

tetrahedral symmetry while the alkali and halogen ions are cubic in shape. Low temperatures, high pressures and anions of small atomic volume cause the shape of the ammonium ion to be a factor of predominant importance in determining the crystal structure. High temperatures, low pressures and anions of large volume make the shape of the ammonium ion of relatively less importance so that under these conditions ammonium salts tend to become isomorphous with the corresponding potassium salts.

The numerical data relating to the crystal structures of the ammonium halides are given in the following table.

TABLE VI.  
Summary of Results.

Salt.	Temp. ° C.	Arrangement of ions.	Distance between like ions. Å.	Distance between unlike ions. Å.	Density (calculated).	Molecular volume.
NH <sub>4</sub> Cl	20	Centered cubic	3.859	3.342	1.536	34.9
NH <sub>4</sub> Cl	250	Simple cubic	4.620	3.266	1.265	42.3
NH <sub>4</sub> Br	20	Centered cubic	3.988	3.453	2.548	38.4
NH <sub>4</sub> Br	250	Simple cubic	4.88	3.45	1.972	49.7
NH <sub>4</sub> I	20	Simple cubic	5.090	3.60	2.563	56.6

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS  
UNIVERSITY.]

## TRIVALENT TITANIUM. I. NOTES ON THE VOLUMETRIC DETERMINATION OF IRON BY MEANS OF TITANOUS SALTS.

BY WILLIAM M. THORNTON, JR., AND JAMES E. CHAPMAN.

Received October 16, 1920.

### I. Introduction.

The use of titanous chloride for the estimation of iron was first suggested by Knecht.<sup>1</sup> A little later Knecht and Hibbert<sup>2</sup> supplied quantitative data, which seemed sufficient to prove that the method was accurate. Since then various analytical processes have been brought forward by Knecht and his co-workers<sup>3</sup> and others,<sup>4</sup> all of which depend, more or less directly, upon the great reducing power of the salts of trivalent titanium. Notwithstanding the many attractive features that these

<sup>1</sup> Knecht, *Ber.*, **36**, 166 (1903).

<sup>2</sup> Knecht and Hibbert, *ibid.*, **36**, 1549 (1903).

<sup>3</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918.

<sup>4</sup> Rothmund, *Z. anorg. Chem.*, **62**, 108 (1909); Radlberger and Siegmund, *Oesterr. Ung. Z. Zuckerind.*, **42**, 34 (1913); Salvaterra, *Chem.-Ztg.*, **38**, 90 (1914); Monnier, *Ann. chim. anal.*, **20**, 1 (1915); **21**, 109 (1916); Mach and Lederle, *Landw. Versuchs.-Stat.*, **90**, 191 (1917); Hackl, *Chem.-Ztg.*, **43**, 9 (1919); Williams, *Chem. News*, **119**, 8 (1919).

methods of analysis present, they have not as yet become popular (at least in America), owing doubtless to an exaggerated idea as to the difficulty in preserving the reagent of constant titer. Largely on this account, according to his own statement, Newton<sup>1</sup> has worked out the determination of iron by titration with permanganate after reduction with titanous sulfate (not of accurately known strength)—the excess being destroyed by bismuth trioxide, which does not affect ferrous iron, and the metallic bismuth thus precipitated and surplus bismuth oxide removed by filtration. In like manner, Newton and Hughes<sup>2</sup> have developed methods for the estimation of both uranium and phosphorus. Although there can be little doubt as to the accuracy of the titanous chloride method, still certain questions regarding suitable conditions for its application do not seem to have been definitely answered. As the result of an experience covering several years, during which many iron and other determinations were made with standard titanium solutions, certain experimental data have accumulated, oftentimes in a rather incidental way, which we have decided to set forth here for the benefit of any who may see fit to give this convenient mode of volumetric procedure a fair trial. Moreover, much of the work, presently to be described, was done with standard solutions of titanium trisulfate, instead of the trichloride; in spite of the fact that all quantitative results published prior to 1920 have been obtained with the chloride. In some cases, as will appear evident, the sulfate has distinct analytical advantages; and, if one has only titanous oxide to start with, it is somewhat easier to prepare.

## II. The Preparation of the Titanous Salts.

A good deal has been written concerning the preparation of titanous chloride and titanous sulfate, which may be found here and there in the literature. No attempt will be made to give a complete account here.

Some time ago a 15% solution of titanous chloride could be purchased, which had been imported from Germany; but, fortunately, American chemists are no longer dependent upon foreign markets for this material, since the titanous salts (both chloride and sulfate) of excellent quality may now be obtained from a domestic source.<sup>3</sup>

Either of these salts, in the form of a strong solution (about 20%), may be diluted with water, after adding the requisite quantity of acid to prevent any possible formation of metatitanic acid by hydrolysis, to the desired concentration.

Knecht and Hibbert<sup>4</sup> have recommended that the solution be boiled for

<sup>1</sup> Newton, *Am. J. Sci.*, [4] 25, 343 (1908).

<sup>2</sup> Newton and Hughes, *THIS JOURNAL*, 37, 1711 (1915). See also Newton, Dissertation, New Haven, 1908, where the estimation of vanadium is described.

<sup>3</sup> The La Motte Chemical Products Co., 13 W. Saratoga St., Baltimore, Md.

<sup>4</sup> *Ber.*, 36, 1550 (1903).

a short time prior to dilution to remove traces of hydrogen sulfide which commercial specimens of titanous chloride are likely to contain. This precaution is, however, quite unnecessary with salts made by the La Motte process.

### III. The Apparatus.

Fig. 1 shows the apparatus employed by us for storing and using the solution of titanous salt. In principle it is quite like the one proposed by Knecht and Hibbert;<sup>1</sup> but there are a few differences in detail. Chief among these is the substitution of the buret with 3 way Stopcock F for the bead valve used by them. This was done with a view to securing a more accurate delivery on the part of the buret and also for greater convenience in filling the same. The solution is charged into the storage bottle S, the volume being so regulated as to fill the bottle to its neck. The cock F is then turned so that the liquid rises in the buret B and on up until hydrostatic equilibrium has been reached. The hydrogen supply having been in the meanwhile turned on from the Kipp generator K, the cock F is turned so as to empty the entire buret and a current of hydrogen is passed over until it is reasonably certain that all air has been displaced from within the system; whereupon the buret B, after having been filled again, will be ready for use.

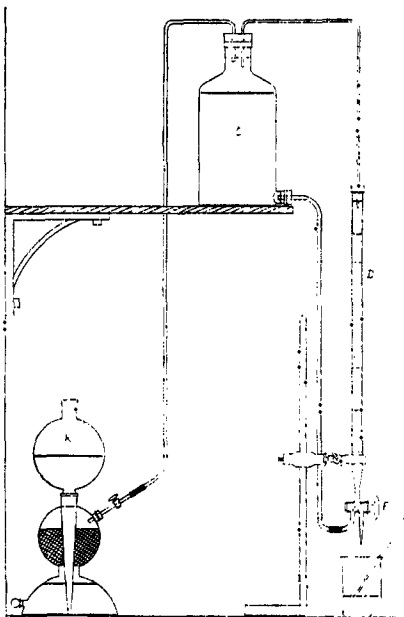


FIG. 1.

### IV. The Permanence of the Standard Solution.

To serve as a counterpart to the titanium solution, it is well to have at hand a solution of ferric ammonium sulfate containing enough sulfuric acid to prevent the formation of basic salt. Since the stability of this solution may safely be assumed, it is an easy matter to detect any change in the reducing power of the titanium solution by titrating the one against the other from time to time. Knecht and Hibbert<sup>2</sup> have recorded experiments which show that a solution of titanous chloride did not undergo any appreciable change during a period of 18 days. Since we have similar

<sup>1</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1918, p. 47.

<sup>2</sup> Knecht and Hibbert, *Ber.* 36, 1551 (1903).

data on a solution of titanous sulfate, it seems well to state the results of our experiments here.

TABLE I.

Expt.	Date.	(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> . Cc. taken.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . Cc. required.
1.....	Feb. 17	25.00	17.72
2.....	Apr. 1	25.00	17.73

From Table I it is evident that the solution kept for 42 days. At the end of that time the particular solution was used up; otherwise it would doubtless have maintained its full strength indefinitely.

### V. The Standardization.

Knecht and Hibbert<sup>1</sup> prescribe ferrous ammonium sulfate as the ultimate standard for all work with titanous chloride. Because of the many objections that have been raised against this salt as an oxidimetric standard, we decided to subject the matter to a rigorous test.<sup>2</sup> For this purpose a solution of c. p. ferrous ammonium sulfate, saturated at 40°, was filtered and allowed to fall into an equal volume of redistilled alcohol with continuous stirring. The fine-grain crystalline precipitate thus produced was filtered by suction and air-dried. This product was so finely divided that, although it contained a little iron in the ferric condition, it seemed rational to suppose that it would be, after thorough mixing, chemically homogeneous. A weighed portion of the precipitated salt was dissolved in water, acidified with 10 cc. of sulfuric acid (1 : 1) and carefully titrated with potassium permanganate, which had in turn been standardized against sodium oxalate<sup>3</sup> according to the technique of McBride,<sup>4</sup> until the end-point was just reached. The solution thus oxidized was boiled to expel dissolved oxygen,<sup>5</sup> cooled, treated with 10 cc. of 10% ammonium thiocyanate solution and titrated with titanous chloride to complete loss of color. On the same day an equal portion of the same ferrous ammonium sulfate was titrated with the same titanous chloride, omitting, however, the preliminary oxidation with permanganate. It is obvious that, if the second small titer be deducted from the first titer, the difference will serve as a basis for calculating the iron value of the titanous chloride with sodium oxalate as the primary standard. On the other hand, the main titer (uncorrected) will give the iron value with ferrous ammonium sulfate as the primary standard. The results of these experiments are set forth in Table II.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Bur. Standards Circ.*, 26, 9 (1913).

<sup>3</sup> *Ibid.*, Standard Sample No. 40.

<sup>4</sup> *THIS JOURNAL*, 34, 393 (1912).

<sup>5</sup> The boiling serves also to remove the small amount of permanganate added in excess by causing it to react with traces of organic matter in the distilled water and reagents.

TABLE II.

Expt.	Value of one cc. of $\text{TiCl}_3$ in a gram of Fe.	
	$\text{Na}_2\text{C}_2\text{O}_4$ Standard.	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Standard.
(1) Titration in Air.		
1.....	0.003753	0.003757
(2) Titration in Carbon Dioxide.		
2.....	0.003761	0.003766

The matter was tested still further, pursuing the same technique, but using the c. p ferrous ammonium sulfate of commerce without any additional purification.

TABLE III.

Expt.	Value of one cc. $\text{TiCl}_3$ in a gram of Fe.	
	$\text{Na}_2\text{C}_2\text{O}_4$ Standard.	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Standard.
Titration in Carbon Dioxide.		
3.....	0.0021035	0.0021050
4.....	.....	0.0021037

The data of Tables II and III seem to warrant the conclusion that any sample of ferrous ammonium sulfate of good quality will serve as a sufficiently accurate standard for titanous salt solutions; since, in this case, the total iron content is of importance and not that actually present in the ferrous condition. Various other methods of standardization naturally suggest themselves; but it is doubtful if any would exceed ferrous ammonium sulfate in point of convenience. Moreover, there are still other ways of checking the values thus obtained, as will be explained later on.

## VI. Comparison of Titrations in Air with Titrations in Carbon Dioxide.

Insofar as the salts of trivalent titanium are powerful reducing agents,

TABLE IV.

Expt.	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ Cc. taken.	$\text{TiCl}_3$ Cc. required.	Room temp. ° C.
(1) Titration in Air.			
1.....	50.00	23.60	24
2.....	50.00	23.57	23
3.....	50.00	23.58	24
4.....	50.00	23.66	21
5.....	50.00	23.62	19
6.....	50.00	23.63	20
7.....	50.00	23.54	30
		Av., 23.60	
(2) Titration in Carbon Dioxide.			
8.....	50.00	23.36	30
9.....	50.00	23.41	25
		Av., 23.385	

they are very sensitive to atmospheric oxidation. The question naturally arises, therefore, as to whether the drops are at all oxidized while falling through the air, or if the ferrous salt formed suffers oxidation in the time required to make the titration. The latter effect is in all probability negligible, since Hillebrand<sup>1</sup> states that, in the absence of hydrofluoric acid, the oxidation of ferrous iron on exposure to air at ordinary temperatures is a very slow process; but the former appears to take place to a certain small but measurable extent, as experiment (see Table IV) has consistently shown.

If these figures may be taken as representative, the average loss incurred by titrating in air is 0.215 cc. of titanous chloride (corresponding to 0.0008 g. of iron), a quantity which could hardly be disregarded where precise work is at stake, if it existed as an absolute error. Good results may be expected, however, in those direct titrations with titanous salt solutions which are carried out at the prevailing atmospheric temperatures, provided both the standardization experiments and the actual determinations be carried out in air. This, indeed, makes for greater convenience; but with the arrangement shown in Fig. 2 there is no diffi-

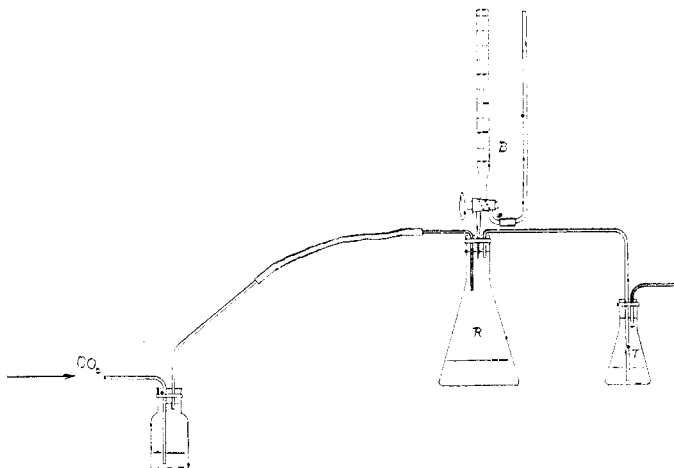


FIG. 2.

culty in accomplishing the titration in the absence of air by simply filling the reaction flask R with carbon dioxide before beginning the delivery of the buret B—the flask T serving as a trap to prevent access of air by backward diffusion. In fact, as Knecht and Hibbert have claimed, in the estimation of certain other substances the carbon dioxide protection is not only desirable but necessary.

#### VII. The Effect of Temperature.

Rhead<sup>2</sup> has considered the influence of temperature upon the titration

<sup>1</sup> Hillebrand, U. S. Geol. Survey, *Bull.* 700, 199 (1919).

<sup>2</sup> Rhead, *J. Chem. Soc.*, 80, 1491 (1906).

and has come to the conclusion that below 30° it may vary without effect. Our own observations are not in exact accord with those of Rhead, and the data of Table IV (2) show a tendency toward a slight lowering of titer with elevation of temperature. The point needs further investigation, so we shall dismiss it for the present.

### VIII. Permissible Volume of the Test Solution.

The volume may vary considerably as proven by experiments recorded in Table V.

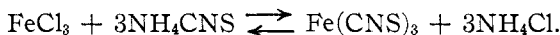
TABLE V.

Expt.	(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> Cc. taken.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cc. required.	Volume. Cc.
1.....	50.00	15.95	500
2.....	50.00	15.97	175

It is inadvisable, however, to titrate with an initial volume greater than 500 cc.; since at that dilution the speed of reaction is perceptibly diminished so that, unless the titration is performed very slowly towards the end, too great a quantity of the titanous salt may easily be added.

### IX. Desirable Amount of the Indicator.

From theoretical considerations it would seem that the amount of thiocyanate added should be large as compared with the volume of the test solution. The formation of the blood-red ferric thiocyanate is the result of a reversible action, which takes place in accordance with the expression



When, towards the end of the titration, the concentration of ferric chloride becomes small, the amount of ferric thiocyanate formed will be excessively small, unless the concentration of the other factor of reaction, *viz.*, ammonium thiocyanate, be kept large; or, speaking in practical terms, a premature end-point will be obtained. The following experimental evidence, bearing on this point, is deemed sufficient.

Fifty cc. of a solution of ferric ammonium sulfate, which had been found from the average of 5 experiments to require 16.40 cc. of the standard titanous sulfate solution for complete reaction, was titrated using only 0.5 cc. of 10% ammonium thiocyanate solution. The color changed from pale orange to colorless when only 16.34 cc. of titanous sulfate had been added. On introducing 10 cc. more of the thiocyanate, the solution turned pink. This was bleached out by adding carefully 0.07 cc. additional of the titanous sulfate—making the whole titer 16.41 cc., which agrees closely with that obtained above when 10 cc. of indicator had been used. Our experience with the matter, then, has led us to believe that, where there is no special objection to the contrary, 10 cc. of a 10% thiocyanate is a safe and ample quantity, and in no case should there be present less than 2.5 cc.

Certain dyestuffs, notably methylene blue, have been used as indicators in the titanium titrations, a few drops only of a weak solution being added. Methylene blue, however, has the disadvantage of not being very sensitive below 35°. <sup>1</sup>

Monnier <sup>2</sup> suggests the possibility of using sodium tungstate as indicator.

### X. The Influence of Certain Acids.

(2) **Hydrochloric Acid.**—Hydrochloric acid may be present in any reasonable concentration and the titers will be almost identical with those obtained in sulfuric acid solutions, a point of practical superiority over the more familiar permanganate titrations.

TABLE VI.

Fifty cc. of Ferric Ammonium Sulfate Used in Each Experiment.

Expt.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cc. required.	HCl (Sp. gr. 1.19). Cc.	H <sub>2</sub> SO <sub>4</sub> (1:1). Cc.
1.....	16.38	25	..
2.....	16.41	50	..
3.....	16.40	50	..
4.....	16.40	25	..
5.....	16.41	..	10
6.....	16.41	..	25

(2) **Nitric Acid.**—The absence of nitric acid has been insisted upon by Rhead. <sup>3</sup> The reasons for this are taken to be self-evident, and will be given no exposition here.

(3) **Hydrofluoric Acid.**—The presence of hydrofluoric acid gives rise to a somewhat striking phenomenon. Instead of getting the characteristic blood-red color of ferric thiocyanate only a yellow coloration is obtained. If, however, a sufficient quantity of boric acid be added, the red color is restored and the end-point is sharp. <sup>4</sup> This action, on the part of boric acid, has been explained by Barnebey <sup>5</sup> on the grounds that the

TABLE VII.

Expt.	Alloy No.	HF (48%) added. Cc.	B(OH) <sub>3</sub> added. G.	Fe found. %.
1.....	6	10	8	19.40
2.....	6	..	..	19.40
3.....	7	10	8	24.39
4.....	7	..	..	24.25
5.....	57	10	Excess	13.50
6.....	57	..	..	13.26

<sup>1</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1918, p. 48. Longmans, Green and Co.

<sup>2</sup> Monnier, *Ann. chim. anal.*, 21, 109 (1916).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Cf. Hackl, *loc. cit.*

<sup>5</sup> Barnebey, *THIS JOURNAL*, 37, 1489 (1915).



slightly dissociated meta-fluoboric acid,  $\text{HBF}_4$ , is formed. The efficiency of this preventive agent was tried out incidentally while analyzing a series of manganese alloys. The test solution was divided into 2 aliquot parts. To one of these hydrofluoric acid was intentionally added while the other was titrated as usual. The results are set forth in Table VII.

### XI. Other Interfering Substances.

As a general rule, any substance that might reduce the iron or oxide the titanous salt must be absent.

Certain forms of organic matter do not affect titanous chloride to any appreciable extent. For instance, in the analysis of nitro compounds, it is often necessary to dissolve the sample in alcohol. The reduction is accomplished with a measured excess of standard titanous chloride<sup>1</sup> or sulfate,<sup>2</sup> and the determination is finished by titrating back with ferric sulfate, after having added the thiocyanate indicator. Moreover, Knecht<sup>3</sup> in his assay of indigo and thio-indigo red employs Rochelle salt for securing a definite end-point.

Copper and doubtless certain other metals of the hydrogen sulfide group, exert an oxidizing action upon the titanous salt. In fact, when copper and iron are present in admixture, the titer corresponds quantitatively to that required for the sum of those 2 metals; provided ammonium thiocyanate be used as indicator.<sup>4</sup>

From moderately dilute solutions titanous chloride precipitates metallic platinum from platinum chloride. It is conceivable then that the traces of platinum that are to be found in the test solution as the result of attack on vessels of that metal by certain reagents might cause an error of small magnitude in the iron determination. Since, however, there is no experimental evidence bearing on this point, it would be idle to discuss the matter further.

Chromic salts do not influence titanous chloride; while chromic acid undergoes quantitative reduction to the trivalent condition.<sup>5</sup>

Titanium, for *a priori* reasons, can do no harm.

Vanadic acid, in a cold solution containing 10% of strong sulfuric acid, is definitely reduced by titanous sulfate to vanadium trioxide,  $\text{V}_2\text{O}_3$ , which is carried back to vanadium pentoxide,  $\text{V}_2\text{O}_5$ , by permanganate.<sup>6</sup>

### XII. The Preliminary Oxidation for the Determination of Total Iron.

Whenever the iron in the sample is present in the ferrous condition

<sup>1</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1918, pp. 25 and 72. Longmans, Green and Co.

<sup>2</sup> Callan, Henderson and Strafford, *J. Soc. Chem. Ind.*, 39, 86 (1920).

<sup>3</sup> Knecht, *J. Soc. Dyers Col.*, 21, 292 (1905); 22, 156 (1906); 25, 135, 160 (1909).

<sup>4</sup> Rhead, *loc. cit.*

<sup>5</sup> Jatar, *J. Soc. Chem. Ind.*, 27, 673 (1908).

<sup>6</sup> Newton, *Dissertation*, New Haven, 1908.

(either in whole or in part), means must be sought for converting it entirely into the ferric state. Herein the method is just the opposite of the permanganate and dichromate processes; but the ferric condition is in general more easily realized and in the presence of air it is certainly more easily maintained. For this purpose Knecht and Hibbert<sup>1</sup> have proposed 3 different modes of oxidation: (1) the solution is boiled with hydrogen peroxide in ammoniacal solution and subsequently acidified with hydrochloric acid; (2) the sulfuric acid solution is treated with potassium permanganate (of unknown strength) until a scarcely perceptible pink color is produced; (3) the solution is heated with potassium chlorate and hydrochloric acid. The second method has seemed to us the nicest and we have used it most often in our work. But in so doing the interfering action of hydrochloric acid in the permanganate titration must be borne in mind. Small concentrations of hydrochloric acid may indeed be offset by adding the Zimmermann-Reinhardt reagent<sup>2</sup> (less phosphoric acid, for fear of precipitating basic titanate phosphate). Moreover, the hydrochloric acid may be displaced by evaporating down with excess of sulfuric acid; water-bath temperatures suffice. Results obtained on the Sibley iron ore<sup>3</sup> are here tabulated (Table VIII).

TABLE VIII.

Analysis.	Fe found. %.	Mode of oxidation.
1	69.26	HCl solution of ore treated with Zimmermann-Reinhardt preventive reagent (less H <sub>3</sub> PO <sub>4</sub> ) and titrated with unknown permanganate to exact end-point.
2	69.38	HCl solution of ore treated with Zimmermann-Reinhardt preventive reagent (less H <sub>3</sub> PO <sub>4</sub> ) and titrated with unknown permanganate to exact end-point.
3	69.51	HCl solution of ore evaporated with H <sub>2</sub> SO <sub>4</sub> and then titrated with unknown permanganate.
Av., 69.38		
Average of the Bureau of Standards. . .		69.26

### XIII. The Direct Determination of Ferric Iron.

The estimation of ferric iron actually existing in the sample needs no special comment. Its application to the analysis of silicates insoluble in acid has been worked out by Hackl;<sup>4</sup> and, needless to say, furnishes a valuable check on the figure usually found as the difference between the ferrous iron and the total.

### XIV. Verifying the Iron Determinations.

A good many ways might be suggested as means of checking the iron

<sup>1</sup> "New Reduction Methods in Volumetric Analysis," 1918, p. 49. Longmans, Green and Co.

<sup>2</sup> "Analytical Chemistry," by Treadwell-Hall, II, 1915, p. 607. John Wiley and Sons, Inc.

<sup>3</sup> Bureau of Standards, Standard Sample No. 27.

<sup>4</sup> *Loc. cit.*

values by independent methods of analysis. Only those that have been actually employed by us will be described here. The iron may first be determined by titration with titanous sulfate. As soon as the end-point is reached, a sufficient quantity of silver nitrate<sup>1</sup> to precipitate the thiocyanate is added and the iron titrated with standard permanganate. A blank experiment must be run on the titanous sulfate solution according to the technique of Newton<sup>2</sup> and a small correction applied for the iron usually contained therein. Because of its very close approach to insolubility, the silver thiocyanate does not react appreciably with permanganate in the time required for conducting the titration—a fact previously utilized by Edgar<sup>3</sup> in his method for copper and iron. Table IX contains some comparative results obtained on manganese alloys in the way given above. It may be well to mention that the titanous sulfate was standardized against C. P. ferrous ammonium sulfate and the potassium permanganate against sodium oxalate.<sup>4</sup>

TABLE IX.

Analysis.	Alloy No.	Fe found. Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . %	Fe found. KMnO <sub>4</sub> . %
1.....	56	14.28	14.29
2.....	57	13.26	13.13
3.....	45	11.41	11.40

Again, the iron may be reduced by hydrogen sulfide, titrated with permanganate and immediately titrated with titanium. Still further, the iron may be determined gravimetrically with the aid of the "cupferron" reagent (ammonium salt of nitrosophenyl-hydroxylamine),<sup>5</sup> which is independent of all standardization. Results on a manganese alloy by 3 different methods are given in Table X.

TABLE X.

Analysis.	Alloy No.	Fe found. Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . %	Fe found. KMnO <sub>4</sub> . %	Fe found. C <sub>6</sub> H <sub>5</sub> .NO.NONH <sub>4</sub> . %
1.....	50	15.37	15.50	15.39

### XV. Determination of Iron and Available Oxygen in Artificial Manganese Peroxide.

In the analysis of prepared manganese peroxide we found it most convenient to determine the available oxygen by dissolving the sample in a weighed excess of sodium oxalate and dil. sulfuric acid and titrating the hot solution with potassium permanganate according to Blair,<sup>6</sup> and,

<sup>1</sup> A 25% solution was used with the 10% ammonium thiocyanate solution, volume for volume.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> THIS JOURNAL, 38, 884 (1916).

<sup>4</sup> Bureau of Standards, Standard Sample No. 40.

<sup>5</sup> Baudisch and King, *J. Ind. Eng. Chem.*, 3, 629 (1911).

<sup>6</sup> Blair, "The Chemical Analysis of Iron," 1918, p. 263. J. B. Lippincott Co.

after cooling, to titrate for iron with titanium. Check determinations with "cupferron" agreed fairly well (Table XI). No doubt the same procedure would serve for the rapid determination of iron in manganese ores.

TABLE XI.

Analysis.	Sample No.	Fe <sub>2</sub> O <sub>3</sub> found. Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . %	Fe <sub>2</sub> O <sub>3</sub> found. C <sub>8</sub> H <sub>5</sub> NO.NONH <sub>4</sub> . %
1.....	13	20.44	20.51

### XVI. Conclusions.

The method of Knecht and Hibbert for the estimation of iron is both rapid and accurate and it may be used with advantage under a great variety of circumstances.

BALTIMORE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

## THE LOWERING OF THE VAPOR PRESSURE OF WATER AT 20° PRODUCED BY DISSOLVED POTASSIUM CHLORIDE.<sup>1</sup>

BY B. F. LOVELACE, J. C. W. FRAZER AND V. B. SEASE.

Received October 23, 1920.

### Introduction.

The work described in this article is a continuation of the measurement of the vapor pressure of solutions by an improved static method devised by Frazer and Lovelace, which has been described in detail in former articles.<sup>2</sup> The chief difficulty encountered in making vapor pressure measurements by this method has been the complete removal of air from the solutions. In the former work it was attempted to rid the solutions of the final traces of air after they had been introduced into the system by an oft-repeated series of operations consisting in expanding the vapor phase into large bulbs, then trapping off the solution and evacuating the bulbs. The residual air pressure was determined by absorbing the water vapor in the bulbs with phosphorus pentoxide and reading the air pressure with a McLeod gage. At that time a period of overnight was thought to be necessary for the absorption of the water vapor, but at the beginning of the work described herein it was established that in this time an appreciable amount of air will be adsorbed on the pentoxide and upon the walls of the system, thus giving an erroneous idea of the amount of air present. It seemed quite certain that some of the former measurements had been inaccurate owing to traces of air, so more rigorous measures

<sup>1</sup> The experimental part of this paper is taken from the dissertation submitted by V. B. Sease to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Frazer and Lovelace, *THIS JOURNAL*, **36**, 2439 (1914); Lovelace, Frazer and Miller, *ibid.*, **38**, 515 (1916).