By addition of these three free energy equations there results

$$Se(s) + 2\ O_2(g) + H_2(g) = H^+ + HSeO_4^- + 107710 \text{ cal.} \qquad (4)$$

That is, $\Delta F_{298} = -107710$ cal. for $HSeO_4^-$ (or for one formula weight of aqueous H_2SeO_4).

Summary

The equilibrium conditions of the reactions

$$Cl_2(g) + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Cl^- \text{ and}$$
$$Br_2 + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Br^-$$

were determined at 25°. The values of the corresponding equilibrium constants were found to be 1.42×10^9 and 0.88, respectively. From each of these constants and known thermodynamic data the reduction potential of the reaction $H_2SeO_3 + H_2O\ (1) = 3H^+ + HSeO_4^- + 2E^-$ was calculated to be -1.088 volts. From this value and existing free energy data, the free energy (ΔF) at 25° of $HSeO_4^-$ (or of one formula weight of aqueous H_2SeO_4) was calculated to be $-107,710$ cal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. IV. THE POTENTIOMETRIC TITRATION OF VANADYL ION ALONE OR IN THE PRESENCE OF FERRIC AND CHROMIC IONS. NOTE ON THE STABILITY OF VANADYL SOLUTIONS[1]

BY N. HOWELL FURMAN

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This communication reports further progress in a study of the direct uses of standard ceric sulfate solutions in volumetric analysis. The apparatus and technique have been described in a former paper.[2]

Experimental

Approximately 0.05 *M* solutions of ceric sulfate in dilute sulfuric acid were prepared and standardized by potentiometric titration with oxalic acid (exactly 0.05 *N*) that had been prepared by dissolving pure, dry sodium oxalate in water acidified with 10 cc. of sulfuric acid (sp. gr. 1.84) per liter.

Note on the Stability of Vanadyl Solutions.—During the course of the investigation observations were made on the stability of vanadyl solutions. The author's findings are in agreement with the conclusions of Stout and Whitaker[3] who stated that vanadyl solutions are stable for six months or more.

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[1] Presented at the spring meeting of the American Chemical Society at St. Louis, Missouri, April, 1928.

[2] Furman, THIS JOURNAL, **50,** 755 (1928).

[3] Stout and Whitaker, *Ind. Eng. Chem.*, **20,** 210 (1928).

Portions of ammonium metavanadate of C.P. grade weighing between 11.7 and 13.8 g. were dissolved in sulfuric acid (30 cc. of concd. acid of sp. gr. 1.84 and about 100 cc. of water). After reduction each solution was diluted to 2 liters. Two methods of reduction to the vanadyl state were employed: (a) the familiar sulfur dioxide method for the preparation of solutions free from chloride;[4] and (b) reduction by shaking with mercury after the addition of 15 cc. of hydrogen chloride of sp. gr. 1.18–1.19.[5]

Weighed portions of the vanadyl solutions were titrated with potassium permanganate which had been standardized against pure sodium oxalate. All end-points were determined potentiometrically.[6] The stability of the vanadyl solutions is evident from the following figures, which are in each instance averages of two concordant determinations.

STABILITY OF VANADYL SULFATE SOLUTIONS

Time, weeks	0	2	5	8	15	65
Normality	0.05739	0.05740	0.05737	0.05740	0.05730	0.05730

The solution that contained hydrochloric acid was equally stable. At the outset its normality was 0.05695 and after sixty-five weeks the value was 0.05683. The solutions were in clear glass bottles that were exposed to diffuse sunlight for six months; during the balance of the period the solutions were in a dark cupboard. A 0.04914 *N* solution free of chloride was used in a portion of the work that was done in Zürich, Switzerland.

Potentiometric Study of the Ceric–Vanadyl Reaction

Measured portions of the vanadyl solutions were titrated with ceric sulfate. All end-points were determined potentiometrically, using a burnished platinum spiral (No. 28 B. and S. gage wire) 6–8 cm. long as indicator electrode and a *N* calomel half-cell as reference electrode. The platinum wire was immersed in chromic acid cleaning solution when not in use. Accurate results are obtained when the vanadyl solution is at room temperature, but it requires several minutes for the potential to become constant in the neighborhood of the end-point. At temperatures between 50 and 60 ° the rate of reaction is rapid and the titration is as satisfactory as the permanganate titration is at 80 °. The break in potential at the end-point per 0.05 cc. of 0.05 *N* ceric solution amounts to 0.025 to 0.1 volt when the initial volume of the solution lies between 200 and 25 cc. Typical titration graphs are shown in Fig. 1, Curves 1 and 2. Representative results are presented in the following table.

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[4] For details see Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1919**, 5th ed., Vol. II, p. 636.

[5] Method of McCay and Anderson, THIS JOURNAL, **44,** 1018 (1922).

[6] A summary of the literature relating to the potentiometric titration of vanadium is to be found on p. 244 of "Potentiometric Titrations," Kolthoff and Furman, published by John Wiley and Sons, Inc., New York.

TABLE I

POTENTIOMETRIC TITRATION OF VANADYL SOLUTIONS WITH CERIC SULFATE

A. Reaction at room temperature. 0.05735 *N* vanadyl and 0.0547 *N* ceric solution

Vanadyl soln., cc......	25	25	10	10	25
Ceric soln. used, cc....	26.15	26.19	10.48	10.49	26.22
Ceric soln. calcd., cc...	26.21	26.21	10.48	10.48	26.21

B. Reaction at 50–60°. Nos. 1–4, vanadyl sulfate 0.04914 *N*, ceric solution 0.05655 *N*. Nos. 5–6, vanadyl chloride 0.05683 *N*, ceric solution 0.05455 *N*

	1	2	3	4	5	6
Vanadyl soln., cc......	25	25	25	50	25	25
Ceric soln. used, cc....	21.73	21.70	21.68	43.39	26.03	26.06
Ceric soln. calcd., cc...	21.71	21.71	21.71	43.42	26.05	26.05

C. Reaction at 50–60°. Trivalent iron and chromium present. Nos. 1–3, 0.04914 *N* vanadyl sulfate, 0.05655 *N* ceric. Nos. 4–6, 0.05735 *N* vanadyl sulfate, 0.04824 *N* ceric. Nos. 7–8, 0.05683 *N* vanadyl chloride, 0.04824 *N* ceric

	1	2	3	4	5	6	7	8
Vanadyl soln., cc......	25	25	50	25	25	10	25	10
Ceric soln. used, cc....	21.73	21.71	43.46	29.70	29.75	11.87	29.51	11.76
Ceric soln. calcd., cc...	21.71	21.71	43.42	29.71	29.71	11.89	29.45	11.78
Iron present, g........	0.14	0.14	1.64	1.14	2.28	1.14	1.14	1.14
Chromium present, g..	.086	.086	0.086	0.35	0.70	0.35	0.35	0.35

The initial volumes ranged from 25 to 125 cc. Near the end-points the ceric solution was added in drops that averaged 0.025 cc. Chromic solutions were prepared by exact reduction of bichromate with ferrous sulfate (potentiometric end-point). It was found possible to control the process of reduction of a large quantity of bichromate so exactly that 50 cc. of the reduced solution (containing 1.14 g. of iron and 0.35 g. of chromium) when treated with one drop of 0.05 *N* ferrous sulfate showed a change of 0.05 volt in oxidation-reduction potential; with one drop of 0.05 *N* ceric solution there was a rise of 0.2 volt.

At temperatures between 50 and 60° vanadyl salts are, therefore, selectively oxidized by ceric sulfate in the presence of large quantities of both chromic and ferric salts. Under these conditions the titration graph is not appreciably modified (see Curve 3, Fig. 1).

The small quantities of hydrochloric acid that were present in one of the vanadyl solutions were without influence upon the accuracy of the method.[7]

Simultaneous Determination of Iron and Vanadium.—The titration of mixtures of ferrous and vanadyl solutions was studied because this problem enters into most of the practical methods for the determination of

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[7] While this article was in preparation the author saw in manuscript, papers by H. H. Willard and Philena Young. These investigators have also studied the use of ceric sulfate as a volumetric reagent and have made a study of the effect of large quantities of hydrochloric acid in certain titrations. It would appear from their results that even very large quantities of hydrochloric acid are without effect. The author has not studied this question in detail, but found in one titration that 10 cc. of concd. HCl (sp. gr. 1.18–1.19) per 100 cc. did not cause any error in the titration of a vanadyl solution.

vanadium in natural and synthetic products. Measured quantities of ferrous and vanadyl solutions were mixed and titrated potentiometrically with ceric solution. The first inflection (complete oxidation of iron) was determined at room temperature.[8] The solution was heated to 50–60° and the titration was continued until the end-point of the oxidation of the vanadyl salts was found. The results are accurate for both iron and vanadium. Curves 4 and 5, Fig. 1, are representative titration graphs.

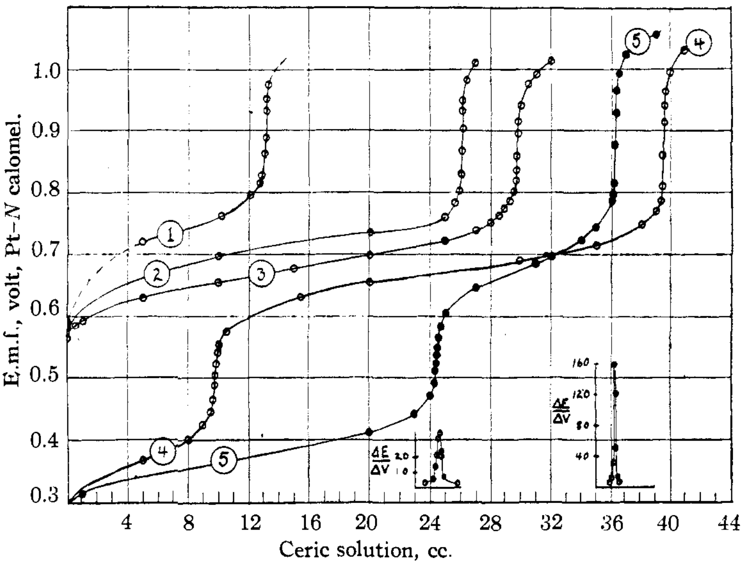

Fig. 1.—Titration of vanadyl and ferrous solutions with ceric sulfate. Curve 1, 25 cc. and Curve 2, 50 cc. of 0.05735 *N* vanadyl sulfate titrated with 0.1092 *N* ceric solution. Curve 3, 25 cc. of 0.05735 *N* vanadyl solution mixed with 100 cc. of a solution containing 2.28 g. of iron and 0.7 g. of chromium and titrated with 0.04824 *N* ceric solution. Curve 4, 10 cc. of 0.04724 *N* ferrous and 25 cc. of 0.05735 *N* vanadyl sulfate titrated with 0.04824 *N* ceric solution. Curve 5, 25 cc. of 0.04764 *N* ferrous and 10 cc. of 0.05683 *N* vanadyl chloride solution titrated with 0.04857 *N* ceric solution. (Values for $\Delta E/\Delta V$ have been multiplied by 100 in constructing the graph.)

It was found advisable to plot the difference quotient ($\Delta E/\Delta V$ where ΔE is the e.m.f. difference per amount of reagent ΔV) against cc. of reagent in order to determine the first inflection. The second inflection is so sharp that it is rarely necessary to plot the values. The results are assembled in Table II.

As a further test of the accuracy of the titration with ceric sulfate of vanadyl salts in the presence of iron, chromium and other components of

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[8] E. Müller and A. Flath, *Z. Elektrochem.*, **29**, 500 (1923), found that the inflection was much sharper at room temperature in the permanganate titration.

Table II

Potentiometric Titration of Mixtures of Ferrous and Vanadyl Salts

	1	2	3	4	5	6	7
Ceric used for Fe^{II}, cc.	9.03	24.49	24.54	24.50	24.48	9.80	9.75
Ceric calcd. for Fe^{II}, cc.	8.99	24.52	24.52	24.52	24.52	9.79	9.79
Ceric used for V^{IV}, cc.	25.99	29.31	11.66	11.84	11.85	29.72	29.67
Ceric calcd. for V^{IV}, cc.	26.05	29.25	11.70	11.87	11.87	29.71	29.71

The vanadyl chloride solution, 0.05683 *N*, was used in determinations 1–3, and 0.05735 *N* vanadyl sulfate in Nos. 4–7. The ceric solutions were: 0.05455 *N* (No. 1), 0.04857 *N* (Nos. 2–3), and 0.04824 *N* (Nos. 4–7).

ferro alloys, the method was applied to U. S. Bureau of Standards ferrovanadium No. 61.

A large sample (3.2768 g.) was brought into sulfuric acid solution. (Nitric acid was used and later expelled. The silica was expelled with hydrofluoric acid and the residue was treated with nitric and sulfuric acids.) The solution was made uniform after dilution to 500 cc. Twenty-five cc. portions of the solution were treated in the following ways.

1. The solution was reduced with a slight excess of ferrous sulfate, using the potentiometric method as indicator. Upon titration with standard ceric solution, the distance between the first inflection (room temperature) and the second (50–60°) gave a measure of the vanadium present. Found: 18.40, 18.30, 18.33 cc. of 0.05455 *N* ceric solution, corresponding to 31.25, 31.08, 31.13% of vanadium (certificate value, 31.15% of vanadium).

2. The solutions were oxidized with persulfate in the presence of silver nitrate. The silver was precipitated and the permanganic acid was reduced upon addition of sodium chloride and a little hydrochloric acid. The excess of $K_2S_2O_8$ was decomposed by boiling.[9] The chromic and vanadic acids were determined together by titration with ferrous sulfate that had been freshly standardized against ceric sulfate. The potentiometric method was used. It was not necessary to remove the silver chloride before titration. The vanadium was then determined by titration with ceric sulfate. Found: Cr, 0.56 and 0.53%; V, 31.16 and 31.20%; certificate values; Cr, 0.52, V, 31.15%.

Further studies of the direct applications of ceric sulfate in volumetric analysis are in progress in this Laboratory.

Acknowledgment.—The author wishes to make grateful mention of the fact that he completed a portion of the material here presented while working as guest in the chemical laboratory of the Eidgenössische Technische Hochschule, Zürich, Switzerland.

Summary

Dilute vanadyl chloride or sulfate solutions (containing free acid) have been shown to be stable for at least a year.

The potentiometric titration of vanadyl solutions with standard ceric sulfate gives accurate results in simple solutions or in the presence of large quantities of ferric and chromic salts. The vanadyl solution should be heated to 50–60°.

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[9] For details see Lundell, Hoffman and Bright, *Ind. Eng. Chem.*, **15,** 1064 (1923).

The titration of mixtures of ferrous and vanadyl solutions yields correct results for both iron and vanadium. This process finds practical application in the direct determination of vanadium and the indirect determination of chromium in ferro alloys.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE STRENGTH OF ACETAMIDE AS AN ACID

BY G. E. K. BRANCH AND J. O. CLAYTON

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Introduction

The determination of the strength of a very weak acid, such as acetamide, through measurements of the electrical conductivity of a solution containing both the weak acid and a strong base, necessitates a knowledge of the equivalent conductivity of the resulting salt. This cannot be obtained directly. Consequently measurements must be made under conditions in which the degrees of neutralization of the base differ, and the resulting equations solved for both the equivalent conductivity of the salt and its hydrolysis constant. Such a solution assumes that neither the mobilities of the ions nor the hydrolysis constant of the salt change when the conditions are varied. It is therefore necessary to correct for or avoid changes in these quantities.

Variation in the concentration of total electrolyte will produce marked changes in the mobilities of the ions and in the hydrolysis constant. Consequently our measurements were made at a constant and low value of the concentration of total electrolyte. Since the salt and the base are strong electrolytes of the same valence type, and are both dilute, variation of the ratio between salt and base will lead to negligible errors.

It did not seem possible to correct in any way for the effect of the change of the concentration of acetamide on the hydrolysis constant. This can be avoided by the use of very dilute solutions of the weak acid, but this cannot be done in the case of acetamide, as appreciable reaction between it and a base can only be obtained with concentrated solutions.

The influence of acetamide on the mobilities of the ions cannot be neglected. This difficulty was overcome by the use of an approximate correction formula. The nature and derivation of this formula are discussed later.

Acetamide is so weak an acid that in aqueous solution containing only small concentrations of base its concentration is always very large in comparison with that of its salt. Consequently the presence of very small traces of impurities which either react with a base or are themselves