Table V also gives the values of f_3'/f_4' computed from equations (24) and (25). It shows, as is to be expected on the theoretical grounds, that the activity coefficient of the trivalent vanadic ion, V^{+++}, is much more sensitive to the ionic strength than is the activity coefficient of the divalent vanadyl ion, VO^{++}.

However, this involved extrapolation may create an uncertainty amounting to millivolts and, therefore, the final results will be expressed more conservatively than the equations given above.

For the cell $\overset{-}{\text{Pt}}$, $VOSO_4$ (c_4) + $^1/_2$ $V_2(SO_4)_3$ (c_3) + H_2SO_4 (c_1), H_2SO_4 (c_1), H_2, $\underset{+}{\text{Pt}}$ and the corresponding cell reaction $V^{+++} + H_2O = VO^{++} + {}^1/_2\ H_2$ the standard potential is

$$\text{At } 25°\text{: } {}_{\text{H}}E_0^{\text{v}} = -0.33_7 \text{ volt}$$

$$\text{At } 0°\text{: } {}_{\text{H}}E_0^{\text{v}} = -0.36_1 \text{ volt}$$

The minus sign means that, at concentrations so chosen that the activities are all unity, the reaction actually tends to go in the opposite direction, namely, $VO^{++} + H^+ + 1^1/_2\ SO_4^{=} + {}^1/_2\ H_2 = V^{+++} + 1^1/_2\ SO_4^{=} + H_2O$ and for this reaction we compute the standard free energy, the entropy and the heat of reaction, and the equilibrium constant, $K = \alpha_4\alpha_{\text{H}}P_{\text{H}_2}/\alpha_3\alpha_{\text{w}}$ (at the concentrations for which the activities are all unity) which are shown in Table VI.

TABLE VI

THERMODYNAMIC QUANTITIES FOR THE REACTION $VO^{++} + H^+ + 1^1/_2 SO_4^{=} + {}^1/_2 H_2 = V^{+++} + 1^1/_2 SO_4^{=} + H_2O$

	25°C.	0°C.
ΔF^0 kilojoules	-32.5	-34.8
ΔF^0 kcal.	-7.7_8	-8.3_2
ΔS joules/deg.	-9_1	
ΔS cal./deg.	-2_2	
ΔH^0 kilojoules	-59.6	
ΔH^0 kcal.	-14.2	
$K = \alpha_4\alpha_{\text{H}}P_{\text{H}_2}/\alpha_3\alpha_{\text{w}}$	$1.9_8 \times 10^{-6}$	$0.21_9 \times 10^{-6}$

Summary

1. The oxidation–reduction potential of tetravalent–trivalent vanadium ions has been determined by potential measurements at 25 and 0° on cells of the type $\overset{-}{\text{Pt}}$, $VOSO_4$ (c_4) + $^1/_2$ $V_2(SO_4)_3$ (c_3) + H_2SO_4 (c_1); H_2SO_4 (c_1), Hg_2SO_4, $\underset{+}{\text{Hg}}$.

2. Combining these data with measurements by Harned and Hamer on the cell $\overset{-}{\text{Pt}}$, H_2, H_2SO_4, Hg_2SO_4, $\underset{+}{\text{Hg}}$, we have estimated the standard potential for a cell dependent on the cell reaction $V^{+++} + H_2O = VO^{++} + 2H^+ + {}^1/_2H_2$, and the equilibrium constant of this reaction.

$${}_{\text{H}}E_0^{\text{v}} = -0.33_7 \text{ volt at } 25°$$

$${}_{\text{H}}E_0^{\text{v}} = -0.36_1 \text{ volt at } 0°$$

$$K = \frac{\alpha_4\alpha_{\text{H}}P_{\text{H}2}}{\alpha_3\alpha_{\text{w}}} = 1.9_8 \times 10^{-6} \text{ at } 25°$$

$$K = \frac{\alpha_4 x_{\text{H}}P_{\text{H}2}}{\alpha_3\alpha_{\text{w}}} = 0.21_9 \times 10^{-6} \text{ at } 0°$$

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 13, 1944

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Electrochemical Studies on Vanadium Salts. II. The Hydrolysis of Vanadyl Sulfate and Vanadic Sulfate Solutions[1]

BY GRINNELL JONES AND WENDELL A. RAY

During the work on the vanadyl–vanadic oxidation–reduction potential described in the preceding paper a knowledge of the extent of hydrolysis of solutions of vanadyl sulfate ($VOSO_4$) and of vanadic sulfate ($V_2(SO_4)_3$) was needed. It is well known that the tetravalent vanadium sulfate is completely hydrolyzed in aqueous solutions to form the vanadyl sulfate, $VOSO_4$. Solutions of the latter salt are acidic indicating that the vanadyl ion, VO^{++}, is further hydrolyzed. The trivalent vanadium ion, V^{+++}, is much less hydrolyzed than the tetravalent vanadium ion, V^{++++}, although some authors assign a formula VO^+ to the trivalent vanadium ion. On the other hand, solutions of vanadic sulfate are more acidic than solutions of vanadyl sulfate. The experiments recorded below were carried out in order to obtain definite information as to the *p*H of solutions of these salts over a wide range of concentration.

The salts designated below as Sample A were prepared by the method described in the preceding paper. However, since these salts were crystallized from a solution containing excess of sulfuric acid, it was feared that there might be sufficient excess of sulfuric acid present in spite of thorough washing to cause a significant error in the *p*H measurements. Therefore, a second sample of each salt, designated as Sample B, was prepared by recrystallization of Sample A from water, followed by centrifugal drainage and washing with alcohol and ether.

Analyses of these salts gave the following results: *Vanadyl Sulfate:* Sample A, V (tetravalent), 23.50, 23.43; SO_4, 44.21, 44.26. Sample B: V, 23.47, 23.45. Calcd. for $VOSO_4 \cdot 3H_2O$: V, 23.47; SO_4, 44.26. *Vanadic Sulfate:* Sample A, V (tri-

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(1) Original manuscript received November 12, 1943.

valent), 18.00, 17.99; SO_4, 50.65, 50.56. Sample B was not analyzed. Calcd. for $V_2(SO_4)_3 \cdot 10H_2O$: V, 17.87; SO_4, 50.54. The results indicate a slight loss of water of crystallization.

As will be seen for the data given below, there was no significant difference between the *p*H of the solutions made from the original samples and those recrystallized from water.

The concentrations, *c*, are expressed in moles of vanadium per liter, *i.e.*, in terms of $VOSO_4$, or of $^1/_2V_2(SO_4)_3$ per liter. The *p*H measurements were made at 25.0° with a Coleman *p*H electrometer using a glass electrode. The instrument was calibrated by the use of a 0.05 molar potassium acid phthalate solution which was assumed to have a *p*H of 4.00 in accordance with the measurements of MacInnes, Belcher and Shedlovsky.[2] The results are shown in Table I.

In the case of vanadyl sulfate a plot of *p*H against log *c* gives a curve which has a slight concavity toward the log *c* axis, especially at the ends. However, within the range $c = 0.0002$ and $c = 0.20$, the straight line whose equation is $pH = 2.58 - 0.543 \log c$, agrees with the observed values with an average deviation of only 0.014 *p*H, which is within the limit of error of the observations. This equation may, therefore, be used for interpolations but it cannot be used safely for extrapolation. The observed values of *p*H at $c = 0.0001$, and at $c = 0.25$ and 0.5 are less than those computed from this equation by more than the probable error of the data. The hydrolysis of vanadyl sulfate is so small that even 0.02 molar sulfuric acid should repress it substantially completely.

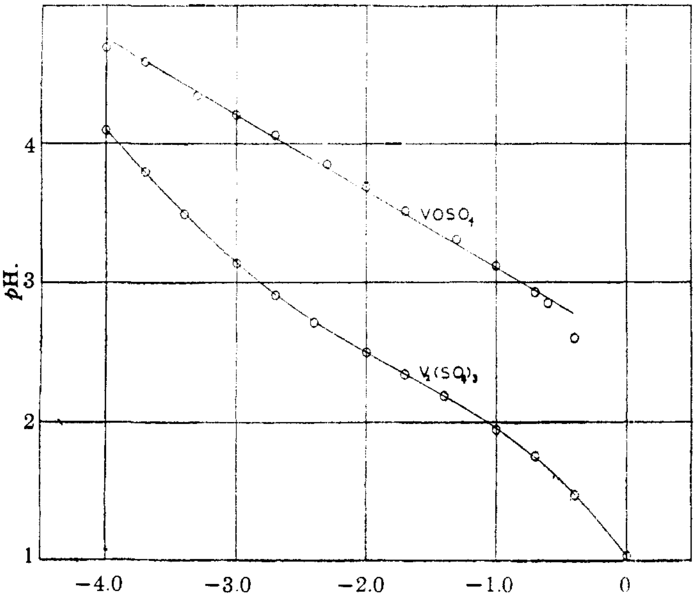

Fig. 1.

TABLE I

*p*H OF SOLUTIONS OF VANADYL SULFATE AND OF VANADIC SULFATE

Concn., *c*	$VOSO_4$ Sample A	$VOSO_4$ Sample B	$^1/_2(V_2(SO_4)_3)$ Sample A	$^1/_2(V_2(SO_4)_3)$ Sample B
1.000	..	..	1.03	..
0.500	2.60	..	..	..
.400	..	..	1.47	..
.250	2.85	..	..	..
.200	2.93	2.92	1.75	..
.100	3.12	3.11	1.94	1.94
.050	3.31	3.30	..	..
.040	..	..	2.18	2.19
.020	3.51	3.51	2.33	2.35
.010	3.69	3.68	2.49	2.50
.005	3.85	3.84	..	..
.004	..	..	2.70	2.72
.002	4.06	4.04	2.91	2.92
.001	4.22	4.20	3.13	3.14
.0005	4.35	4.35	..	..
.0004	..	..	3.49	3.49
.0002	4.60	4.60	3.79	3.79
.0001	4.70	4.70	4.07	4.10

A similar plot of the data for $V_2(SO_4)_3$ is clearly not a straight line but has a reverse curvature with a point of inflection at about $c = 0.02$.

These results show that although the hydrolysis of vanadic sulfate is substantial, it is not sufficient to support the view that trivalent vanadium exists in solution mainly as the VO^+ ion as has been suggested by Gerke,[3] who writes vanadic sulfate as $(VO)_2SO_4$.

Thus for a tenth formal solution of vanadic sulfate ($c = 0.1$) the *p*H is 1.94. If the hydrolysis of the vanadic ion were complete in accordance with the equation, $V^{+++} + H_2O + {}^3/_2SO_4^{=} = VO^+ + 2H^+ + {}^3/_2SO_4^{=}$, the solution would really be 0.1 molar in sulfuric acid plus 0.1 molar in $(VO^+ + {}^1/_2SO_4^{=})$. A 0.1 molar solution of pure sulfuric acid (*i.e.*, free from admixed vanadium salts) would have a *p*H of 0.99. If we let α_H' represent the activity of the hydrogen ion in the vanadium solution and α_H the activity of the hydrogen ion in the acid of the concentration which would be formed by complete hydrolysis, then we have for 0.1 molar solution

$$pH = -\log \alpha_H' = 1.94$$
$$pH = -\log \alpha_H = 0.99$$
$$\log \alpha_H'/\alpha_H = -0.95$$
$$\alpha_H'/\alpha_H = 0.11$$

For a 0.001 molar solution the corresponding figures are

$$pH = -\log \alpha_H' = 3.13$$
$$pH = -\log \alpha_H = 2.79$$

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[2] D. A. MacInnes, D. Belcher and T. Shedlovsky, THIS JOURNAL, **60**, 1099 (1938).

[3] R. H. Gerke, *Chem. Rev.*, **1**, 390 (1925); "Intern. Crit. Tables," **VI**, 332 (1929).

$$\log \alpha'_H/\alpha_H = -0.44$$
$$\alpha'_H/\alpha_H = 0.36$$

We cannot evaluate quantitatively the influence of the presence of the V^{+++} and VO^+ ions on the activity coefficients of the hydrogen ion and therefore cannot compute the concentration of the hydrogen ion produced by hydrolysis or the degree of hydrolysis and the relative amounts of the V^{+++} and VO^+ ions. However, the data indicate that the concentration of the V^{+++} must be many times that of the VO^+ ion.

Some attempt has been made to compute hydrolysis constants from these data but the computed "constants" showed a systematic trend, presumably due to the unreliability of the assumptions which were made as to the activity coefficients. These computations are therefore not published at this time.

Summary

*p*H measurements have been made at 25° on solutions of vanadyl sulfate, $VOSO_4$, and on vanadic sulfate, $V_2(SO_4)_3$, which show that these solutions are acid owing to hydrolysis.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 13, 1944

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Electrochemical Studies on Vanadium Salts. III. The Vanadic–Vanadous Oxidation-Reduction Potential[1]

BY GRINNELL JONES AND JOHN HENRY COLVIN

The earlier papers of this series[1a] describe measurements of the vanadyl (IV)–vanadic (III) oxidation–reduction potential, and of the hydrolysis of vanadyl sulfate and vanadic sulfate solutions. In the present paper the work is extended by similar methods to the measurement of the vanadic (III)–vanadous (II) oxidation–reduction potential.

The history of the researches on the vanadic–vanadous potential closely parallels that for the vanadyl–vanadic potential. The earliest investigator was Rutter,[2] who studied the cell

$$\overset{-}{\mathrm{Pt}},\ {}^1/_2V_2(SO_4)_3 + VSO_4 + \underset{+}{H_2SO_4}\ (0.25\ \text{molar}),$$

H_2SO_4 (0.25 molar), Hg_2SO_4, Hg. The sum of the divalent and trivalent vanadium was kept at 0.1 molar but the ratio varied from equality to a ratio of 1:3. His measurements in which divalent and trivalent vanadium were both 0.05 molar give the value $E_0 = +0.210$ referred to the Nernst zero point of the potential scale.

Abegg, Auerbach and Luther (1911) in their compilation of standard potentials give +0.2 for this potential and this figure is given unchanged by Drucker[3] in his second supplement to this work.

Gerke[4] in his compilation for the "International Critical Tables" (1929) gives $VSO_4 + H_2O\ (l) = {}^1/_2(VO)_2SO_4 + 2H^+ + {}^1/_2SO_4^= + e;\ E_0 = 0.2_1$.

Foerster and Böttcher[5] have made a few measurements similar to those of Rutter. They point out that variable potentials were obtained when using a platinum or other solid metal electrode owing to the evolution of hydrogen but that the difficulty was diminished by using a mercury electrode. Unfortunately they used different concentrations of sulfuric acid in their vanadium solutions and in their sulfuric acid, mercurous sulfate, mercury reference electrodes thereby introducing a liquid junction potential for which they make no correction.

Latimer[6] gives $V^{++} = V^{+++} + e$, $E_0 = +0.20$ with a reference to the above work of Foerster and Böttcher as his authority.

Experimental Procedures

Potential measurements were made on the cell

$$\overset{-}{\mathrm{Hg}},\ {}^1/_2V_2(SO_4)_3\ (c_3) + \underset{+}{VSO_4}\ (c_2) + H_2SO_4\ (c_1),$$

H_2SO_4 (c_1), Hg_2SO_4, Hg at total vanadium concentrations ranging from 0.005 to 0.141 *c* in solutions of sulfuric acid of concentrations 0.05, 0.1, 0.2, 0.5 and 1.0 *c*. Solutions of different vanadium concentrations in sulfuric acid of a particular concentration constitute a series.

Preparation of Materials

Vanadous Sulfate (Divalent Vanadium Sulfate) $VSO_4 \cdot 7H_2O$.—78.5 g. of C. P. vanadium pentoxide was suspended in 25 cc. of concentrated sulfuric acid diluted with about 300 cc. of water and sulfur dioxide passed through the solution until the vanadium pentoxide was completely reduced to vanadyl sulfate as indicated by the clear blue solution. A small amount of vanadium pentoxide was then added to use all the excess of sulfur dioxide and the clear blue solution of vanadyl sulfate, with practically no excess sulfuric acid, was filtered from the excess vanadium pentoxide through a sintered glass filter. The vanadyl sulfate was reduced at a mercury cathode in a divided cell with the platinum anode inside a porous porcelain cup. In going through the trivalent state considerable precipitate was formed which finally required the addition of about 15 cc. more of concentrated sulfuric acid. Continued reduction for about three or four days with 2 amperes re-

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(1) Original manuscript received November 12, 1943.

(1) (a) Grinnell Jones and John H. Colvin, THIS JOURNAL, **66**, 1563 (1944); (b) Grinnell Jones and Wendell A. Ray, *ibid.*, **66**, 1571 (1944).

(2) T. F. Rutter, *Z. anorg. Chem.*, **52**, 373 (1907).

(3) R. Abegg, F. Auerbach and R. Luther, "Messungen elektromotorische Kräfte galvanische Ketten." W. Knapp, Halle, 1911, p. 204; second supplement to the above by C. Drucker, Verlag Chemie, Berlin, 1929, p. 222.

(4) "International Critical Tables," 1929, Vol. VI, p. 332.

(5) F. Foerster and F. Böttcher, *Z. physik. Chem.*, **151A**, 321 (1930).

(6) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 243, 295.