[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Electrochemical Studies on Vanadium Salts. I. The Vanadyl–Vanadic Oxidation–Reduction Potential[1]

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This paper gives the results of some new measurements on the oxidation–reduction potential between the tetravalent and trivalent states of vanadium in aqueous solutions. Similar measurements on the trivalent–divalent transformation are reported in a subsequent paper.

The first study of this potential was made by Rutter[1a] on the cell

$$\overset{-}{\text{Pt}},\ VOSO_4 + V_2(SO_4)_3 + H_2SO_4\ (0.25\ \text{molar}),\ H_2SO_4\ (0.25\ \text{molar}),\ Hg_2SO_4,\ \overset{+}{\text{Hg}}$$

The total vanadium concentration was always 0.1 molar in vanadium, but the ratio of tetravalent to trivalent vanadium was varied over a wide range. All measurements were made at 25°. He did not attempt to compute a normal potential.

However, Abegg, Auerbach and Luther,[2] in their compilation of standard potentials, use Rutter's data to compute the standard potential of the reaction

$$V^{+++} + H_2O = VO^{++} + 2H^+ + e;\ E_h = -0.4\ \text{volt}$$

Gerke,[3] in his compilation for the "International Critical Tables," writes the reaction and gives the potential as follows

$$1/2\ (VO)_2SO_4 + 1/2\ SO_4^{=} = VOSO_4 + e;\ E_h = -0.3_0\ \text{volt}$$

This result is based entirely on Rutter's measurements.

Foerster and Böttcher[4] have made measurements similar to those of Rutter except that they maintained the concentration of the trivalent vanadium equal to that of the tetravalent vanadium, but varied the concentration both of the vanadium salts and of the sulfuric acid. Unfortunately, the concentration of the acid was not the same at the two electrodes, thus introducing a large liquid junction potential for which no precise correction can be made. They found the measured potentials to be little influenced by the change in the total concentration of the vanadium but much influenced by the variation in the concentration of the sulfuric acid used. The measurements were made at 18°.

Latimer and Hildebrand[5] give $V^{+++} + H_2O = VO^{++} + 2H^+ + e$; $E_0 = -0.314$ volt, and without quoting any authority. Latimer[6] gives $V^{+++} + H_2O = VO^{++} + 2H^+ + e$, $E_0 = -0.31$ volt, with a reference to Foerster and Böttcher.

Experimental Procedure

Preparation of Materials

Vanadyl Sulfate ($VOSO_4 \cdot 3H_2O$).—About 50 g. of C. P. vanadium pentoxide obtained from the Vanadium Corporation of America was suspended in about 300 ml. of water and 14 ml. of concentrated sulfuric acid and then dissolved and reduced to the tetravalent condition by passing sulfur dioxide gas through the solution. The solution was filtered through a sintered glass filter, then evaporated on the steam-bath with occasional addition of sulfur dioxide gas until an abundant crop of blue crystals could be obtained on cooling. The crystals were filtered on sintered glass, washed with ethyl alcohol to remove excess of sulfuric acid and then washed with ethyl ether and dried in a vacuum desiccator over sulfuric acid. The salt was analyzed for tetravalent vanadium by titration with potassium permanganate and for sulfate by the barium sulfate method with the following results: vanadium (tetravalent), 23.58, 23.59; sulfate (SO_4), 44.27, 44.20. Calcd. for $VOSO_4 \cdot 3H_2O$: V, 23.48; SO_4, 44.27.

Vanadic (trivalent) Sulfate, $V_2(SO_4)_3 \cdot 10H_2O$.—Fifty grams of C. P. vanadium pentoxide was suspended in 300 ml. of water and 40 ml. of concentrated sulfuric acid and reduced to the tetravalent condition with sulfur dioxide. The solution was then filtered through a fritted glass filter, and evaporated to approximately one-half its volume on a steam-bath. The reduction to the trivalent condition was accomplished by electrolysis in a divided cell, using a platinized platinum cathode. The electrolysis was continued until some divalent vanadium had been formed. The cathode solution was allowed to stand in contact with a strip of platinized platinum, which resulted in liberation of hydrogen gas and oxidation of the divalent vanadium to trivalent vanadium. Upon cooling the solution to about 0° a good yield of grayish-violet colored crystals was obtained. The crystals were filtered on a fritted glass filter, washed with ethyl alcohol, and then with ether, and dried in a vacuum desiccator over sulfuric acid. Analysis of the dried crystals gave the following results: vanadium (trivalent) 17.93, 17.97, 17.87; sulfate, 50.65, 50.55, 50.61. Calcd. for $V_2(SO_4)_3 \cdot 10H_2O$: V, 17.87; SO_4, 50.52. The vanadic sulfate is extremely soluble in water, giving solutions which are very dark in color, but which become bright green upon the addition of a small amount of acid. The solid vanadic sulfate is stable to oxidation in dry air, but its solutions absorb oxygen and, therefore, must be protected from air during the potential measurements and analysis.

Mercury.—The mercury was purified according to the directions given by Mack and France.[7] Mercurous sulfate for use in the reference half cell was made by anodic oxidation on the purified mercury in sulfuric acid according to the directions of Hulett[8] and recommended by Harned and Hamer. The sulfuric acid, mercurous sulfate, mercury reference electrodes were constructed as shown in Fig. 1. The ground joint, M, was a No. 15 standard taper with a grinding 18 mm. long. These half cells when

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(1) Original manuscript received November 12, 1943.

(1a) T. F. Rutter, *Z. anorg. Chem.*, **52**, 377 (1907); H. Hofer and F. Jakob, *Ber.*, **41**, 3189 (1908).

(2) R. Abegg, F. Auerbach and R. Luther, "Messungen elektromotorischer Kräfte galvanische Ketten," W. Knapp, Halle, 1911, page 204. The potential is recorded with a positive sign but the sign has been changed above to conform to the convention customary in the American literature. Their definition of the reference hydrogen electrode is not the same as that now in use.

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

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

(5) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," 2nd ed., The Macmillan Company, New York, N. Y., 1940, pp. 339, 475.

(6) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, pp. 243, 296.

(7) E. Mack and W. G. France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., p. 240.

(8) G. A. Hulett, *Phys. Rev.*, **32**, 257 (1911).

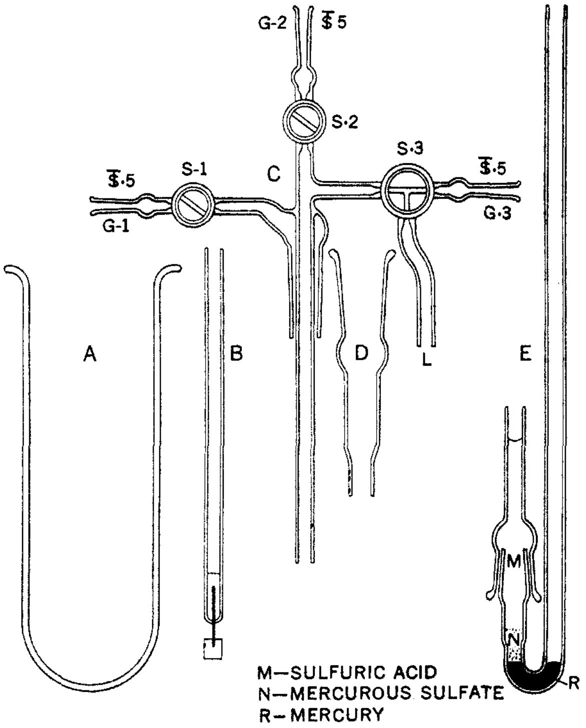

Fig. 1. Apparatus.

immersed in a solution containing the vanadium solutions gave a liquid junction inside the grinding and since the sulfuric acid in the two halves of the cell was always the same concentration these liquid junction potentials must have been small and were eliminated by extrapolation as shown below. Diffusion of the vanadium ions through the ground joint to the mercury electrode did not occur for more than twenty-four hours. The internal resistance through this film in the ground joint was not too great to prevent a sensitivity of 0.01 millivolt in the potential readings. Three replicates were always prepared but never showed a significant difference among themselves.

The Cell.—The vanadium electrodes, B, consisted of small pieces of platinum foil about 0.5 sq. cm. immersed in the mixed vanadyl–vanadic sulfate solutions. It was found by experience that it was better to platinize these electrodes.

Apparatus was built which made it possible to prepare the solutions quantitatively from the weighed solid salts and standard acid, and then to transfer it to the electrolytic cell, and after making the potential measurements at both 25 and 0° to remove samples for analysis, without exposure to air.

The cell (as shown in Fig. 1, with the parts disassembled) consisted of a large Pyrex glass tube, A, having the form of a test-tube, 5 cm. in diameter and 22 cm. long into which was placed the mercurous sulfate, mercury reference electrode, E, two platinum electrodes, B, a thermometer and suitable tubes, C, D, for filling the cell with the desired vanadium–sulfuric acid solution, sweeping out the apparatus with oxygen-free nitrogen and removing a sample for analysis after the potential measurements without exposing the solutions to air. The upper end of the tube above the mercury electrode extended above the level of the solution in the cell A so that the liquid junction between the two half cells was entirely in the ground joint, M, and the potential measurements were made through this ground joint. All of these parts were inserted into the tube, A, through a rubber stopper which, however, never came in contact with the solutions.

The manipulation and behavior of the cell can be described best by the following typical specific example. In this particular case it was desired to make a solution which would be 0.1 molar in tetravalent vanadium (vanadyl ion VO^{++}), 0.1 molar in trivalent vanadium (vanadic ion V^{+++}), and 0.5 molar in sulfuric acid; 125 ml. of 1 *C* sulfuric acid was added to a 250-ml. volumetric flask. Oxygen-free nitrogen, which was obtained by passing the gas from a cylinder of compressed nitrogen over red-hot freshly reduced copper, was bubbled through the acid to remove oxygen from the acid and the flask. 5.4253 g. of $VOSO_4 \cdot 3H_2O$ and 7.1263 g. of $V_2(SO_4)_3 \cdot 10H_2O$ were added, and after dissolving the crystals the flask was filled to the mark with oxygen-free water, and the neck of the flask swept out with nitrogen. The cell was assembled with a reference electrode, E, containing 0.5 molar sulfuric acid and two platinized platinum electrodes, B, and then swept out with oxygen-free nitrogen. The prepared vanadium solution was transferred to the cell by the use of nitrogen pressure and the cell closed and placed in a thermostat adjusted to 25.0°.

The electromotive force was measured by a calibrated Wolff potentiometer using a Weston standard cell as a reference standard.

Within one hour after placing the cell in the constant temperature bath at 25°, the cell potential reached a constant value of 0.3453_9 volt, with either platinum electrode, and retained that potential until the cell was removed from the 25° bath one hour later. The cell was then packed in an ice-bath and the cell potential determined at intervals. Within one-half hour the cell potential, with either platinum electrode, was constant at a value of 0.3204 volt, which was retained at least four hours longer.

It was found that bubbling the nitrogen through the solution in the cell hastened the attainment of constant readings, but that after temperature equilibrium had been reached it made no difference whether the nitrogen was bubbling through the cell or not.

In cells containing lower concentrations of the vanadium ions, it is more difficult to obtain constancy and agreement in the potential readings and in the analyses.

The concentrations of trivalent and tetravalent vanadium in the cell solution was determined by adjusting the temperature to 25°, removing a measured quantity of the solution by means of pipet attached at joint G-2 while maintaining an inert atmosphere, and titrating to the pentavalent state with standardized permanganate in a solution acidified with sulfuric acid. The vanadium was reduced then to the tetravalent state with sulfur dioxide, the excess sulfur dioxide removed, and the solution titrated again with permanganate to oxidize the vanadium to the pentavalent state.

In the special case referred to above the concentration of the trivalent vanadium was 0.1007 mole per liter, and the tetravalent vanadium was 0.1006 mole per liter; hence $VO^{++}/V^{+++} = c_4/c_3 = 0.9988$.

There is evidence in the literature[9] that the tetravalent vanadium ion, V^{++++}, is practically completely hydrolyzed in aqueous solutions to the vanadyl ion, VO^{++}, and solutions of vanadyl sulfate are slightly acid owing to further hydrolysis (see the following paper). Measurements of the *p*H of vanadyl and vanadic sulfate solutions which are reported in the following paper, show that a 0.1 *C* solution of $VOSO_4$ has a *p*H of 3.11, which indicates that it is only about 1% hydrolyzed and its hydrolysis is presumably practically completely repressed by even 0.01 *C* H_2SO_4. However, with the vanadic sulfate the situation is much more unfavorable. A solution which is 0.1 molar in trivalent vanadium ($^1/_2$ $V_2(SO_4)_3$) has a *p*H of 1.94. A 0.02 *C* sulfuric acid solution which has a *p*H of about 1.6, would be expected to repress the hydrolysis of a 0.1 molar vanadic sul-

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(9) H. T. S. Britton and G. Welford, *J. Chem. Soc.*, 758 (1940).

fate solution to a substantial degree but perhaps not completely enough to prevent the hydrolysis influencing the potential. In the potential measurements reported below the concentration of sulfuric acid was varied from 1 *C* to 0.02 *C* and the concentration of the vanadium salts from 0.1 *C* to 0.005 *C* in the hope that the effect of hydrolysis on the potentials could be eliminated by suitable extrapolation. It, therefore, seems probable that the measured potential of the cell, ${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$, of the type

$$\overset{-}{\mathrm{Pt}},\ \mathrm{VOSO_4}\ (c_4) + 1/2\ \mathrm{V_2(SO_4)_3}\ (c_3) + \mathrm{H_2SO_4}\ (c_1),\ \mathrm{H_2SO_4}\ (c_1),\ \mathrm{Hg_2SO_4},\ \overset{+}{\mathrm{Hg}}:\ {}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$$

will be determined by the cell reaction

$$\mathrm{V^{+++} + H_2O + 1/2\ Hg_2SO_4 = VO^{++} + 2H^+ + 1/2\ SO_4^{=} + Hg}$$

and the potential of the vanadium half-cell by the electrode reaction $\mathrm{V^{+++} + H_2O = VO^{++} + 2H^+ + e}$, as was assumed by Abegg, Auerbach and Luther, and by Latimer and Hildebrand.

The electromotive force of this cell will be given by the equation

$${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}} = {}_{\mathrm{Hg}}E^{\mathrm{v}}_{0} + E_{\mathrm{L}} + \frac{RT}{F}\ln\frac{\alpha_3\alpha_{\mathrm{w}}}{\alpha_4\alpha_{\mathrm{H}}^2\alpha_{\mathrm{s}}^{1/2}} \qquad (1)$$

where α_{H}, α_3, α_4, α_{s} and α_{w} are the activities of the hydrogen ion, the vanadic ion, the vanadyl ion, the sulfate ion and the water, respectively. E_{L} is the liquid junction potential. ${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$ is the measured potential of the vanadyl–vanadic electrode measured against the sulfuric acid–mercurous sulfate–mercury electrode. ${}_{\mathrm{Hg}}E^{\mathrm{v}}_{0}$ is the normal potential of this cell (with all the activities unity).

It is now convenient to introduce the stoichiometrical activity coefficients which can be defined by the equations

$$\begin{aligned} \alpha_3 &= c_3f_3 = \rho_0m_3\gamma_3 \\ \alpha_4 &= c_4f_4 = \rho_0m_4\gamma_4 \\ \alpha_{\mathrm{H}} &= c_{\mathrm{H}}f_{\mathrm{H}} = \rho_0m_{\mathrm{H}}\gamma_{\mathrm{H}} \end{aligned} \qquad (2)$$

where *m* refers to the concentration expressed in moles per thousand grams of water and *c* to the concentration expressed in moles per liter. The ratio of *m* to *c* is never greater than 1.0372 in any of the cases considered and it approaches $1/\rho_0$ with dilution of the solutions. It should also be noted that in all cases $m_4/m_3 = c_4/c_3$ and therefore

$$\gamma_4/\gamma_3 = f_4/f_3 \qquad (3)$$

The concentrations of the ion constituents are computed from analytical data alone without allowance for partial ionization or hydrolysis and therefore the activity coefficients are stoichiometrical activity coefficients which by definition include the influence of partial ionization and hydrolysis as well as interionic effects. In a pure solution of sulfuric acid of concentration m_1 (containing no vanadium salts) by definition

$$m_{\mathrm{H}} = 2m_1 \quad \text{and} \quad \alpha_{\mathrm{H}} = 2\rho_0m_1\gamma_{\mathrm{H}} \qquad (4)$$

Introducing these activity coefficients for the VO^{++}, and V^{+++} and rearranging gives equation (5)

$${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}} + \frac{RT}{F}\ln c_4/c_3 = {}_{\mathrm{Hg}}E^{\mathrm{v}}_{0} + E_{\mathrm{L}} - \frac{RT}{F}\ln f_4/f_3 + \frac{RT}{F}\ln \alpha_{\mathrm{w}} - \frac{RT}{F}\ln \alpha_{\mathrm{H}}^2\alpha_{\mathrm{s}}^{1/2} \qquad (5)$$

In order to test the hypothesis that our cells were really functioning as a tetravalent–trivalent oxidation–reduction cell, we made potential measurements on a series of cells of the type given in which the concentration of the sulfuric acid was maintained at a fixed value of $c_1 = 1.000$ or $m_1 = 1.0372$ and the total vanadium concentration $(c_3 + c_4)$ at about 0.04 molar, but the ratio of the concentration of the tetravalent vanadium (c_4) to the trivalent vanadium (c_3) was varied over a wide range so as to produce a variation in the measured potential of nearly 0.1 volt. The results are shown in Table I.

Since in this series the sulfuric acid in both half cells was always 1 molar $(c_1 = 1)$ and the variable concentration of the vanadium ions was always much smaller, the ionic strength was approximately constant throughout the series and therefore we may regard all of the activity coefficients as approximately constant in this series. The liquid junction potentials should be small and not appreciably variable.

The approximate constancy of the figures in the last column of Table I is proof that we are really dealing with a tetravalent–trivalent oxidation–reduction cell.

TABLE I

POTENTIAL, ${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$, AT 25° OF THE CELL: Pt, $\mathrm{VOSO_4}$ (c_4) + 1/2 $\mathrm{V_2(SO_4)_3}$ (c_3) + $\mathrm{H_2SO_4}$ $(c_1 = 1)$, $\mathrm{H_2SO_4}$ $(c_1 = 1)$, $\mathrm{Hg_2SO_4}$, $\overset{+}{\mathrm{Hg}}$

c_4	c_3	${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$ volts	${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}} + \frac{RT}{F}\ln\frac{c_4}{c_3}$
0.0350	0.0050	0.2555	0.3055
.0300	.0100	.2780	.3062
.01928	.01983	.3066	.3059
.01027	.02994	.3337	.3062
.00534	.03466	.3531	.3051

In the remaining measurements the concentrations of the tetravalent and of the trivalent vanadium were always as nearly equal as was feasible. In order to determine the effect of variation in concentration of the acid, several series of measurements were carried out in which the acid concentration was varied from $c_1 = 1$ to $c_1 = 0.02$. In order to minimize the liquid junction potentials in every case the acid concentration in the $\mathrm{H_2SO_4}$, $\mathrm{Hg_2SO_4}$, Hg half-cell was the same as in the vanadium half-cell. Within each series the concentration of the vanadium salts $(c_3 + c_4)$ was varied from 0.2 molar to 0.01 molar. In each case after the potential measurements were obtained at 25° the cell was transferred to an ice-bath and potential measurements made at 0°

TABLE II

VANADYL–VANADIC OXIDATION–REDUCTION POTENTIALS AT 25 AND 0°

			25°		0°	
c_1	$c_4 + c_3$	c_4/c_3	${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$, v.	E_c, v.	${}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}}$, v.	E_c, v.
1.000	0.2014	1.001	0.3033	−0.3718	0.2810	−0.3988
1.000	.1018	0.965	.3058	− .3702	.2834	− .3972
1.000	.0391	.972	.3066	− .3692	.2841	− .3964
1.000	.02005	.988	.3066	− .3688	(.2847)	(− .3954)
1.000	.00998	.996	.3066	− .3686	.2838	− .3961
			$E_c = -0.3685 - 0.0166\ (c_3 + c_4)$		$E_c = -0.3959 - 0.0139\ (c_3 + c_4)$	
0.500	0.2013	0.999	0.3454	−0.3502	0.3204	−0.3787
.500	.1010	.993	.3465	− .3493	.3216	− .3777
.500	.1008	1.002	.3473	− .3483	.3222	− .3769
.500	.04036	1.001	.3478	− .3478	.3227	− .3764
.500	.02020	1.023	.3478	− .3473	.3225	− .3761
.500	.01025	1.007	.3484	− .3470	.3232	− .3757
			$E_c = -0.3470 - 0.0170\ (c_3 + c_4)$		$E_c = -0.3758 - 0.0139\ (c_3 + c_4)$	
0.200	0.2011	0.996	0.3940	−0.3256	0.3660	−0.3554
.200	.1008	1.003	.3954	− .3240	.3675	− .3537
.200	.1000	1.000	.3958	− .3237	.3676	− .3537
.200	.0400	1.000	.3966	− .3229	.3686	− .3527
.200	.02056	1.002	.3969	− .3228	.3689	− .3524
.200	.01043	0.993	.3978	− .3219	.3695	− .3520
.200	.01000	1.000	.3974	− .3221	.3693	− .3520
			$E_c = -0.3219 - 0.0182\ (c_3 + c_4)$		$E_c = -0.3519 - 0.0175\ (c_3 + c_4)$	
0.100	0.2027	1.006	0.4284	−0.3084	0.3987	−0.3389
.100	.2000	1.000	.4299	− .3071	.3989	− .3388
.100	.1012	1.016	.4305	− .3061	.4010	− .3384
.100	.1000	1.000	.4300	− .3070	.3997	(− .3381)
.100	.04168	1.000	.4309	− .3061	.4011	− .3367
.100	.04056	1.022	.4303	− .3062	.4008	− .3365
.100	.02087	1.043	.4305	− .3054	.4016	− .3353
.100	.02000	1.000	.4325	− .3045	.4024	− .3354
.100	.0100	1.000	.4325	− .3045	.4029	− .3349
.100	.0100	1.000	.4322	− .3048	.4026	− .3352
			$E_c = -0.3048 - 0.0186\ (c_3 + c_4)$		$E_c = -0.3351 - 0.0190\ (c_3 + c_4)$	
0.0500	0.2026	1.002	0.4615	−0.2927	0.4314	−0.3230
.0500	.1018	1.002	.4652	− .2890	.4341	− .3203
.0500	.04086	1.029	.4668	− .2867	.4356	− .3181
.0500	.02037	1.028	.4673	− .2862	.4362	− .3176
.0500	.01120	1.062	.4676	− .2851	.4370	− .3160
			$E_c = -0.2851 - 0.03076\ (c_3 + c_4)$		$E_c = -0.3163 - 0.0355\ (c_3 + c_4)$	
0.0200	0.2000	1.000	0.4987	−0.2798	0.4714	−0.3061
.0200	.1014	1.003	.5072	− .2712	.4770	− .3004
.0200	.04004	1.000	.5132	− .2653	.4806	− .2969
.0200	.02040	1.04	.5138	− .2637	.4818	− .2957
			$E_c = -0.2619 - 0.0897\ (c_3 + c_4)$		$E_c = -0.2945 - 0.0580\ (c_3 + c_4)$	

$E_c = {}_{\mathrm{Hg}}E^{\mathrm{v}}_{\mathrm{m}} + {}_{\mathrm{H}}E^{\mathrm{Hg}}_{\mathrm{m}} - \frac{RT}{F}\ln\frac{c_3}{c_4}$; $2.30258\,\frac{RT}{F} = 0.059138$ at 25°C.; 0.054179 at 0°. Values for ${}_{\mathrm{H}}E^{\mathrm{Hg}}_{\mathrm{m}}$ given in Table III.

Then a sample was withdrawn and analyzed for c_4 and c_3. A correction, $(RT/F)\ln c_4/c_3$, was applied to the measured potential to compensate for any unequality in c_4 and c_3. This correction never amounted to more than 0.0015 volt, and was usually less than 0.001 volt. The average correction was 0.00025 volt. The results are shown in Table II.

In order to refer the results to the standard hydrogen electrode, we will make use of the measurements of Harned and Hamer[10] on the cell.

$$\overset{+}{\mathrm{Hg}},\ \mathrm{Hg_2SO_4},\ \mathrm{H_2SO_4}\ (m_1),\ \overset{-}{\mathrm{Pt}},\ \mathrm{H_2}:\ {}_{\mathrm{H}}E^{\mathrm{Hg}}_{\mathrm{m}}$$

In this cell the cell reaction is $\mathrm{H^+ + Hg + {}^1/_2\ SO_4^{=} = {}^1/_2\ H_2 + {}^1/_2\ Hg_2SO_4}$.

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[10] H. S. Harned and W. J. Hamer, THIS JOURNAL, 57, 27 (1935).

TABLE III

MEAN STOICHIOMETRIC ACTIVITY COEFFICIENTS OF SULFURIC ACID SOLUTIONS BASED ON HARNED AND HAMER'S DATA

		At 25°		At 0°	
c_1	m	${}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}}$	$\gamma'_{\pm}$	${}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}}$	$\gamma'_{\pm}$
	1.0	−0.67600	0.130	−0.68068	0.173
1.0	1.0372	− .67507	.1283	− .67980	.1705
	0.50	− .69609	.154	− .69958	.202
0.5	.5100	− .69558	.1532	− .69910	.2007
	.2	− .71970	.209	− .72151	.271
.2	.2019	− .71946	.2083	− .72128	.2705
	.1	− .73714	.265	− .72791	.341
.1	.10061	− .73698	.2652	− .73776	.3404
	.05	− .75434	.340	− .75455	.426
.05	.05022	− .75423	.3396	− .75444	.4251
	.02	− .77861	.453	− .77760	.554
.02	.02007	− .77852	.4525	− .77752	.5533

The electromotive force of this cell is

$$ {}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}} = {}_{\mathrm{H}}E_{0}^{\mathrm{Hg}} + \frac{RT}{F}\ln \alpha_{\mathrm{H}}\alpha_{\mathrm{s}}^{1/2} \qquad (6) $$

where ${}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}}$ is the measured potential of the mercury, mercurous sulfate, sulfuric acid (m_1), hydrogen cell. (Note that sign of the potential given by Harned and Hamer must be changed to negative because we find it convenient to write the cell in the reversed fashion.)

${}_{\mathrm{H}}E_{0}^{\mathrm{Hg}}$ is the standard potential of the sulfate ion, mercurous sulfate, mercury electrode referred to the standard hydrogen electrode which is assumed to be zero.

Adding equations (1) and (6) gives

$$ {}_{\mathrm{Hg}}E_{\mathrm{m}}^{\mathrm{v}} + {}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}} = {}_{\mathrm{H}}E_{0}^{\mathrm{v}} + {}_{\mathrm{H}}E_{0}^{\mathrm{Hg}} + E_{\mathrm{L}} + \frac{RT}{F}\ln\frac{\alpha_3\alpha_{\mathrm{w}}}{\alpha_4\alpha_{\mathrm{H}}} \qquad (7) $$

and the corresponding cell reaction is $V^{+++} + H_2O = VO^{++} + H^+ + {}^1/_2H_2$. But the standard potential of the vanadyl–vanadic electrode measured against the standard hydrogen, hydrogen ion electrode is

$$ {}_{\mathrm{H}}E_{0}^{\mathrm{v}} = {}_{\mathrm{Hg}}E_{0}^{\mathrm{v}} + {}_{\mathrm{H}}E_{0}^{\mathrm{Hg}} \qquad (8) $$

$$ {}_{\mathrm{Hg}}E_{\mathrm{m}}^{\mathrm{v}} + {}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}} = {}_{\mathrm{H}}E_{0}^{\mathrm{v}} + E_{\mathrm{L}} + \frac{RT}{F}\ln\frac{\alpha_3\alpha_{\mathrm{w}}}{\alpha_4\alpha_{\mathrm{H}}} \qquad (9) $$

The data of Harned and Hamer which we are using are given for round values of m whereas we have found it convenient in our experiments to use round values of c. However, Harned and Hamer's measurements of ${}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}}$ give approximately a straight line when plotted against log m and it was therefore easy to find the proper value of ${}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}}$ for the particular concentration which was used in our experiments. The maximum correction required for this purpose was only 0.00093 volt and this small correction should be sufficiently precise for our purpose.

The results together with the corresponding values of the mean stoichiometric activity coefficients, $\gamma\pm$, are shown in Table III.

Then making these substitutions in equation (7) gives

$$ E_{\mathrm{c}} = {}_{\mathrm{Hg}}E_{\mathrm{m}}^{\mathrm{v}} + {}_{\mathrm{H}}E_{\mathrm{m}}^{\mathrm{Hg}} - \frac{RT}{F}\ln\frac{c_3}{c_4} = {}_{\mathrm{H}}E^{\mathrm{v}} + E_{\mathrm{L}} + \frac{RT}{F}\ln\frac{f_3}{f_4} - \frac{RT}{F}\ln \rho_0 2m_1\gamma_{\mathrm{H}} + \frac{RT}{F}\ln \rho_0\alpha_{\mathrm{w}} \qquad (10) $$

We can assign a numerical value to all of the terms on the left-hand side for any cell whose potential is measured and thus obtain the values of E_{c} as shown in columns 5 and 7 of Table II. For any series in which the concentration of sulfuric acid (m_1) is held constant the left side of the equation, E_{c}, may be plotted against $c_3 + c_4$ giving approximately a straight line which may be extrapolated to $c_3 + c_4 = 0$, thus giving an intercept which is designated E'_{c}, as shown in Fig. 2 and Fig. 3. The effect of this extrapolation is to eliminate the liquid junction potential and also the secondary effects of the presence of the vanadium salts on the several activity coefficients and on the activity of water. However, the extrapolation does not eliminate the effect of the presence of the sulfuric acid on the activity coefficients of the vanadyl, vanadic and hydrogen ions and on the activity of the water because the concentration of the acid is a constant within any series and, therefore, these activity coefficients are not

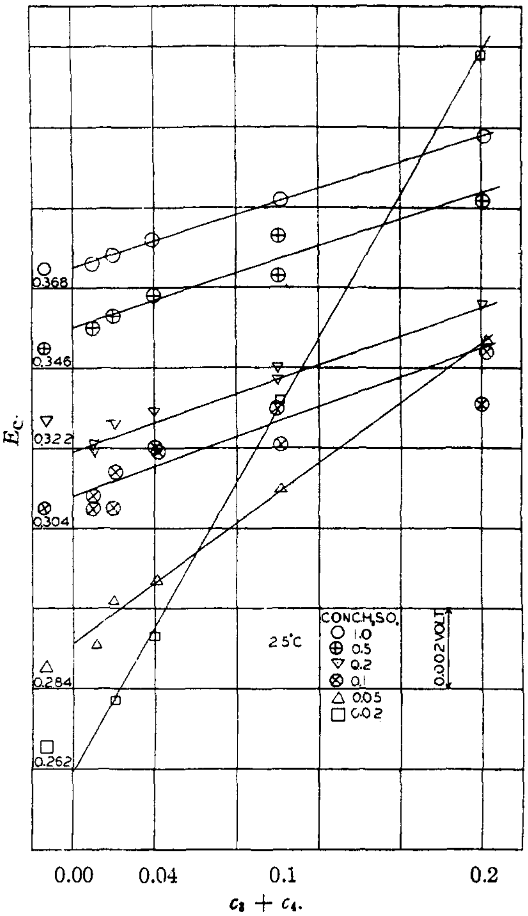

Fig. 2.

TABLE IV

c_1	$E_c' + A\,(c_3 + c_4)$	$\frac{RT}{F}\ln 2m_1\gamma'_{\pm}$	$\frac{RT}{F}\ln \alpha_w'$	E_c''
		At 25°		
1.0	$-0.3685 - 0.0166\,(c_3 + c_4)$	−0.0076	+0.0010	−0.3751
0.5	$-.3470 - .0170\,(c_3 + c_4)$	− .0236	+ .0005	− .3701
.2	$-.3219 - .0182\,(c_3 + c_4)$	− .0434	+ .0002	− .3651
.1	$-.3048 - .0186\,(c_3 + c_4)$	− .0583	+ .0001	− .3630
.05	$-.2851 - .0376\,(c_3 + c_4)$	− .0729	0	− .3580
.02	$-.2619 - .0897\,(c_3 + c_4)$	− .0928	0	− .3547
		At 0°		
1.0	$-0.3959 - 0.0139\,(c_3 + c_4)$	−0.0036	+0.0009	−0.3986
0.5	$-.3758 - .0139\,(c_3 + c_4)$	− .0184	+ .0004	− .3938
.2	$-.3519 - .0175\,(c_3 + c_4)$	− .0367	+ .0002	− .3884
.1	$-.3351 - .0190\,(c_3 + c_4)$	− .0504	+ .0001	− .3854
.05	$-.3163 - .0355\,(c_3 + c_4)$	− .0641	0	− .3804
.02	$-.2945 - .0580\,(c_3 + c_4)$	− .0826	0	− .3771

changed by this kind of extrapolation. We may express this mathematically by the relation

$$f_3 = f_3'k_3 \qquad (11)$$

where f_3 is the activity of the vanadic ion in the actual working solutions as defined above and f_3' is the limiting value of the activity coefficient of the vanadic ion in a solution of sulfuric acid of concentration m_1 as the concentration of the vanadium salts $(c_3 + c_4)$ approaches zero. k_3 is a correcting factor which expresses the influence of the vanadium salts on the activity coefficient of the vanadic ion. Then as $c_3 + c_4$ approaches zero k_3 approaches unity and at the limit becomes unity, but f_3' does not approach unity.

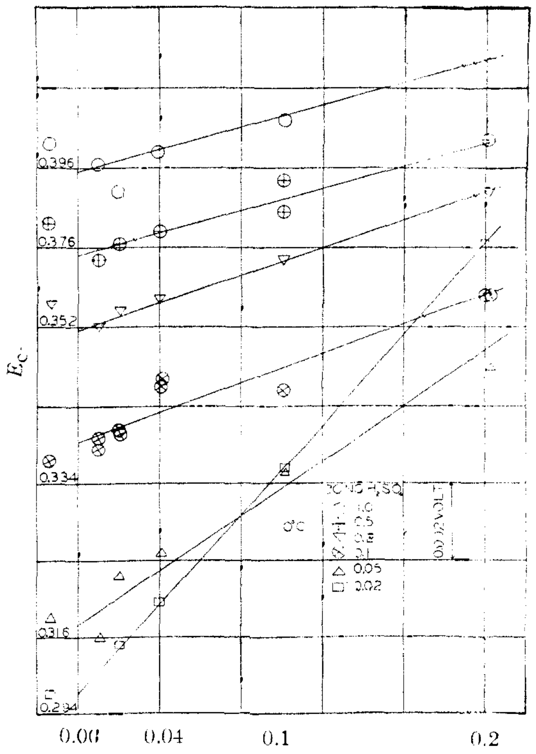

Fig. 3.

In an analogous manner we write

$$\begin{aligned} f_4 &= f_4'k_4 \\ \gamma_H &= \gamma_H'k_H \qquad (12) \\ \alpha_w &= \alpha_w'k_w \end{aligned}$$

Making these substitutions, equation (10) becomes

$$E_c = {}_{Hg}E^v_m + {}_HE^{Hg}_m + \frac{RT}{F}\ln\frac{c_4}{c_3} = {}_HE^v_0 + E_L + \frac{RT}{F}\ln\frac{f_3'k_3}{f_4'k_4} - \frac{RT}{F}\ln \rho_0 2m_1\gamma_H'k_H + \frac{RT}{F}\ln \rho_0\alpha_w'k_w \quad (13)$$

We have a definite numerical value for the left side of this equation for each experiment, as shown in Table III. When these values, for any series of experiments for which m_1 is constant but c_3 and c_4 are variable, are plotted against $c_3 + c_4$ they give straight lines which may be represented by the equation

$$E_c = {}_{Hg}E^v_m + {}_HE^{Hg}_m + \frac{RT}{F}\ln\frac{c_4}{c_3} = E_c' + A_c(c_3 + c_4) \quad (14)$$

The average deviation between the observed points and these lines is only 0.00025 volt at 25° and 0.00031 volt at 0°, and the maximum deviation out of seventy-four cases is only 0.0014 volt. These plots are shown on a reduced scale in Fig. 2 for 25° and in Fig. 3 for 0°, and the corresponding equations are given in Table II.

We may identify the term $A_c(c_3 + c_4)$ with the sum of all the terms on the right-hand side of equation (13) which are dependent on the concentration of the vanadium ions giving

$$A_c(c_4 + c_3) = E_L + \frac{RT}{F}\ln\frac{k_3k_w}{k_4k_H} \qquad (15)$$

It should be noticed that the values of A_c decrease with the increasing concentration of the acid especially in the dilute range. This is reasonable since this term measures the secondary effects of the presence of the variable concentration of vanadium ions on the liquid junction potentials and on the several activity coefficients. The higher the concentration of the acid the more these secondary effects will be suppressed or minimized by the dominant influence of the ions derived from the sulfuric acid. The negative sign of A_c is also in accord with the general experience and theory as to the influence of increasing ionic strength on the activity coefficients. It is to be expected that the activity coefficient of the triply charged vanadic ion would be more sensitive to changes in ionic strength than the doubly charged vanadyl ion and the hydrogen ions and that therefore an increase in the ionic strength should cause a greater decrease in f_3 than in f_4 and γ_H thus giving a negative sign to A_c.

In a similar manner we may identify the intercept of these straight lines, E'_c, with the sum of all of the terms in equation (13) which are independent of the concentration of the vanadium ions giving

$$E'_c = {}_{\mathrm{H}}E^{\mathrm{v}}_0 + \frac{RT}{F}\ln\frac{f'_3}{f'_4} - \frac{RT}{F}\ln \rho_0 2m_1\gamma'_{\mathrm{H}} + \frac{RT}{F}\ln \rho_0\alpha'_{\mathrm{w}} \tag{16}$$

For each series of experiments with a definite value of the acid concentration (m_1), we now have a definite numerical value for E'_c. We also have definite numerical values for the last two terms of equation (16) from the work of Harned and Hamer[10] who have determined the activity of water in sulfuric acid solutions, $\gamma'_{\pm}$, at both 0 and 25°. By definition

$$\gamma'_{\pm} = \sqrt[3]{\gamma'^2_{\mathrm{H}}\gamma'_{\mathrm{s}}} \tag{17}$$

It is now necessary to introduce the non-thermodynamic assumption based on the Debye interionic attraction theory[11] that

$$\gamma'_{\mathrm{s}} = \gamma'^4_{\mathrm{H}} \tag{18}$$

and therefore

$$\gamma'_{\pm} = \gamma'^2_{\mathrm{H}} \text{ or } \gamma'_{\mathrm{H}} = \gamma'^{1/2}_{\pm} \tag{19}$$

Introducing equation (19) into equation (16) and rearranging gives

$$E''_c = E'_c - \frac{RT}{F}\ln \rho_0\,\alpha'_{\mathrm{w}} + \frac{RT}{F}\ln 2m_1\,\rho_0\,\gamma'^{1/2}_{\pm} = {}_{\mathrm{H}}E^{\mathrm{v}}_0 + \frac{RT}{F}\ln\frac{f'_3}{f'_4} \tag{20}$$

which serves as a definition of a new quantity E''_c which has a definite value for each series of constant acid strength and temperature.

The values for $\gamma'_{\pm}$ and for α'_{w} are taken from Harned and Hamer with a slight correction for the difference between the exact values of m used in our experiments and in theirs as shown in Table III. The values of E''_c are shown in Table IV and as will be seen show a systematic trend with the concentration of the acid varying at 25° from -0.3751 when $c_1 = 1.0$ to -0.3547 when $c_1 = 0.02$. At 0° the trend is slightly greater from -0.3986 to -0.3771 over the same range of concentration. As is apparent from equation (20) this variation is due to the term $RT/F \ln f'_3/f'_4$.

In order to evaluate this term and thereby obtain the desired standard potential we take advantage of the well-known Hückel relationship

$$\log f_i = \frac{-Az_i^2\sqrt{\omega}}{1 + Ba_i\sqrt{\omega}} + \beta\omega \tag{21}$$

where ω is the ionic strength of the solution, z_i the valence and a_i the average distance of nearest approach of the ions, A and B are constants for any solvent and temperature, and β is a constant for any given solvent, temperature and ion. The theoretical limiting slope of the curve obtained by plotting $\log f_i$ against $\sqrt{\omega}$ is $-A$. Numerical values for A and B can be computed from theoretical considerations. a_i and β must be evaluated from the data. a_i is not a characteristic property of each ion but is theoretically the distance of closest approach of the ions in the solution. We shall, therefore, assume that a_i is the same for the trivalent ion as for the divalent ion since they are present together in the same solution. Although this assumption may not be wholly unobjectionable, the data do not permit a separate evaluation of a_i for each ion so that this approximation must be made, and the results indicate that it is good enough for the purpose.

We can, therefore, write

$$\log f'_3/f'_4 = \frac{-9A\sqrt{\omega}}{1 + Ba_i\sqrt{\omega}} + \beta_3\omega + \frac{4A\sqrt{\omega}}{1 + Ba_i\sqrt{\omega}} - \beta_4\,\omega \tag{22}$$

and combining with (20) gives

$$E''_c = {}_{\mathrm{H}}E^{\mathrm{v}}_0 - \frac{5\,RT\,2.30259\,A\sqrt{\omega}}{F(1 + Ba_i\sqrt{\omega})} - \frac{RT\,2.30259\,(\beta_3 - \beta_4)\omega}{F} \tag{23}$$

Then the experimental values are substituted in this equation and plotting E''_c against $\sqrt{\omega}$ and extrapolating to $\sqrt{\omega} = 0$ in such a way that the limiting slope at $\sqrt{\omega} = 0$ is A, the value of ${}_{\mathrm{H}}E^{\mathrm{v}}_0$ can be determined. According to Manov, Bates, Hamer and Acree[12] at 25°: $-A = 0.5092$, and $RT\ 2.30259/F = 0.059138$; and at 0°: $A = 0.4883$, and $RT\,2.30259/F = 0.054179$. For convenience, we write $G = RT\ 2.30259/F(\beta_3 - \beta_4)$. Making these substitutions gives

$$\text{At 25°:}\quad E''_c = {}_{\mathrm{H}}E^{\mathrm{v}}_0 - \frac{0.1505\sqrt{\omega}}{1 + Ba_i\sqrt{\omega}} + G\omega \tag{24}$$

$$\text{At 0°:}\quad E''_c = {}_{\mathrm{H}}E^{\mathrm{v}}_0 - \frac{0.1323\sqrt{\omega}}{1 + Ba_i\sqrt{\omega}} + G\omega \tag{25}$$

In order to estimate the ionic strength, ω, it seems desisable to assume that the dissociation of the first hydrogen of sulfuric acid is complete but that the dissociation of the second hydrogen is incomplete and increases on dilution. Fortunately the dissociation constant of the second hydrogen of sulfuric acid has been determined at both 25 and 0° by Hamer.[13] According to his measurements

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[11] See D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 224.

[12] G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, THIS JOURNAL, 65, 1766 (1943).

[13] W. J. Hamer, *ibid.*, 56, 860 (1934); see also, J. Shrawder, Jr., and I. A. Cowperthwaite, *ibid.*, 56, 2340 (1934).

$$K_2 = \frac{\alpha_H \alpha_s}{\alpha_{HSO_4}} = \frac{m_H m_s}{m_{HSO_4}} \frac{\gamma_H \gamma_s}{\gamma_{HSO_4}} = 0.012 \text{ at } 25°\text{, and}$$
$$K_2 = 0.0148 \text{ at } 0° \quad (26)$$

Noyes and Sherrill[13a] report approximately the same value at 25°, namely, $K_2 = 0.0115$. Klotz[14] and Singleterry[15] found at 25° $K_2 = 0.0102$.

Assuming with Hamer that the first dissociation is complete and the second is partial with the fraction ionized represented by h, we have

$$m_H = m(1 + h) \quad (27)$$
$$m_s = mh \quad (28)$$
$$m_{HSO_4} = m(1 - h) \quad (29)$$
$$\omega = 1/2[m(1 + h) + m(1 - h) + 4mh] = m(1 + 2h) \quad (30)$$

We will also have to assume that in any given solution $\gamma_H = \gamma_{HSO_4}$ which is plausible on the basis of the Debye interionic attraction theory. Making these substitutions in equation (22) gives

$$\ln K_2 = \ln \frac{mh(1 + h)}{1 - h} + \ln \gamma_s \quad (31)$$

where according to Hamer, $K_2 = 0.012$ at 25° and $K_2 = 0.0148$ at 0°.

From Harned and Hamer's measurements of the cell Hg^+, Hg_2SO_4, H_2SO_4 (m_1), H_2^-; ${}_HE_m^{Hg}$, we have

$${}_HE_m^{Hg} = {}_HE_0^{Hg} + \frac{RT}{2F} \ln \alpha_H^2 \alpha_s \quad (32)$$

$${}_HE_m^{Hg} = {}_HE_0^{Hg} + \frac{RT}{2F} \ln m^2 (1 + h)^2 mh + \frac{RT}{2F} \ln \gamma_H^2 \gamma_s \quad (33)$$

We must also assume on the basis of the interionic attraction theory that $\gamma_s = \gamma_H^4$, hence

$$\frac{4F}{RT} ({}_HE_m^{Hg} - {}_HE_0^{Hg}) = 6 \ln m + 2 \ln (1 + h)^2 h + 2 \ln \gamma_s \quad (34)$$

Now eliminating $\ln \gamma_s$ between equations (27) and (30) and converting from natural logarithms to common logarithms gives

$$3 \log m + 3 \log K_2 - \frac{4F}{2.302585\, RT} ({}_HE_m^{Hg} - {}_HE_0^{Hg}) = \log \frac{h}{(1 - h)^3(1 + h)} \quad (35)$$

where ${}_HE_0^{Hg}$ is −0.61515 at 25° and −0.63495 at 0° according to Harned and Hamer. The values for h for each concentration of sulfuric acid were computed by this equation by the use of the measured values of the potentials given in Table III. The results are shown in Table V. As will be seen the values for the degree of dissociation at 25° vary from about 2% at 1 molar to about 42% at 0.02 molar. Similar calculations at 0° give results for the degree of dissociation of sulfuric acid which are substantially less than at 25°.

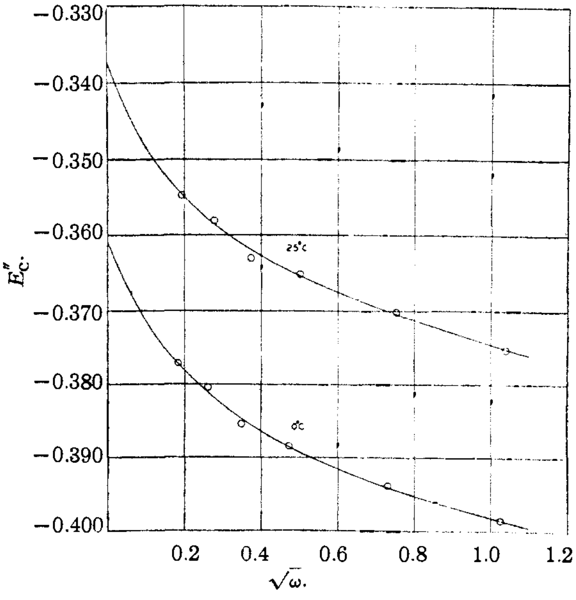

Fig. 4.

Then the values of the parameters ${}_HE_0^v$, βa_i and G in equations (24) and (25), were determined from the data shown in Table V, giving

TABLE V

c_1		ω	E_c'' obs.	$\Delta E_c''$ obs.-comp.	f_3'/f_4'
		At 25°			
1.0	0.02082	1.0804	−0.3571	−0.0001	0.23
0.5	.05591	0.56703	− .3701	+ .0003	.28
.2	.1221	.25120	− .3651	+ .0003	.33
.1	.1916	.13917	− .3630	− .0011	.38
.05	.2723	.07757	− .3580	+ .0006	.44
.02	.4238	.03708	− .3547	− .0001	.51
0	Extrap.		− .3373	Av. .0004	
		At 0°			
1.0	0.00729	1.0523	−0.3986	−0.0001	0.20
0.5	.02231	0.5328	− .3938	+ .0002	.24
.2	.05583	.2244	− .3884	+ .0001	.31
.1	.10278	.1213	− .3854	− .0008	.36
.05	.1775	.06805	− .3804	+ .0006	.42
.02	.3385	.03366	− .3771	− .0001	.50
0	Extrap.		− .3608	Av. .0003	

$$\text{At } 25°\text{: } E_c'' = {}_HE_0^v + \frac{RF}{T} \ln \frac{f_3'}{f_4'} = -0.3373 - \frac{0.1505 \sqrt{\omega}}{1 + 3.573 \sqrt{\omega}} - 0.0042\, \omega \quad (24')$$

$$\text{At } 0°\text{: } E_c'' = {}_HE_0^v + \frac{RT}{F} \ln \frac{f_3'}{f_4'} = -0.3608 - \frac{0.1323 \sqrt{\omega}}{1 + 2.750 \sqrt{\omega}} - 0.0021\, \omega \quad (25')$$

The maximum deviation between the observed values of E_c'' and those computed by the equations is 0.0011 volt at 25° and 0.0008 volt at 0°; and the average deviations are 0.0004 volt at 25° and 0.0003 volt at 0°.

The plot of E_c'' against $\sqrt{\omega}$ corresponding to these data and equations is shown in Fig. 4.

[13a] A. A. Noyes and M. S. Sherrill, THIS JOURNAL, **48**, 1873 (1926).

[14] I. M. Klotz, Diss., Univ. of Chicago (1940).

[15] C. R. Singleterry, Diss., Univ. of Chicago (1940).

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, $\overset{+}{\text{Pt}}$ and the corresponding cell reaction $V^{+++} + H_2O = VO^{++} + {}^1/_2 H_2$ the standard potential is

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

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

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, $\overset{+}{\text{Hg}}$.

2. Combining these data with measurements by Harned and Hamer on the cell $\overset{-}{\text{Pt}}$, H_2, H_2SO_4, Hg_2SO_4, $\overset{+}{\text{Hg}}$, 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-

[1] Original manuscript received November 12, 1943.