analysis*).

*Acetic Acid*.—Operate upon about 1 gramme of glacial acid, about 20 grammes of dilute acid, or about 3 grammes of ordinary acetic acid.



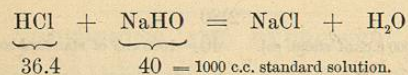
Acetic Acid, U. S. P., should contain 36 per cent of real acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ); Dilute Acetic Acid, U. S. P., 6 per cent; Glacial Acetic Acid, U. S. P., 99 per cent.

*Citric Acid*.—Operate on about 1 gramme. The reaction is expressed by the following equation, etc.:



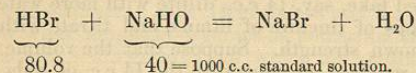
Citric Acid, U. S. P., should be pure (= 100 per cent.  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ ).

*Hydrochloric Acid*.—Operate on from 1 to 2 grammes of the concentrated acid or on about 4 grammes of the dilute acid.



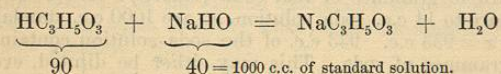
Hydrochloric Acid, U. S. P., should contain 31.9 per cent. of real acid (HCl), and Dilute Hydrochloric Acid, U. S. P., 10 per cent.

*Dilute Hydrobromic Acid*.—Operate on from 8 to 12 c.c.



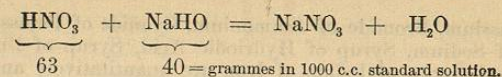
Dilute Hydrobromic Acid, U. S. P., should contain 10 per cent. of real acid (HBr).

*Lactic Acid*.—Operate on 1.5 to 2 grammes. The reaction is expressed by the following equation:—



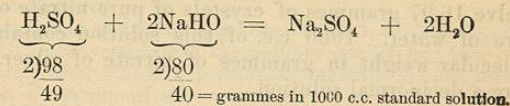
Lactic Acid, U. S. P., should represent 75 per cent. of absolute lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ).

*Nitric Acid*.—Operate on from 1 to 2 grammes of concentrated or on from 4 to 5 grammes of dilute acid.



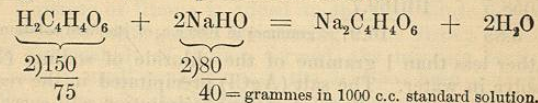
Nitric Acid, U. S. P., should contain 69.4 per cent., and Dilute Nitric Acid, U. S. P., 10 per cent., of real acid ( $\text{HNO}_3$ ).

*Sulphuric Acid*.—Operate upon from .5 to 1 gramme of concentrated acid or from 4 to 5 grammes of either Dilute or Aromatic Sulphuric Acid.



Sulphuric Acid, U. S. P., should contain not less than 96 per cent., Dilute, U. S. P., 10 per cent. of real acid, and Aromatic, U. S. P., 18 per cent., of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), partly as ethyl-sulphuric acid.

*Tartaric Acid*.—Operate upon about 1 gramme of the acid. The following equation, etc. represents the reaction:—



Tartaric Acid, U. S. P., should contain 100 per cent. of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

*Notes*.—1. Pure acetates, citrates, more especially, tartrates, and some other organic salts have an alkaline action on litmus, but not to an important extent. If the soda solution be added to acetic, citric, or tartaric acid containing litmus until the liquid is fairly blue, the operator will obtain trustworthy results. In delicate experiments turmeric, "methyl-orange," "phenolphthalein," etc. may be used instead of litmus.

2. The operations for the quantitative analysis or measurement of acids are often collectively spoken of under the name of *acidimetry*.

#### QUESTIONS AND EXERCISES.

1012. Calculate the percentage of real acid present in diluted sulphuric acid, 30 grammes of which are neutralized by 84 c.c. of the official volumetric solution of soda. *Ans.* 13.72.

1013. Show how much real nitric acid is contained in a solution 36 grammes of which are saturated by 94 c.c. of the standard solution of soda. *Ans.* 16.45 per cent.

#### ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY NITRATE OF SILVER.

The purity of many salts and the strength of their solutions may be determined by this process. Diluted Hydrocyanic Acid, Bromide



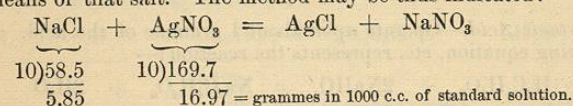
of Potassium, Bromide of Ammonium, Cyanide of Potassium, Bromide of Sodium, Syrup of Hydriodic Acid, Syrup of Bromide of Iron, and Syrup of Iodide of Iron are quantitatively analyzed by standard solution of nitrate of silver.

## STANDARD SOLUTION OF NITRATE OF SILVER.

(Nitrate of Silver,  $\text{AgNO}_3 = 169.7$ .)

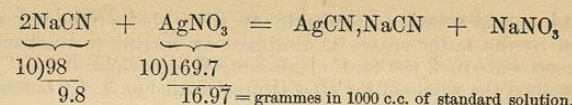
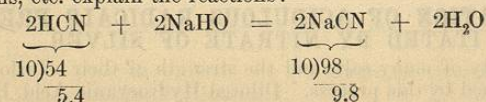
Dissolve 16.97 grammes of crystals of pure nitrate of silver in 1 litre of water. 1000 c.c. of this solution contain  $\frac{1}{10}$  of the molecular weight in grammes of nitrate of silver. It is therefore a decinormal solution.

Pure crystals of nitrate of silver can readily be obtained. When this is not the case, and pure chloride of sodium is at hand, a solution may be made of approximate strength, and then be standardized by means of that salt. The method may be thus indicated:—



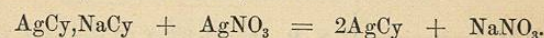
Take rather less than 1 gramme of the chloride of sodium ( $\text{NaCl}$ ) and dissolve in water. The salt ( $\text{AgCl}$ ) precipitated in the reaction is an insoluble salt, and the end of its precipitation will serve as a good indication of the completion of the reaction. A better indicator, however, is a few drops of neutral chromate of potassium (which should previously be purified by recrystallization). The nitrate of silver does not act upon the chromate until all the chloride is converted into chloride of silver, after which a deep-red precipitate of chromate of silver is produced. This indication is extremely delicate, and in practice is noticed when the white color due to chloride of silver changes to yellowish from formation of the first traces of chromate of silver. The titration being accomplished, suppose that .1 gramme of the chloride of sodium has taken 17 c.c. of the nitrate of silver solution of unknown strength: how many c.c. of the solution are equivalent to 5.85 of the chloride of sodium? that is, how many c.c. of solution contain 16.97 grammes of nitrate of silver? As .1 gramme of  $\text{NaCl}$  is to 17 c.c., so are 5.85  $\text{NaCl}$  to  $x$  c.c. = 994 c.c. 994 c.c. of the solution of nitrate of silver are equivalent, therefore, to 1000 c.c. of official standard solution, and contain 16.97 grammes of the nitrate of silver. They may be diluted to 1000 c.c. if desired.

*Hydrocyanic Acid.*—Three to four grammes of the dilute acid form a convenient quantity to operate upon. The  $\text{HCN}$  is first converted into  $\text{KCN}$  or  $\text{NaCN}$  with potash or soda. The following equations, etc. explain the reactions:—



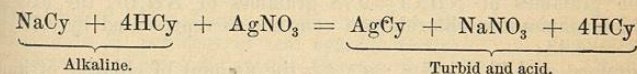
It is seen that 5.4 grammes of real hydrocyanic acid ( $\text{HCy}$ ) are equivalent to 9.8 grammes of cyanide of sodium, and represent 16.97 grammes of nitrate of silver, or 1000 c.c. of standard solution of nitrate of silver.

The cyanide of sodium having been obtained, the titration is carried on until it is converted into the soluble double salt ( $\text{NaCy, AgCy}$ ), immediately after which a permanent turbidity occurs, due to precipitation of cyanide of silver, thus:—



This turbidity affords a delicate and satisfactory proof of the completion of the above reaction, which is the B. P. process.

There is, however, a difficulty in the conversion of the acid into the cyanide (Siebold) to which it is necessary to pay particular attention. Tincture of litmus is added to the acid diluted largely with water, and the soda poured in. Owing to the strong alkaline reaction of the cyanide of sodium formed, the mixture becomes blue when only a small proportion of the acid has been converted. If then the titration be conducted until the turbidity appears, only the cyanide of sodium will be estimated, leaving free hydrocyanic acid still unacted upon. Indeed, cyanide of sodium may be estimated in presence of hydrocyanic acid in this way. Thus the following reaction (expressed approximately) might occur:



In this case only one-fifth of the acid originally present would be estimated. The mixture would, however, become acid. If this acidity be prevented all difficulty is overcome. The following details (Senier) will be found to answer well: To the diluted hydrocyanic acid add soda solution to a strong alkaline reaction, determined by means of tincture of litmus. Then add the silver solution, drop by drop, from the burette, when in most cases the mixture will become acid. When it does so, add more soda solution, and repeat this process until the final reading, when the solution must be alkaline. In this way the addition of too much soda at the commencement, which would use up silver solution and make the reading a trifle too high, is avoided.

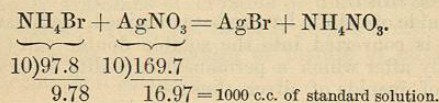
Dilute Hydrocyanic Acid, U. S. P., should contain 2 per cent. of real acid ( $\text{HCN}$ ), as shown by the following process:—

The following is the quantitative test of purity ordered by the United States Pharmacopœia:—"6.75 gm. diluted with 30 c.c. of water, and mixed with enough of an aqueous suspension of magnesia to make the mixture quite opaque, and afterward with a few drops of solution of chromate of potassium, should require 50 c.c. of

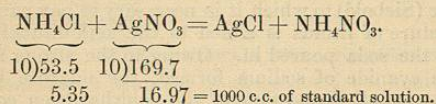


the volumetric solution of nitrate of silver before the red color caused by the latter ceases to disappear on stirring (corresponding to the presence of 2 per cent. of absolute Hydrocyanic Acid). By this method the whole of the HCy is precipitated as AgCy before the chromate of silver is permanently precipitated.

*Bromide of Ammonium.*—Operate upon .075 to .1 gramme of the salt, using chromate of potassium (or Bichromate, U. S. P.) as an indicator of the close of the reaction:—



Bromide of Ammonium, U. S. P., should be of 97 per cent. purity, but as the impurity is chloride of ammonium, this too will be precipitated by the nitrate of silver, and must be calculated in finding the percentage of bromide.



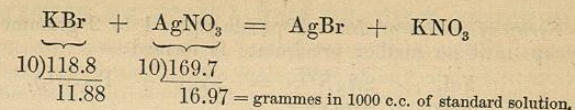
The amount of the salt equivalent to 1000 c.c. of standard solution is first calculated by simple proportion: Let  $x$  represent this; then  $9.78 - x = y$ , the excess of standard solution used up by the chloride of ammonium, reckoned in terms of bromide ( $\text{NH}_4\text{Br}$ ); and since 5.35 grammes of  $\text{NH}_4\text{Cl} = 9.78$  grammes of  $\text{NH}_4\text{Br}$ , the excess which ammonium chloride can consume is represented by  $9.78 - 5.35 = 4.43$ ;

therefore, as  $4.43 : 5.35 :: y : z =$  the amount of chloride of ammonium present in  $x$  grammes of the sample taken; lastly, the percentage is calculated by simple proportion:

As  $x : 100 :: z : p =$  percentage. For example: .075 gramme of the salt required, 7.8 c.c. of standard solution,

1.  $7.8 : 1000 :: .075 : x$ ;  
 $x = 9.615$ .
2.  $9.78 - 9.615 = y$ ;  
 $y = .165$ .
3.  $4.43 : 5.35 :: .165 : z$ ;  
 $z = .19926$ .
4.  $9.615 : 100 :: .19926 : p$ ;  
 $p = 2.072$  per cent. of  $\text{NH}_4\text{Cl}$ .

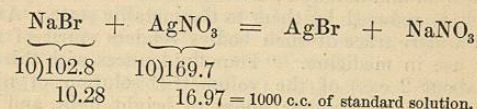
*Bromide of Potassium.*—Operate upon rather less than .1 gramme, and conduct the titration in the same manner as with chloride of sodium, using chromate of potassium as an indicator of the close of the reaction:—



To calculate the KCl, proceed as for  $\text{NH}_4\text{Cl}$ , 74.5 of KCl being equal to 118.8 of KBr.

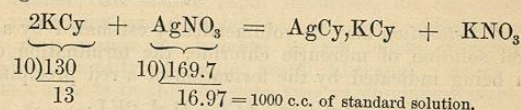
The United States Pharmacopœia requires Bromide of Potassium to contain 97 per cent. of the salt.

*Bromide of Sodium.*—Operate upon .1 gramme, and proceed exactly as for bromide of ammonium:—



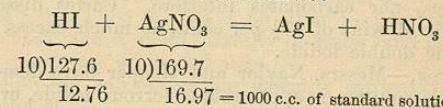
Bromide of Sodium, U. S. P., should be of 97 per cent. purity, and the chloride may be calculated in the same manner as chloride of ammonium, 5.85 grammes of chloride being equal to 10.28 grammes of bromide of sodium.

*Cyanide of Potassium.*—Operate upon from .1 to .2 gramme of the salt, conducting the titration as for hydrocyanic acid. The following reaction occurs:—



The United States Pharmacopœia requires Cyanide of Potassium to contain 90 per cent. of real cyanide (KCy).

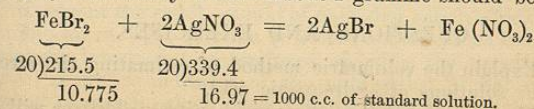
*Syrup of Hydriodic Acid.*—Operate upon 10 to 15 grammes. The reaction which occurs is as follows:—



The close of the reaction is shown by the cessation of the formation of iodide of silver, the nitric acid liberated rendering chromate of potassium inadmissible as an indicator.

*Syrupus Acidi Hydriodici*, U. S. P., should contain 1 per cent. of anhydrous hydriodic acid (HI).

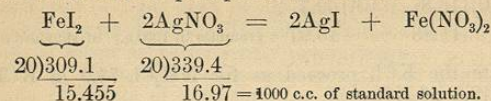
*Syrup of Bromide of Iron.*—About 1 gramme should be used:—



It should correspond to 10 per cent. of bromide of iron ( $\text{FeBr}_2$ ) to fulfil the requirements of the United States Pharmacopœia.



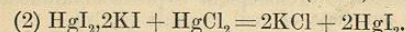
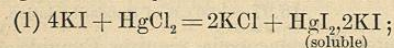
*Syrup of Iodide of Iron.*—Operate upon 1 to 2 grammes of the syrup until no further precipitate is formed:—



*Syrupus Ferri Iodidi*, U. S. P., should contain 10 per cent. of iodide of iron ( $\text{FeI}_2$ ).

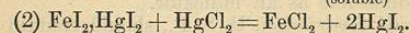
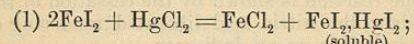
*Spirit of Wine* (*Spiritus Rectificatus*, B. P.) may contain traces of amylic alcohol and aldehyd; these may be detected by nitrate of silver, which is reduced by them to the metallic state. Any quantity beyond a mere trace of such bodies renders spirit of wine too impure for use in medicine. "Four fluidounces with thirty grain-measures (about 2 c.c.) of the volumetric solution of nitrate of silver exposed for twenty-four hours to bright light, and then decanted from the black powder which has formed, undergoes no further change when again exposed to light with more of the test."—B. P. "If 20 c.c. are shaken in a glass-stoppered vial, previously well rinsed with the same alcohol, with 2 c.c. of test-solution of nitrate of silver, the mixture should not be rendered more than faintly opalescent during one day's exposure to direct sunlight (abs. of more than traces of foreign organic matters, fusel oil, etc.)."—U. S. P.

*Iodide of Potassium* may be volumetrically estimated by a semi-decinormal solution of mercuric chloride, the termination of the operation being indicated by the formation of a red precipitate:—



The author of this process, M. Personne, states that neither chlorides, bromides, nor carbonates interfere. Carles dissolves the iodide in spirit of wine of  $17\frac{1}{2}$  per cent., as much excess of water decomposes the double iodide.

*Iodide of Iron.*—Messrs. Naylor and Hooper have demonstrated that Personne's solution is applicable to ferrous iodide, even in the state of syrup:—



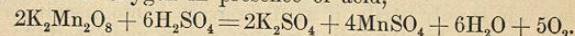
#### QUESTIONS AND EXERCISES.

1014. Explain the volumetric method of estimating the strength of aqueous solutions of hydrocyanic acid.

1015. Work a sum showing how much nitrate of silver will indicate, by the official volumetric process, the presence of 1 part of real hydrocyanic acid. *Ans.* 6.2853 parts.

#### ESTIMATION OF SUBSTANCES READILY OXIDIZED.

Any deoxidizer—that is, any substance which quickly absorbs a definite amount of oxygen or is susceptible of any equivalent action—may be quantitatively tested by ascertaining how much of an oxidizing agent of known power must be added to a given quantity before complete oxidation is effected. The oxidizing agents employed for this purpose in the United States Pharmacopœia are iodine and the red chromate of potassium. Permanganate of potassium is often used for the same purpose. Iodine acts indirectly by taking hydrogen from water and liberating oxygen; the red chromate of potassium directly, by the facility with which it yields three-sevenths of its oxygen, as indicated by the equations and statements given on p. 575; permanganate of potassium, by affording five-eighths of its oxygen in presence of acid,



#### STANDARD SOLUTION OF IODINE.

(Iodine, I = 126.6.)

If pure iodine be not at hand, it may be prepared by mixing the commercial article with about a fourth of its weight of iodide of potassium and subliming. Sublimation may be effected by gently warming the mixture in a beaker the mouth of which is closed by a funnel; the iodine vapor condenses on the funnel, while fixed impurities are left behind, and any chlorine which the iodine may contain is absorbed by the iodide of potassium, an equivalent quantity of iodine being liberated. Small quantities may be similarly treated between two watch-glasses placed edge to edge. Any trace of moisture in the resublimed iodine is removed by exposure for a few hours under a glass shade near a vessel containing oil of vitriol.

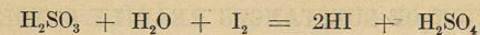
Place 12.66 grammes of pure iodine and about 18 grammes of pure iodide of potassium (an aqueous solution of which is the best solvent of iodine; the salt plays no other part in these operations) in a litre flask, add a small quantity of water, and agitate until the iodine is dissolved; dilute to 1 litre.

The following substances are officially estimated by this volumetric solution:—

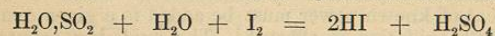
*Sulphurous Acid.*—Operate on about .5 of a gramme of the acid, and dilute with water as usual. If the sulphurous acid be diluted to a less degree than .04 or .05 per cent., there will be some risk of the sulphuric acid formed being again reduced to sulphurous acid, with liberation of iodine. In delicate experiments the distilled water used for dilution should previously be freed from air by boiling, to prevent the small amount of oxidizing action which dissolved air would exert. The solution of iodine is then added until a slight permanent brown tint is produced, showing the presence of free iodine. A better indicator of the termination of the reaction is mucilage of starch, which gives a blue color with the slightest trace of free iodine.

The following equations, etc. show the reaction that takes place:—





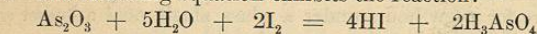
$$\begin{array}{r} 20 \overline{)82} \\ 4.1 \end{array} \quad \begin{array}{r} 20 \overline{)253.2} \\ 12.66 = \text{grms. in 1000 c.c. of standard solution.} \end{array}$$



$$\begin{array}{r} 20 \overline{)64} \\ 3.2 \end{array} \quad \begin{array}{r} 20 \overline{)253.2} \\ 12.66 = \text{grms. in 1000 c.c. of standard solution.} \end{array}$$

The official (U. S. P.) sulphurous acid should contain 3.5 per cent. of sulphurous anhydride ( $\text{SO}_2$ ).

*Arsenic*.—About .1 gramme of *solid arsenic*, accurately weighed, should be dissolved in the usual quantity of water, heated to boiling, by help of about .5 gramme of bicarbonate of sodium. The arsenious acid is only partly, if at all, converted into arsenite or arseniate of sodium, but the iodine reaction occurs more readily in an alkaline solution. When the liquid is quite cold, mucilage of starch is added, and the iodine solution allowed to flow in until, after well stirring, a permanent blue color is produced. The official *solution of arsenite of potassium*, already containing some carbonate of potassium, requires somewhat less. 10 grammes is a convenient quantity to operate upon. To this should be added the usual quantity of water and about .3 of a gramme of bicarbonate of sodium. After boiling and cooling the titration is carried on as before.—About 10 grammes of the official *solution of arsenic in dilute hydrochloric acid* is also a convenient quantity to operate upon. This quantity requires about .6 gramme of bicarbonate of sodium. The usual quantity of water is added, and the titration performed as before. The following equation exhibits the reaction:—

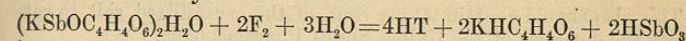


$$\begin{array}{r} 40 \overline{)197.8} \\ 4.945 \end{array} \quad \begin{array}{r} 40 \overline{)506.4} \\ 12.66 = \text{grms. in 1000 c.c. of standard solution.} \end{array}$$

Arsenic, U. S. P., should contain 97 per cent., and both solutions, U. S. P., contain .97 per cent. of arsenic.

In the foregoing operation, if ebullition be continued longer than is necessary for the solution of the arsenic, more monocarbonate of sodium may be formed than will be reconverted into bicarbonate by the liberated carbonic acid; loss of iodine will then ensue. E. J. Woolley has shown that borax may be usefully employed in the place of the bicarbonate of sodium. *Antimony* also passes from lower to higher active quantivalence under the influence of nascent oxygen, iodine, or an equivalent acidulous radical. The following equation illustrates the reaction with tartar emetic and iodine. The student should make several determinations on, say, 20 c.c. of a solution of 2 grammes of pure crystals of tartar emetic in 200 c.c. of water. To the 20 c.c. add about an equal amount of strong solution of bicarbonate of sodium, a couple of c.c. of starch mucilage, and then the iodine solution, until, after stirring, the blue color is fairly persistent. The whole operation should be quickly conducted or a

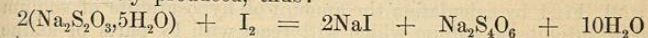
precipitate of antimonious hydrate will be formed; and it is only when in solution that the antimony is properly attacked. This process is by Mohr. It has been tested by Fresenius and in the Research Laboratory of the Pharmaceutical Society of Great Britain, and is trustworthy:—



$$\begin{array}{r} 40 \overline{)664} \\ 16.6 \end{array} \quad \begin{array}{r} 40 \overline{)506.4} \\ 12.66 \text{ grammes in 100 c.c. of s. s.} \end{array}$$

*Hyposulphite of Sodium*.—About .4 of a gramme is a convenient quantity to employ. It is dissolved in water, starch mucilage added, and the iodine solution slowly run in, the whole being frequently stirred, until a permanent blue color is produced. This is the B. P. process; the U. S. P. orders a solution of sodium hypsulphite to be shaken with solid iodine.

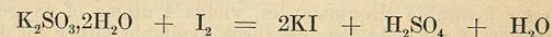
In the previous reactions iodine has acted as an indirect oxidizing agent by uniting with the hydrogen and thus liberating the oxygen of water. In the present case it unites with an analogue of hydrogen—namely, sodium—a new salt (tetrathionate of sodium) being simultaneously produced, thus:—



$$\begin{array}{r} 20 \overline{)496} \\ 24.8 \end{array} \quad \begin{array}{r} 20 \overline{)253.2} \\ 12.66 = \text{grms. in 1000 c.c. of standard solution.} \end{array}$$

The United States Pharmacopoeia requires 98 per cent. purity in the case of hypsulphite of sodium.

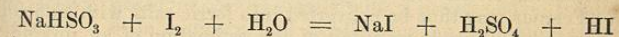
*Sulphite of Potassium*.—About .1 gramme is a convenient quantity to take, using starch paste as an indicator, as before. The reaction as below occurs:—



$$\begin{array}{r} 2.0 \overline{)19.4} \\ 9.7 \end{array} \quad \begin{array}{r} 20 \overline{)253.2} \\ 12.66 = 1000 \text{ c.c. of standard solution.} \end{array}$$

Sulphite of potassium, U. S. P., should contain 90 per cent. of the crystallized salt ( $\text{K}_2\text{SO}_3, 2\text{H}_2\text{O}$ ).

*Bisulphite of Sodium*.—Operate upon .05 to .07 gramme, as before:—

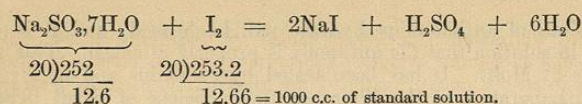


$$\begin{array}{r} 20 \overline{)104} \\ 5.2 \end{array} \quad \begin{array}{r} 20 \overline{)253.2} \\ 12.66 = 1000 \text{ c.c. of standard solution.} \end{array}$$

The United States Pharmacopoeia requires bisulphite of sodium to contain 90 per cent. of the pure salt ( $\text{NaHSO}_3$ ).

*Sulphite of Sodium*.—Use for this estimation about 1. to .15 gramme, and proceed as before:—





This also should contain 90 per cent. of the crystallized salt to satisfy the demands of the United States Pharmacopæia.

#### QUESTIONS AND EXERCISES.

1016. Give equations illustrative of the reactions on which the use of a standard volumetric solution of iodine is based.

1017. From what point of view may iodine be regarded as an oxidizing agent?

1018. What reagent indicates the termination of the reaction between deoxidizing substances and moist iodine?

1019. How much sulphurous acid gas will cause the absorption of 2.54 parts of iodine in the volumetric reaction? *Ans.* .642.

1020. What quantity of iodine will be required, under appropriate conditions, to oxidize 5 parts of arsenic? *Ans.* 12.008.

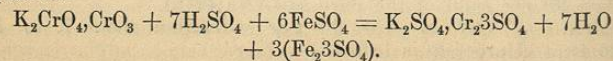
1021. Find by calculation the amount of hyposulphite of sodium and of sulphite of sodium which will react with 13 parts of iodine in volumetric analysis. *Ans.* 25.466 and 12.9384.

#### VOLUMETRIC SOLUTION OF RED CHROMATE OF POTASSIUM.

(Red Chromate of Potassium,  $\text{K}_2\text{Cr}_2\text{O}_7 = 294.8$ .)

One molecule of red chromate of potassium in presence of an acid, under favorable circumstances, yields 4 atoms of oxygen to the hydrogen of the acid, leaving three available either for direct oxidation or for combination with the hydrogen of more acid, an equivalent proportion of acidulous radical being liberated for any required purpose.

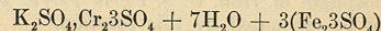
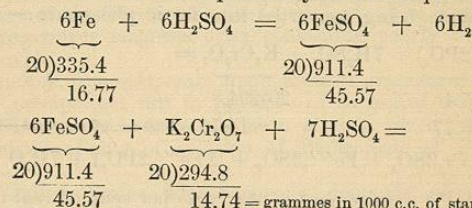
When used as a volumetric agent the red chromate always yields the whole of its oxygen to the hydrogen of the accompanying acid, a corresponding quantity of acidulous radicals being set free—four-sevenths of this radical immediately combining with the potassium and chromium of the red chromate, three-sevenths becoming available. Ferrous may thus be converted into ferric salts with sufficient rapidity and exactitude to admit of the estimation of an unknown quantity of iron by a known quantity of the red chromate. As 1 atom of any liberated bivalent acidulous radical will convert 2 molecules of ferrous into 1 of ferric salt, 1 molecule of red chromate causes 6 of ferrous to become 3 of ferric, as shown in the following equation:—



The volumetric solution is made by dissolving 14.74 grammes ( $\frac{1}{20}$  of a molecular weight in grammes) of red chromate of potassium in water, and diluting to one litre. It is used in determining the strength of the ferrous preparations. It is known that the whole of the ferrous has been converted to ferric salt when a small drop of the liquid placed in contact with a drop of fresh and very dilute solution of ferridcyanide of potassium on a white plate ceases to strike a blue color.

If the red chromate employed in making this standard solution is not known to be pure and dry, the strength of the solution may be checked by dissolving a small, accurately weighed piece of pianoforte wire (0.4 or 0.5 gramme) in diluted sulphuric acid in a small flask, warming, and then running in the solution of red chromate until conversion is effected.

The reactions which take place may be thus expressed:—



It is evident that 16.77 grammes of iron are equivalent in the reactions to 14.74 of red chromate or 1000 c.c. of standard solution of the chromate. Now suppose that 0.5 of a gramme of pianoforte wire has been employed, and the quantity of solution of red chromate of unknown strength used has been 28 c.c. How many c.c. of this solution contain 14.74 of red chromate? that is, how many c.c. must be required to oxidize ferrous salt containing 16.77 of iron? As .5 of iron is to 28 c.c. sol., so are 16.77 of iron to  $x$  c.c. sol. = 939.12 c.c. Of the supposed solution, then, 939.12 c.c. would contain 14.74 grammes of red chromate, and would be equivalent to 1000 c.c. of standard solution. It might be employed without being diluted, or, better, be diluted to official standard strength.

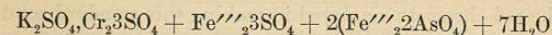
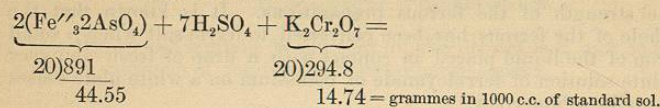
Special care should be taken in all these estimations of substances readily oxidized to avoid atmospheric oxidation. Flasks may usually be loosely corked, or corked closely with a gas exit-tube passing just beneath a little mercury, and in all cases the estimation should be performed quickly. When standardizing with iron wire any slight oxidation may be remedied by a fragment of zinc, the last portions of which must be removed or dissolved before the titration is commenced.

The ferrous salt in the following substances is estimated by this solution.

*Arsenate of Iron.*—Operate upon 1 to 2 grammes. Dissolve in excess of dilute sulphuric or hydrochloric acid. Sulphuric acid is preferable in most cases, because ferrous sulphate absorbs oxygen

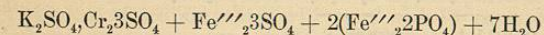
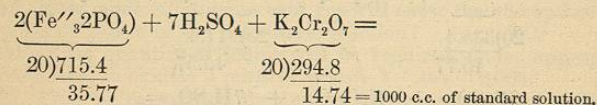


much less readily than ferrous chloride. The reaction that occurs is shown in the following equation, the ferrous arseniate being converted into ferric arseniate:—



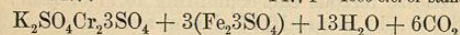
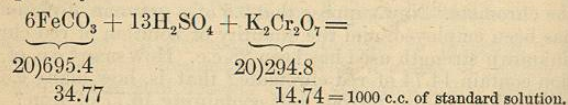
Arseniate of Iron, B. P., is supposed to contain 37.9 per cent. of ferrous arseniate. The compound is more nearly a ferric than a ferrous arseniate.

*Phosphate of Iron.*—Operate upon 1 to 2 grammes. Proceed as with arseniate. The following equation indicates the reaction, the ferrous phosphate being converted into ferric phosphate:—



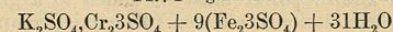
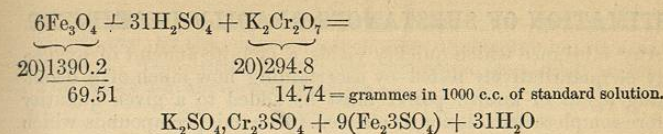
The official (B. P.) requirement is nearly 45 per cent. of real ferrous phosphate. Phosphate of Iron, U. S. P., is *Ferric Phosphate*, and therefore cannot be estimated by this solution.

*Saccharated Carbonate.*—Proceed as with arseniate, using about the same quantity:—

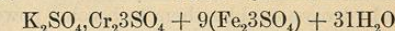
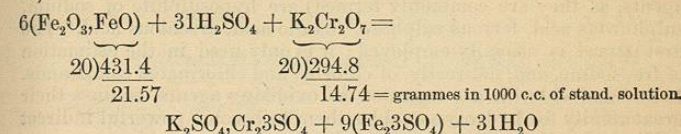


The official (U. S. P.) strength is 15 per cent. Trade samples yield from 20 to 30, and sometimes 35, per cent., according to the care with which oxidation has been prevented. The theoretical percentage obtainable from the ingredients is 45.5, the quantity that would be present if the compounds were anhydrous and unoxidized—conditions never obtained in practice. Howie has suggested that as hydrochloric acid is known to so rapidly convert ordinary sugar into inverted sugar as to render it easily attacked by chromic acid, while phosphoric acid very slowly affects sugar, the latter acid instead of the former should be employed in dissolving the saccharated carbonate of iron for volumetric analysis. Another mode of eliminating the action of sugar is to char with oil of vitriol before analyzing.

*Magnetic Oxide of Iron.*—Use about the same quantity, and proceed as with arseniate or phosphate. The reaction may thus be shown:—



or,



Absolutely pure magnetic oxide of iron contains 31 per cent. of ferrous oxide. Oxidation occurs, however, during manufacture, as in the case of the ferrous salts just described. The British Pharmacopœia recognizes magnetic oxide containing nearly 25 per cent. of ferrous oxide.

*Sulphate of Iron.*—Operate upon about 1 gramme of the crystallized or precipitated salt in presence of excess of sulphuric acid; the reaction which occurs has been already given when treating of the standardizing of solution of Bichromate of Potassium on page 575.

The United States Pharmacopœia demands almost absolute purity for both *Ferri Sulphas* and *Ferri Sulphas Precipitatus* ( $\text{FeSO}_4, 7\text{H}_2\text{O}$ ).

*Note.*—The use of this volumetric solution in quantitative analysis admits of great extension. The student should at least employ it in the case of a few iron ores.

#### QUESTIONS AND EXERCISES.

1022. Write equations explanatory of the oxidizing power of red chromate of potassium.

1023. One hundred cubic centimetres of an aqueous solution of red chromate of potassium contain  $\frac{1}{250}$  of the molecular weight of the salt in grammes; with what weight of metallic iron, dissolved in hydrochloric acid, will this volume react? *Ans.* 1.677 grammes.

1024. If 8.34 grammes of impure crystallized ferrous sulphate, dissolved in acidulated water, require 93 c.c. of the standard solution of chromate for complete conversion into ferric salt, what percentage of ferrous sulphate is present? *Ans.* 92.966.

1025. Work a sum showing how much red chromate of potassium is required for the conversion of 10 parts of ferrous sulphate into ferric salt. *Ans.* 1.768.

1026. Show what quantity of pure ferrous carbonate is indicated by 1.475 parts of red chromate as applied in volumetric analysis. *Ans.* 3.479.

1027. Prove what amount of official saccharated carbonate of iron is equivalent to .7375 part of red chromate in the volumetric reaction. *Ans.* 11.598.