tion of both gelatinous hydrated iron and aluminum oxides, that of iron being more efficient.

2. A method suitable for application to the extraction of gallium from low grade ores has been suggested.

ITHACA, N. Y. RECEIVED OCTOBER 4, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Phenanthroline-Ferrous Ion. III. A Silver Reductor. The Direct Determination of Iron in the Presence of Vanadium[1]

BY GEORGE H. WALDEN, JR., LOUIS P. HAMMETT AND SYLVAN M. EDMONDS

Our potential measurements at high acidities[2] have shown that the oxidimetric determination of ferrous ion using the phenanthroline-ferrous ion indicator will not be interfered with by the presence of tetravalent vanadium provided that the titration be made in the presence of 5 molar sulfuric acid. To make the fullest practical application of this knowledge it is extremely desirable to have a method of reducing iron to the ferrous state and vanadium to the tetravalent state without further reduction of the vanadium and without reduction of tetravalent titanium, which shall be highly precise and at the same time as rapid and convenient as the Jones reductor.

The Silver Reductor

We have therefore developed a silver reductor which not only satisfies all of these requirements but also appears to be the cheapest and most convenient reductor for the determination of iron yet devised. The use of silver as a reducing agent in the determination of iron has never become popular, although it has been suggested.[3,4] This is probably due as much to the difficulty caused in the subequent titration by the chloride ion necessarily present as it is to the feeling that silver must be too expensive a reagent. Chloride ion does not, however, interfere in the titration of iron with ceric sulfate using the phenanthroline ferrous indicator, and the cost of the silver for a reductor is very small since less than an ounce is required.

To obtain a sufficiently low oxidation potential with silver it must be used in contact with a solution containing an ion of a highly insoluble silver salt. When the reduction is carried out in one molar hydrochloric acid, a satisfactory acid concentration, the oxidation potential is given by the e. m. f. of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl}\ 1\ M\ \mathrm{HCl} \parallel 1\ M\ \mathrm{HCl} \mid \mathrm{H_2(Pt)}$$

At 25° the potential[5] is 0.2329 volt, a value amply below that required for the quantitative reduction of ferric ion. We might expect, however, from a consideration of Fig. 1 of the previous paper[2] that in 1 M acid solution vanadium should be quantitatively reduced to V^{+++} at this potential (-0.53 volt referred to quinhydrone). Actually this reduction does not take place.[6] The reaction is probably very slow so that in the time required for the solution to pass through the silver reductor no measurable amount of the trivalent ion is formed.

Construction of the Reductor.—A reductor column of the usual Jones reductor type with an inside tube diameter of 2 cm. is recommended. Although the length of the column is immaterial it need be no longer than 12 cm. A reservoir bulb of 50–75 cc. capacity is most satisfactory. Approximately 18 g. of silver is precipitated from silver nitrate with copper. For this purpose a piece of electrolytic sheet copper about 10 cm. square is suspended in a solution of 29 g. of silver nitrate in 400 cc. of water to which has been added a few drops of nitric acid. The reaction is allowed to proceed with continuous vigorous mechanical stirring until a test shows the absence of silver ion in the solution. The silver is then washed by decantation with dilute sulfuric acid until most of the copper is removed. A small plug of glass wool is inserted in the lower end of the reductor column. The silver is suspended in water, the mixture poured into the reductor and the solution allowed to drain to the top of the silver column. The column is then rinsed with dilute sulfuric acid until a test shows the absence of copper in the wash liquid. Care should always be taken not to allow the liquid in the column to drain below the top of the silver.

---

[1] This article is based upon part of a dissertation submitted by Sylvan M. Edmonds to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington meeting of the American Chemical Society, March, 1933.

[2] THIS JOURNAL, **56**, 57 (1934).

[3] Hoenig, *Z. anal. Chem.*, **54**, 441 (1915).

[4] Edgar and Kemp, THIS JOURNAL, **40**, 777 (1918); Edgar, *ibid.*, **38**, 1297 (1916).

[5] Scatchard, *ibid.*, **47**, 641 (1925).

[6] In 6 M hydrochloric acid or in a solution five molar in sulfuric acid and also one molar in hydrochloric acid, there is partial reduction to the trivalent ion.

Although air introduces no blank, its presence in the column sometimes causes pockets to form that interfere with the proper flow of liquid. Should the column inadvertently be allowed to fill with air the latter may be readily removed by adding sufficient water to cover the silver and half fill the reservoir, stoppering the top of the reductor and vigorously shaking. In this way, the silver is suspended in the liquid. The column, when allowed to settle, will be free of all air bubbles. Although the silver is in a finely divided state, solutions flow readily through the reductor and suction is not required.

When a hydrochloric acid solution of ferric or vanadate ion is passed through the reductor the silver at the very top of the column darkens with the formation of silver chloride. A black ring is formed a few millimeters in depth and extending completely around the column. With further use, the dark area slowly extends down the column with a sharply defined boundary at a rate of about 3 or 4 mm. per determination (50 cc. of 0.05 *M* $FeNH_4(SO_4)_2$). The color of the coated silver serves as a striking indication of the behavior of the reductor. When the silver chloride extends over three-quarters of the length, the column is regenerated by filling with dilute sulfuric acid (0.1 *M*) and inserting a zinc rod into the reductor so that it touches the silver. This rapidly reduces the silver chloride to silver and thus the over-all process removes none of the metal from the column except the extremely small amount due to the solubility of silver chloride. Also, no foreign substance is introduced into the solution to be reduced except this trace of silver chloride.

Experiments showed that after 50 cc. of a 0.05 *M* $FeNH_4(SO_4)_2$ solution had been passed through the column, 150 cc. of 1 *M* hydrochloric acid was sufficient to remove the last traces of iron. The hydrochloric acid is added in several small portions, each being allowed to drain down to the top of the column before the next is added.

Blank Correction with the Silver Reductor.—To determine whether any blank correction was required with the silver reductor, 150 cc. of 1 *M* hydrochloric acid was allowed to flow through the column at the rate of 30 to 40 cc. per minute[7] and the solution then titrated with ceric sulfate. When the reductor was first used one washing with 150 cc. of acid introduced a blank of one or two drops of 0.1 *M* $Ce(SO_4)_2$. A second 150 cc. almost invariably contained so little reductant that a fraction of a drop of the ceric sulfate bleached the indicator. It was found most convenient to keep the reductor at all times filled with 1 *M* hydrochloric acid. In several months of use it was seldom that the first washing did not show the absence of any blank. Thus, unlike other reductors, the silver reductor introduces no blank correction and is always ready for use.

Determination of Iron

The method for the direct determination of iron in the presence of vanadium depends upon the reduction of both elements in the silver reductor followed by the titration of the iron with ceric sulfate after the solution has been treated with sufficient sulfuric acid to make it 5 molar. With phenanthroline-ferrous ion as the indicator, the end-point is sharp and vivid and occurs when the iron is quantitatively oxidized and the vanadium still entirely in the vanadyl stage.

Materials.—Ceric sulfate and ammonium vanadate solutions were those used in the work described in the previous paper.[2] A 0.1 *M* ammonium vanadate solution was also prepared by dissolving the required amount of the salt in warm water and then adding sufficient sulfuric acid to yield on proper dilution a solution containing one mole of the acid per liter. An approximately 0.1 *M* $FeNH_4(SO_4)_2$ solution in 0.2 *M* sulfuric acid was prepared from the C. P. salt. Chemical tests showed the absence of vanadium and titanium in this solution. It was standardized by reduction in the Jones reductor and titration with ceric sulfate using the phenanthroline-ferrous ion indicator. A 0.1 *M* titanium sulfate solution in 1 *M* sulfuric acid was prepared from C. P. $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ after the oxalate had been destroyed by evaporation to sulfur trioxide fumes; 0.017 *M* potassium dichromate and 0.1 *M* manganous chloride solutions were made up from the C. P. salts.

Method of Analysis.—Fifty cc. of a one molar hydrochloric acid solution of the sample was poured through the reductor at a rate of about 30 cc. per minute. The reduced solution was caught in a 600-cc. beaker. The column was then washed with 150 cc. of 1 *M* hydrochloric acid. The solution was treated with 200 cc. of 10 *M* sulfuric acid and the mixture thoroughly cooled. One drop of 0.025 *M* phenanthroline-ferrous ion was added and the solution titrated with 0.1 *M* $Ce(SO_4)_2$.

To test the procedure mixtures were analyzed containing in 50 cc., 25.00 cc. of $FeNH_4(SO_4)_2$ solution and 25 cc. of one of the following solutions: ammonium vanadate, titanium sulfate, potassium dichromate and manganous chloride. A mixture of 10.00 cc. of $FeNH_4(SO_4)_2$ solution and 10 cc. of each of the test solutions was also analyzed in the same way. The results are summarized in Table I.

Controls.—As a further check on the behavior of vanadium, titanium, chromium and manganese in the silver reductor and subsequent oxidation with ceric sulfate in five molar sulfuric acid, separate controls were made employing 50 cc. of a 1 *M* hydrochloric acid solution containing 25 cc. of each of the test solutions. The solutions were passed through the reductor and analyzed by the method given above. In all cases, a fraction of a drop of 0.1 *M* ceric sulfate, added to the final solution, bleached the indicator.

Effect of Small Amounts of Nitric Acid.[8]—As much as 0.2 g. of nitric acid in 50 cc. of 1 *M* hydrochloric acid when passed through the reductor introduces no substance capable of oxidation by ceric sulfate. The presence of this amount of nitric acid does not interfere in the quantitative reduction of iron and the subsequent titration with $Ce(SO_4)_2$ in either 1 *M* hydrochloric acid or 5 *M* sulfuric acid. In Table I are also listed the results of a series of test analyses of mixtures that contained in 50 cc., 25.00

---

[7] Since the rate of flow by gravity alone is considerably greater than this, the proper adjustment must be made by partially closing the stopcock.

[8] Nitric acid is reduced in the Jones reductor to very easily oxidizable substances so that the acid, if present, must be removed before the reduction. Actually, the complete removal of nitric acid by evaporation to sulfur trioxide fumes is difficult and very time-consuming.

cc. of $FeNH_4(SO_4)_2$ solution, 0.2 g. of nitric acid and sufficient hydrochloric acid to yield an acid concentration of 1 *M*.

Behavior of Molybdenum in the Silver Reductor.—When a dilute ammonium molybdate solution in 1 *M* hydrochloric acid is passed through the reductor, the molybdenum is reduced from the hexavalent state to the pentavalent, as is evidenced by the deep brown color of the reduced solution. This solution may then be oxidized back with ceric sulfate using the phenanthroline-ferrous ion indicator. The end-point is sharp but the ceric ion oxidation is slow so that when the end-point is neared several seconds must be allowed after the addition of each drop. The reduction and reoxidation with standard ceric sulfate yields values for the molybdenum that are only roughly quantitative. When widely different amounts of molybdenum as ammonium molybdate are taken for analysis, the titer varies by several per cent. in a very erratic fashion. It is evident that iron cannot be determined directly in the presence of molybdenum. Fortunately, the element is not a usual constituent of iron ores or minerals. Moreover, iron may be readily separated from molybdenum by a double ammonium hydroxide precipitation.[9] In such a separation vanadium is precipitated along with the iron.

Analyses of Standard Samples

Two iron ores, B. S. Nos. 27a and 29, and ferrovanadium, B. S. No. 61, were analyzed for iron. The ores (0.3-g. samples) were taken into solution in the usual way by heating with hydrochloric acid and fusing the insoluble residue with sodium carbonate. The combined hydrochloric acid solution was evaporated to 10 cc., diluted to 50 cc. and then passed through the reductor as described above and the final titration with standard ceric sulfate made in 5 *M* sulfuric acid solution.

In the analysis of ferrovanadium a 0.3-g. sample was taken into solution with hydrofluoric acid and sulfuric acid. The mixture was evaporated to sulfur trioxide fumes, diluted to 400 cc., heated to boiling and concentrated ammonium hydroxide added until alkaline and then 40 cc. in excess. The precipitate was washed twice with hot dilute ammonia and redissolved in 1 : 1 hydrochloric acid. After dilution to 400 cc. the iron and vanadium were reprecipitated in the same way and the precipitate washed with hot dilute ammonia. The first washing, after acidification, was tested for molybdenum with potassium thiocyanate and zinc and showed the absence of the element. The precipitate was dissolved in 1 : 1 hydrochloric acid, the solution evaporated to 10 cc., diluted to 50 cc. and the iron determined as above.

The results of these analyses are given in Table II together with the corresponding certificate values.

Application of the Silver Reductor to the Determination of Small Amounts of Iron.—The method of analysis that has been devised for the determination of large amounts of iron is directly applicable to the precise estimation of much smaller quantities provided 0.01 *M* ceric sulfate is employed for the final titration. A blank, measured as the volume of 0.01 *M* $Ce(SO_4)_2$ required to bleach completely the indicator color in 200 cc. of 1 *M* hydrochloric acid that had been previously passed through the reductor, amounts to two- to three-tenths of a cc. This represents the indicator blank plus that due to the traces of iron in the C. P. hydrochloric acid. In Table III are given the results of two series of test analyses where the test mixtures were analyzed by exactly the same method that has been described above with the exception that standard 0.01 *M* $Ce(SO_4)_2$ was used for the final titration instead of the 0.1 *M* reagent.

Table I

0.1 *M* $FeNH_4(SO_4)_2$, cc.	Soln. added		No. of detns.	Molarity of $FeNH_4(SO_4)_2$	Av. dev., pts. 1000
25			6	0.09716	0.8
25	0.05 *M* NH_4VO_3	25 cc.	6	.09716	.9
25	0.1 *M* NH_4VO_3	25 cc.	3	.09716	.2
25	0.1 *M* $Ti(SO_4)_2$	25 cc.	6	.09724	.4
25	0.017 *M* $K_2Cr_2O_7$	25 cc.	6	.09710	.5
25	0.1 *M* $MnCl_2$	25 cc.	6	.09726	1.2
10	0.1 *M* NH_4VO_3, $Ti(SO_4)_2$, $MnCl_2$; 0.017 *M* $K_2Cr_2O_7$ 10 cc. each		6	.09718	2.0
25	HNO_3, 0.2 g.		3	.09704	1.2
25	Jones Reductor Standardization		5	.09712	0.6

Table II

Sample	% Iron (certificate)	% Iron (found)	No. of detns.	Av. dev., pts. 1000
B. S. Iron Ore 27a	68.57	68.55	3	0.8
B. S. 29; Magnetite	55.75	55.71	3	1.3
B. S. 61; Ferrovanadium	52.8	52.81	2	0.8

Table III

V present, mg.	Iron (taken), mg.	Iron (found), mg.	No. of detns.	Av. dev., pts. 1000
0	13.57	13.54	4	1.2
13	13.57	13.56	3	0.7

Summary

1. A new reductor employing silver is described. Iron is quantitatively reduced in this reductor while vanadium is reduced solely to the

---

(9) *U. S. Bureau of Mines, Bull.* 212 (1923).

tetravalent state. The silver reductor offers many advantages over other reductors.

2. A method has been devised for the direct determination of iron in the presence of vanadium, titanium, chromium and manganese.

NEW YORK, N. Y. RECEIVED OCTOBER 7, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Vapor–Liquid Equilibria in the System Nitrogen–Water

BY ARTHUR W. SADDINGTON AND NORMAN W. KRASE

Introduction

Within recent years an increased amount of fundamental data on systems under pressure have been collected. Several papers upon the solubility relations of gases at high pressures in various liquids have appeared.[1] Among these is the work of Goodman and Krase,[2] who pointed out the existence at constant pressure of a minimum solubility point for nitrogen in liquid water at about 80°. Henry's law "constants" showed a wide variation and no definite trend. The most recent work has been reported by Wiebe[3] and his collaborators on nitrogen–water, hydrogen–water and nitrogen–liquid ammonia systems. These results for the first named equilibria did not agree closely with those of Goodman and Krase, but the evidence in favor of a minimum solubility point was further strengthened. Henry's law was of little value in predicting these results.

At various times reports[4] have appeared dealing with the vapor content of compressed gases in contact with the liquid phase. Recently Bartlett[5] published results showing the concentration of water vapor in compressed hydrogen, nitrogen and a 3:1 mixture of these gases in equilibrium with condensed water. As usually had been found in previous work, the water vapor concentration was much larger than that calculated by the ordinary methods. Poynting's relation did not predict the effect of pressure upon this system and the magnitude of the variation depended upon the nature of the indifferent gas. In the following year, J. J. Van Laar[6] using Bartlett's data demonstrated that his complex equation of state for gas mixtures in equilibrium with a condensed phase was able to predict the effect of the compressed gas upon the vapor pressure of water. Similar calculations have been made by Gillespie and his collaborators with the Beattie–Bridgeman equation of state and good agreement with experimental results was obtained where constants were available. A thermodynamic treatment of gas mixtures was given and it was shown that Dalton's law, the Gibbs–Dalton law and the Lewis and Randall fugacity rule were only approximations at elevated pressures. A method for the numerical calculations of the equilibrium pressures of a gas mixture was outlined.[7]

The various work mentioned above gives an incomplete understanding of the equilibrium relationships of the nitrogen–water system. In the present work an effort was made to extend this knowledge with the idea of bringing to light any basic quantitative laws. Measurements of gaseous and liquid phase compositions have been extended to about 240° at pressures to 300 atmospheres. Incidentally, an apparatus was designed capable of extending such researches to other systems.

A possible quantitative solution of the problem, however, seems to rest upon density measurements of both liquid and vapor phases. For example, the application of Poynting's relation to the gas phase depends upon the evaluation of β, the compressibility coefficient of the liquid. Actually a limited amount of data for pure water only is available. The method evidently falls into considerable error at this point for the compressibility of a solution of gas in a liquid cannot

---

(1) W. Sander, *Z. physik. Chem.*, **78**, 514 (1912); Frolich, *et al.*, *Ind. Eng. Chem.*, **23**, 548 (1931); V. Ipatiev, *et al.*, *Ber.*, **65B**, 568 (1932); B. Zuskend, *et al.*, *Z. anorg. allgem. Chem.*, **200**, 279 (1931).

(2) J. Goodman and N. W. Krase, *Ind. Eng. Chem.*, **23**, 401 (1931).

(3) R. Wiebe, V. Gaddy and C. Heins, *Ind. Eng. Chem.*, **24**, 823 (1932); **24**, 927 (1932); THIS JOURNAL, **55**, 947 (1933); R. Wiebe and T. Tremearne, *ibid.*, **55**, 975 (1933).

(4) H. Braune and F. Strassman, *Z. physik. Chem.*, **143A**, 225 (1929); A. Eucken and F. Bresler, *ibid.*, **134**, 230 (1928); A. Larson and C. Black, THIS JOURNAL, **47**, 1015 (1925); Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 768 (1924); I. McHaffie, *Phil. Mag.*, [VII] 1, 561 (1926).

(5) E P. Bartlett, THIS JOURNAL, **49**, 65 (1927).

(6) J. J. Van Laar, *Z. physik. Chem.*, **137**, 421 (1928); **145**, 207 (1929).

(7) E. Lurie and L. J. Gillespie, THIS JOURNAL, **49**, **1146** **(1927)**; L. J. Gillespie, *Phys. Rev.*, **36**, 121 (1930); H. T. Gerry and L. J. Gillespie, *ibid.*, **40**, 269 (1932).