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

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.

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[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

$\overset{-}{\mathrm{Pt}}$, $^1/_2V_2(SO_4)_3 + VSO_4 + H_2SO_4$ (0.25 molar), H_2SO_4 (0.25 molar), Hg_2SO_4, $\overset{+}{\mathrm{Hg}}$. 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 $VSO_4 + H_2O\ (l) = {}^1/_2(VO)_2SO_4 + 2H^+ + {}^1/_2SO_4^{=} + e;\ E_0 = 0.21$.

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 $\overset{-}{\mathrm{Hg}}$, $^1/_2V_2(SO_4)_3\ (c_3) + VSO_4\ (c_2) + H_2SO_4\ (c_1)$, $H_2SO_4\ (c_1)$, Hg_2SO_4, $\overset{+}{\mathrm{Hg}}$ 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.

sulted in a concentrated, pure violet colored solution. The solution was siphoned into a flask containing 95% ethyl alcohol, care being taken to insure that the vanadous solution be in the bottom of the flask and under the alcohol and not mixed with the alcohol. If the vanadous sulfate solution is shaken with the alcohol very fine needle-like crystals of vanadous sulfate are obtained with which it is very difficult to work on account of the rapidity with which they are attacked by traces of oxygen. The flask was filled almost completely and then stoppered to prevent access of air. Upon standing the slow mixing with the alcohol by diffusion was effective in causing the practically complete crystallization of the vanadous sulfate in comparatively large crystals. The insolubility of the vanadous sulfate and the solubility of vanadic sulfate in alcohol make it a very simple matter to remove small amounts of oxidized product due to the oxidizing action of air that might come in contact with the crystals during handling in air.

Anal. Calcd. for $VSO_4 \cdot 7H_2O$: V^{++}, 18.66; $SO_4^{=}$, 35.2. Found: V^{++}, 18.8, 18.5; $SO_4^{=}$, 35.87, 35.80.

All other materials were prepared as described in the first paper of this series.

Solutions of vanadous sulfate readily absorb oxygen from the air and are converted into vanadic sulfate according to the reaction $4V^{++} + 4H^+ + 6SO_4^= + O_2 = 4V^{+++} + 6SO_4^= + 2H_2O$. The cell must therefore be designed so as to protect the solutions from the air at all times. Although this is a nuisance it presents no fundamental difficulties. A more serious difficulty is that solutions of vanadous sulfate are inherently unstable, tending to evolve hydrogen and change to vanadic sulfate according to the reaction $2V^{++} + 2H^+ + 3SO_4^= = 2V^{+++} + 3SO_4^= + H_2$.

In the absence of a catalyst and at room temperature this reaction does not occur at a significant speed but in the presence of platinum this reaction occurs rapidly. However, by taking advantage of the high over-voltage of hydrogen on mercury this difficulty can be substantially reduced although not entirely eliminated. This device was used by Forbes and Bartlett for the analogous case of stannic-stannous potential and by Forbes and Richter for the chromic-chromous potential, and by Forbes and Hall for the potential between trivalent and divalent titanium ions,[7] and also by Foerster and Böttcher[5] for the measurement on vanadous salts. These earlier experimenters used a large stationary pool of mercury at the bottom of their cells as the electrode. However, we have found that higher and more reproducible potentials can be obtained by using a form of electrode having a surface of about 1 sq. cm. which can be renewed by admitting more mercury thereby causing the mercury to overflow and giving a fresh surface. On standing the potentials tend to decrease slowly at irregular and non-reproducible rates, but when a fresh surface was created the potential rose. In some cases a visible bubble of gas, presumably hydrogen, appeared on the mercury electrode. The maximum values obtained on fresh surfaces are more reproducible than the potentials on old surfaces and are believed to be nearer the true reversible potentials than the potentials of the old surface. For any given cell these potentials appear to be definite within a few tenths of a millivolt provided successive measurements are made in rapid succession, but if the measurements are prolonged over several hours or days the values on fresh surfaces show a progressive decrease. By removing portions of the solution from the cell from time to time and titrating them it was shown that there is a progressive change of vanadous salt into vanadic salt and these changes in composition can be correlated to the changes in potential. However, the analysis and plotting of the data shows that the results are not as consistent as the analogous data which we obtained for the vanadyl-vanadic potential. This is not surprising because of the unstable character of solutions containing vanadous salts.

The same cell, including the parts, was used in this work as was used in the previous work on the vanadyl–vanadic combination, and shown in Fig. 1 of the first paper of this series, except that the platinum electrodes were replaced by a mercury electrode having a surface of about 1 sq. cm. and so arranged that the surface could be renewed at will during the measurements by opening a stopcock which permitted more mercury to flow to the electrode and thereby causing the mercury at the surface to overflow and fall to the bottom of the cell.

All of the apparatus was essentially the same as that used in the previous work, with minor alterations. The technique for the preparation and handling of the solutions was similar except that special precautions were taken to protect the vanadous sulfate from oxidation by the air. The vanadous sulfate, prepared in the form of comparatively large crystals, was kept stored under ethyl alcohol in which it is almost insoluble but in which any vanadic sulfate which might be formed by oxidation is readily soluble. A suitable quantity was transferred under alcohol to a special weighing bottle filled with alcohol. Then by working in an atmosphere of oxygen-free nitrogen most of the alcohol was removed by suction and the remainder by evaporation. The salt was then weighed in a nitrogen atmosphere. The appropriate amount of vanadic sulfate was then weighed out to give the desired ratio between the two salts (usually 1:1) and the vanadic sulfate dissolved in the sulfuric acid of the desired concentration and the solution swept out with nitrogen. Then the weighed vanadous sulfate was added to the solution with only the momentary exposure to air while it was being transferred from its weighing bottle to the flask containing the acid and vanadic salt. After the vanadous salt had dissolved and the solution had been well mixed by a current of nitrogen, the solution was blown into the cell by the pressure of nitrogen gas. The cell was then mounted in the thermostat and after waiting for temperature equilibrium the potential was measured with repeated renewal of the mercury surface as described above. Then a part of the solution was blown out of the cell for analysis. This analysis was carried out by titration with potassium permanganate to the pentavalent condition, followed by reduction to the tetravalent condition by means of a stream of sulfur dioxide gas, removal of excess of sulfur dioxide, and another titration with potassium permanganate. In some cases the solution was allowed to stand in the cell overnight or longer and new measurements of potential and titrations were made. In such cases the potentials on the fresh mercury surfaces were always lower but the titrations showed that the vanadic salt had increased at the expense of the vanadous salt. After making the measurements at 25° the cell was packed in ice and water and measurements of potential made at 0° followed by the removal of another sample for analysis.

Interpretation of the Data

For the reasons given in the first paper of this series it seems clear that in the presence of excess sulfuric acid to repress hydrolysis the vanadium salts will be present almost entirely as the ions V^{++} and V^{+++}, respectively. Therefore, for the cell

$$\overset{-}{Hg}, VSO_4\ (c_2) + {}^1/_2\ V_2(SO_4)_3\ (c_3) + H_2SO_4\ (c_1),$$
$$H_2SO_4\ (c_1),\ Hg_2SO_4,\ \overset{+}{Hg};\quad {}_{Hg}E$$

the cell reaction will be $V^{++} + {}^1/_2Hg_2SO_4 = V^{+++} + {}^1/_2SO_4^= + Hg$ and the potential will be

$$ {}_{Hg}E^{v}_{m} = {}_{Hg}E^{v}_{0} + E_L + \frac{RT}{F} \ln \frac{\alpha_2}{\alpha_3 \alpha_s{}^{1/2}} \qquad (1)$$

The meaning of the terms will be clear by analogy with the similar case described in the first paper of this series.

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[7] G. S. Forbes and E. P. Bartlett, THIS JOURNAL, **36**, 2030 (1914); G. S. Forbes and H. W. Richter, *ibid.*, **39**, 1140 (1917); G. S. Forbes and L. P. Hall, *ibid.*, **46**, 385 (1924).

In order to evaluate the activity of the sulfate ion, α_s, and also to refer to the measurements of the standard hydrogen electrode we will make use of the data of Harned and Hamer[8] on the cell $\overset{+}{Hg}$, Hg_2SO_4, H_2SO_4 (m), $\overset{-}{Pt}$, H_2; ${}_{H}E_{m}^{Hg}$. For this cell the reaction is $H^+ + Hg + {}^1/_2SO_4^{=} = {}^1/_2H_2 + {}^1/_2Hg_2SO_4$ and the electromotive force

$$ {}_{H}E_{m}^{Hg} = {}_{H}E_{0}^{Hg} + \frac{RT}{F} \ln \alpha_H \alpha_s^{1/2} \qquad (2)$$

Adding equations (1) and (2) gives

$$ {}_{Hg}E_{m}^{v} + {}_{H}E_{m}^{Hg} = {}_{Hg}E_{0}^{v} + {}_{H}E_{0}^{Hg} + E_L + \frac{RT}{F} \ln \frac{\alpha_2 \alpha_H}{\alpha_3} \qquad (3)$$

and the corresponding cell reaction is

$$V^{++} + H^+ = V^{+++} + 1/2H_2$$

Then introducing the stoichiometrical activity coefficients into equation (3) gives

$$E_c = {}_{Hg}E_{m}^{v} + {}_{H}E_{m}^{Hg} + \frac{RT}{F} \ln \frac{c_3}{c_2} = {}_{H}E_{0}^{v} + E_L + \frac{RT}{F} \ln \frac{f_2}{f_3} + \frac{RT}{F} \ln 2\rho_0 m_1 \gamma_H \qquad (4)$$

For any experimental cell we can assign a definite numerical value to all of the terms on the left side of this equation from our measurements or from the measurements of Harned and Hamer after applying a slight correction to adjust the data to the exact concentrations of acid used as is explained in more detail in the first paper of this series (Table IV).

In order to test the hypothesis that we really had a trivalent–divalent oxidation–reduction cell we made potential measurements of three cells of the type given in which the concentration of the sulfuric acid (c_1) was maintained at 1 molar, and the total vanadium concentration ($c_3 + c_2$) at about 0.038 molar, but the ratio of the concentration of the trivalent vanadium (c_3) to the divalent vanadium (c_2) was varied over a wide range. The results are shown in Table I.

TABLE I

POTENTIALS AT 25 AND 0° OF THE CELL $\overset{-}{Hg}$, $1/2V_2(SO_4)_3$ $(c_3) + VSO_4(c_2) + H_2SO_4(c_1 = 1)$, $H_2SO_4(c_1 = 1)$, $\overset{+}{Hg_2SO_4}$, Hg

		At 25°		At 0°	
c_3	c_2	${}_{Hg}E_{m}^{v}$	${}_{Hg}E_{m}^{v} + \frac{RT}{F} \ln \frac{c_3}{c_2}$	${}_{Hg}E_{m}^{v}$	${}_{Hg}E_{m}^{v} + \frac{RT}{F} \ln \frac{c_3}{c_2}$
0.0064	0.0322	0.9943	0.9529v.	1.0082	0.9702v.
.0185	.0192	.9529	.9521	0.9701	.9694
.0290	.0094	.9232	.9520	.9429	.9694

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 much smaller, the ionic strength was approximately a constant at each temperature throughout the series and, therefore, we may regard all of the activity coefficients as approximately constant in this series for each temperature. The liquid junction potentials should be small and not appreciably

TABLE II

VANADIC-VANADOUS OXIDATION-REDUCTION POTENTIALS AT 25°

$c_3 + c_2$	c_3/c_2	${}_{Hg}E_{m}^{v}$, v.	E_c, v.
c_1 = 1.000 molar H_2SO_4		${}_{H}E_{m}^{Hg} = -0.6751$ volt	
0.1046	1.054	0.9543	0.2806
.0661	0.996	.9537	.2785
.0377	.966	.9529	.2769
.01217	.945	.9517	.2752
.00523	.972	.9512	.2754
		$E_c = 0.2749 + 0.0550\ (c_3 + c_2)$	
c_1 = 0.500 molar H_2SO_4		${}_{H}E_{m}^{Hg} = -0.6956$ volt	
0.1361	1.027	0.9584	0.2635
.0879	0.943	.9585	.2614
.0647	0.968	.9571	.2607
	1.094	.9535	.2602
.0342	1.068	.9527	.2588
.02053	0.858	.9587	.2592
	0.993	.9550	.2592
		$E_c = 0.2581 + 0.0383\ (c_3 + c_2)$	
c_1 = 0.200 molar H_2SO_4		${}_{H}E_{m}^{Hg} = -0.7195$ volt	
0.1101	0.918	0.9644	0.2427
	0.972	.9629	.2427
.0764	1.000	.9603	.2408
.0610	1.099	.9591	.2420
.0598	0.903	.9627	.2406
	1.111	.9582	.2414
	1.292	.9540	.2411
.0310	1.079	.9565	.2390
.02586	1.105	.9573	.2394
.01609	0.890	.9616	.2391
	1.076	.9576	.2400
		$E_c = 0.2387 + 0.0365\ (c_3 + c_2)$	
c_1 = 0.100 H_2SO_4		${}_{H}E_{m}^{Hg} = -0.7370$ volt	
0.1410	1.023	0.9647	0.2283
.0931	0.979	.9641	.2266
	1.047	.9610	.2252
.0627	0.962	.9632	.2252
	1.090	.9590	.2242
.0613	0.987	.9609	.2236
.0431	0.964	.9611	.2232
.0280	0.946	.9614	.2230
	1.144	.9545	.2210
.02188	0.964	.9603	.2224
.01084	0.932	.9601	.2213
		$E_c = 0.2212 + 0.0511\ (c_3 + c_2)$	
c_1 = 0.0500 molar H_2SO_4		${}_{H}E_{m}^{Hg} = -0.7542$	
0.1298	0.999	0.9664	0.2122
.0588	.981	.9638	.2091
.0415	.868	.9648	.2069
.02873	.816	.9647	.2053
	1.039	.9587	.2055
.02086	0.867	.9612	.2033
	1.028	.9570	.2035
.01467	0.886	.9597	.2024
		$E_c = 0.2025 + 0.0820\ (c_3 + c_2)$	

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

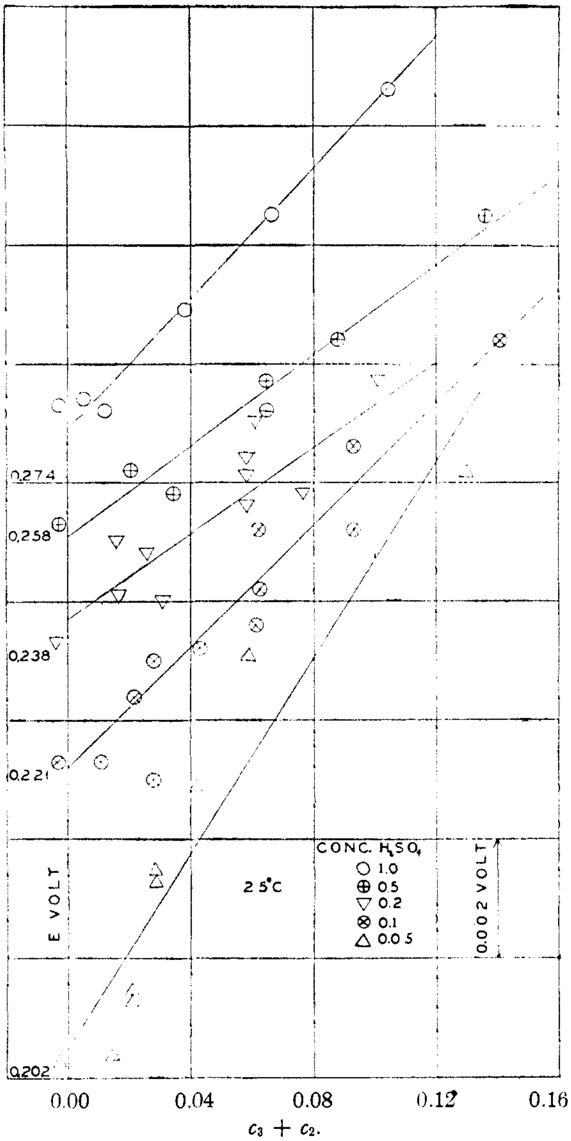

Fig. 1.

variable. Therefore, each side of equation (4) should be approximately a constant. The approximate constancy of the figures in columns 4 and 6 of Table I proves that we are really dealing with a trivalent–divalent potential. This is confirmed by some of the data given in Tables II and III which show the proper correlation between the change in potential on standing and the change of vanadous salt into vanadic salt which occurs on standing.

The experimental data are summarized in Tables II and III and shown in Figs. 1 and 2, which give also the values of E_c as defined by equation (4). For any given series in which the concentration of sulfuric acid is a constant, E_c may be plotted against $c_2 + c_3$ giving approximately a straight line which may be extrapolated to $c_2 + c_3 = 0$, thus giving an intercept which is

TABLE III

VANADIC-VANADOUS OXIDATION-REDUCTION POTENTIALS AT 0°

$c_3 + c_2$	c_3/c_2	$_{Hg}E^{V}_{m}$, v.	E_c, v.
c_1 = 1.000 molar H_2SO_4		$_{H}E^{Hg}_{m}$ = −0.6798 volt	
0.1046	1.054	0.9712	0.2926
.0661	0.996	.9708	.2910
.0377	.966	.9701	.2895
.01217	.945	.9692	.2881
.00523	.972	.9685	.2880
	$E_c = 0.2877 + 0.0480\ (c_3 + c_2)$		
c_1 = 0.500 molar H_2SO_4		$_{H}E^{Hg}_{m}$ = −0.6991 volt	
0.1361	1.027	0.9748	0.2763
.0879	1.023	.9742	.2756
.0647	1.001	.9725	.2734
.0342	1.093	.9687	.2717
.02053	0.858	.9740	.2713
	$E_c = 0.2706 + 0.0447\ (c_3 + c_2)$		
c_1 = 0.200 molar H_2SO_4		$_{H}E^{Hg}_{m}$ = −0.7213 volt	
0.0764	1.181	0.9753	0.2579
.0452	1.264	.9720	.2562
.02590	1.896	.9615	.2552
.01609	0.914	.9772	.2538
.00616	0.847	.9797	.2545
	$E_c = 0.2537 + 0.0555\ (c_3 + c_2)$		
c_1 = 0.100 molar H_2SO_4		$_{H}E^{Hg}_{m}$ = −0.7378 volt	
0.1410	1.023	0.9782	0.2409
.0931	0.994	.9757	.2378
	1.074	.9735	.2374
.0627	0.971	.9762	.2377
.0613	.924	.9767	.2370
.0431	.964	.9761	.2374
.0280	.994	.9741	.2362
.02188	.964	.9753	.2366
.01084	.942	.9757	.2365
	$E_c = 0.2357 + 0.0296\ (c_3 + c_2)$		
c_1 = 0.0500 molar H_2SO_4		$_{H}E^{Hg}_{m}$ = −0.7544 volt	
0.1298	1.044	0.9765	0.2231
.0588	1.112	.9750	.2231
.0415	1.007	.9774	.2232
.02873	0.919	.9765	.2201
.02086	0.932	.9745	.2184
.01467	0.998	.9715	.2171
	$E_c = 0.2187 + 0.0440\ (c_3 + c_2)$		

designated E_c' as is shown in Fig. 2 and Fig. 3. The effect of this extrapolation is to eliminate the liquid junction potential and also the secondary effect of the presence of the vanadium salts on the several activity coefficients. However, this extrapolation does not eliminate the effect of the presence of the sulfuric acid on the activity coefficients of the vanadous, vanadic and hydrogen ions because the concentration of the acid is held constant within any series. Introducing the correcting factors as explained in the first paper of this series

$$f_3 = f_3'k_3;\ f_2 = f_2'k_2;\ \gamma_H = \gamma_H'k_H \qquad (5)$$

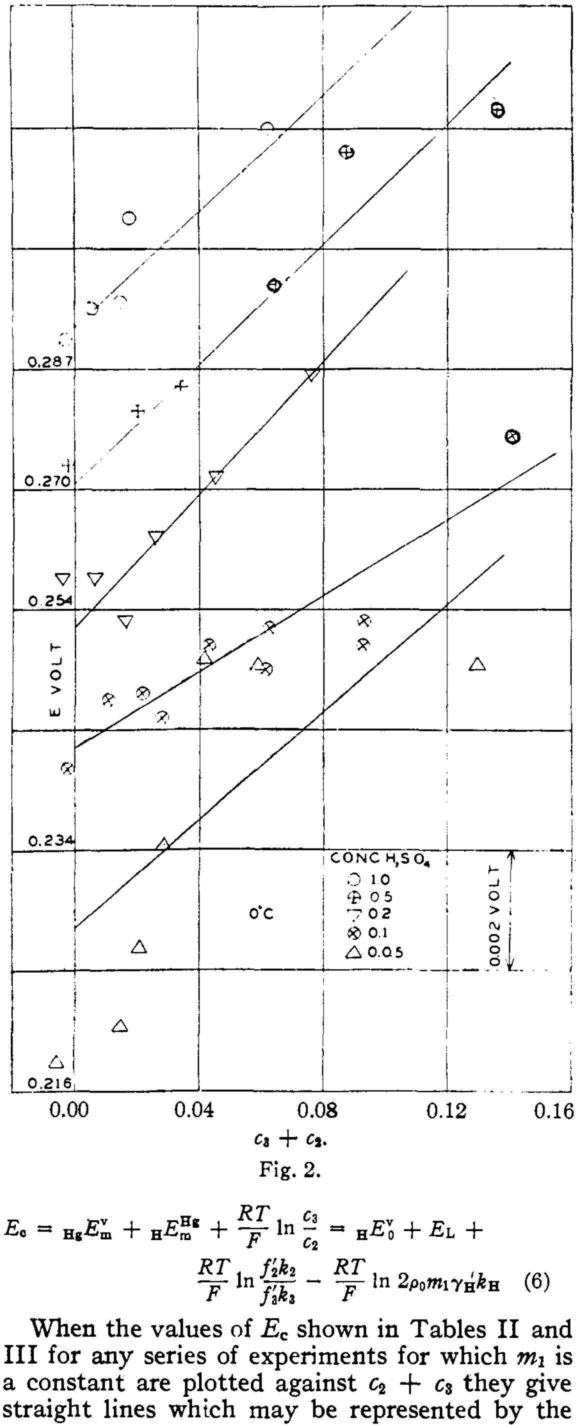

Fig. 2.

$$E_c = {}_{\text{Hg}}E^{\text{V}}_{\text{m}} + {}_{\text{H}}E^{\text{Hg}}_{\text{m}} + \frac{RT}{F}\ln\frac{c_3}{c_2} = {}_{\text{H}}E^{\text{V}}_0 + E_{\text{L}} + \frac{RT}{F}\ln\frac{f_2'k_2}{f_3'k_3} - \frac{RT}{F}\ln 2\rho_0 m_1\gamma_{\text{H}}'k_{\text{H}} \quad (6)$$

When the values of E_c shown in Tables II and III for any series of experiments for which m_1 is a constant are plotted against $c_2 + c_3$ they give straight lines which may be represented by the equation

$$E_c = {}_{\text{Hg}}E^{\text{V}}_{\text{m}} + {}_{\text{H}}E^{\text{Hg}}_{\text{m}} + \frac{RT}{F}\ln\frac{c_3}{c_2} = E_c' + A_c(c_2+c_3) \quad (7)$$

These equations with numerical values for E_c' and A_c are given in Tables II and III. The average deviation between the observed values and these lines is 0.00053 volt at 25° and 0.00065 volt at 0°. These average deviations are about twice as great as for the vanadyl–vanadic potentials which is presumably due to the unstable character of the vanadous salts.

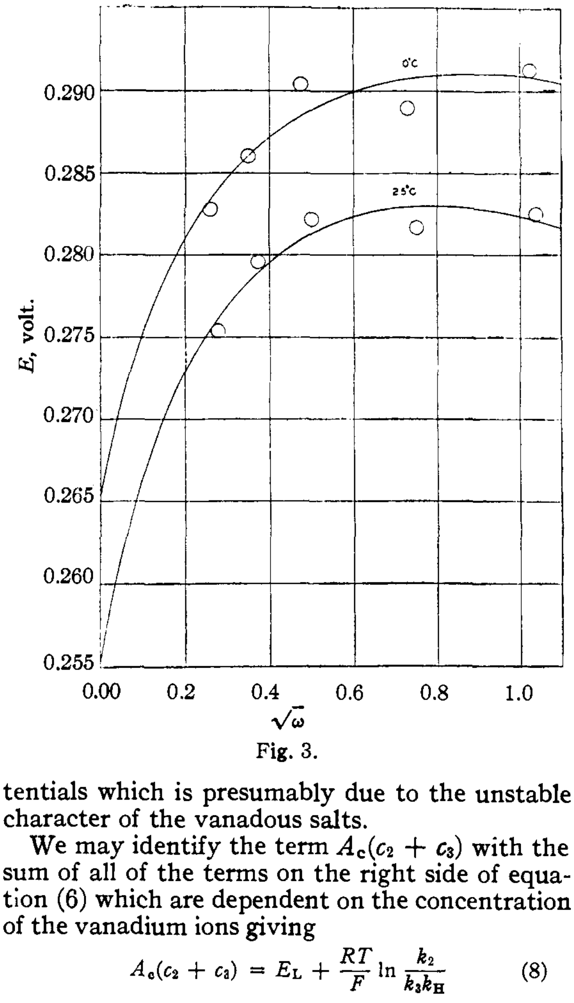

Fig. 3.

We may identify the term $A_c(c_2 + c_3)$ with the sum of all of the terms on the right side of equation (6) which are dependent on the concentration of the vanadium ions giving

$$A_c(c_2 + c_3) = E_{\text{L}} + \frac{RT}{F}\ln\frac{k_2}{k_3k_{\text{H}}} \quad (8)$$

The positive sign found for A_c is in accord with the expectation that $k_2 > k_3k_{\text{H}}$ since the activity coefficient of the trivalent ion is more decreased by the increase in ionic strength due to the presence of acid than is the activity coefficient of the divalent ion.

In a similar manner we may identify the intercept of these straight lines with the sum of all of the terms in equation (6) which are independent of the concentration of the vanadium ions giving

$$E_c' = {}_{\text{H}}E^{\text{V}}_0 + \frac{RT}{F}\ln\frac{f_2'}{f_3'} - \frac{RT}{F}\ln 2m_1\gamma_{\text{H}}' \quad (9)$$

A definite numerical value can be assigned to the term

$$\frac{RT}{F}\ln 2m_1\gamma_{\text{H}}' = \frac{RT}{F}\ln 2m_1\gamma'_{\pm}{}^{1/2} \quad (10)$$

from the work of Harned and Hamer as is explained in detail in the first paper of this series.

Introducing (10) into (9) and rearranging gives

$$E_c'' = E_c' - \frac{RT}{F}\ln 2\rho_0 m_1\gamma'_{\pm}{}^{1/2} = {}_{\text{H}}E^{\text{V}}_0 + \frac{RT}{F}\ln\frac{f_2'}{f_3'} \quad (11)$$

The values for E_c'' are shown in Table IV, and as will be seen show a systematic trend with the con-

TABLE IV

c_1	m_1	$\gamma'_\pm$	$E' + A\ (c_3 + c_2)$	$-\frac{RT}{F} \ln 2m_1\rho_0\gamma'_\pm{}^{1/2}$	E''_c
			At 25°		
1.0	1.0372	0.1283	+0.2749 + 0.0550 $(c_3 + c_2)$	0.0077	0.2826
0.5	0.5100	.1532	.2581 + 0.0383 $(c_3 + c_2)$	.0237	.2818
.2	.2019	.2083	.2387 + 0.0314 $(c_3 + c_2)$	.0435	.2822
.1	.10061	.2652	.2212 + 0.0511 $(c_3 + c_2)$	.0583	.2795
.05	.05022	.3396	.2025 + 0.0820 $(c_3 + c_2)$	.0730	.2755
			At 0°		
1.0	1.0372	0.1705	0.2877 + 0.0480 $(c_3 + c_2)$	0.0036	0.2913
0.5	0.5100	.2007	.2706 + 0.0447 $(c_3 + c_2)$	.0184	.2890
.2	.2019	.2705	.2537 + 0.0555 $(c_3 + c_2)$	.0367	.2904
.1	.10061	.3404	.2357 + 0.0296 $(c_3 + c_2)$	.0504	.2861
.05	.05022	.4251	.2187 + 0.0440 $(c_3 + c_2)$	.0641	.2828

centration of the acid, varying at 25° from 0.2826 when $c = 1.0$ to 0.2755 when $c = 0.05$; and at 0° from 0.2913 to 0.2828 over the same range of concentration. This trend is due to the term $RT/F \ln f'_2/f'_3$. As explained in the first paper of this series this term is expressed as a function of the ionic strength by the Hückel equation and the numerical values of the ionic strength evaluated by the use of Hamer's data and the value of the parameters in the Hückel equation and the value of ${}_{\text{H}}E^{\text{v}}_0$ determined by the method of least squares with the results shown in Table V and in Fig. 3. This method of determining ${}_{\text{H}}E^{\text{v}}_0$ assumes that the plot of log f_1 against the square root of the ionic strength has the theoretical limiting slope.

The results are as follows

$$\text{At } 25°\text{:}\quad E''_c = E^{\text{v}}_0 + \frac{RT}{F} \ln \frac{f'_2}{f'_3} = +\,0.2553 + \frac{0.1505\sqrt{\omega}}{1 + 3.438\sqrt{\omega}} - 0.00688\,\omega \qquad (12)$$

$$\text{At } 0°\text{:}\quad E''_c = +\,0.2654 + \frac{0.1323\sqrt{\omega}}{1 + 3.357\sqrt{\omega}} - 0.0049\,\omega \qquad (13)$$

Table V also shows the values of f'_2/f'_3 computed from equations (12) and (13) above. This table shows that the activity coefficient of the trivalent vanadic ion, V^{+++}, is much more sensitive to the ionic strength than that of the divalent vanadous ion, V^{++}.

However, the involved extrapolation may create an uncertainty amounting to millivolts and the data themselves are less reliable than for the vanadyl–vanadic case so the final results should be expressed more conservatively than in the above equation. For the cell $\overset{-}{\text{Hg}}$, $VSO_4(c_2)$ + $^1/_2$-$V_2(SO_4)_3$ (c_3) + H_2SO_4 (c_1): H_2SO_4 (c_1), $\overset{+}{\text{Pt}}$, H_2 and the corresponding cell reaction $V^{++} + H^+ = V^{+++} + {}^1/_2H_2$ the standard potential is

At 25°: ${}_{\text{H}}E^{\text{v}}_0$ = + 0.255 volt
At 0°: ${}_{\text{H}}E^{\text{v}}_0$ = + 0.265 volt

This means that in a mixed solution of vanadous sulfate, vanadic sulfate and sulfuric acid of such a concentration that the activities are all unity, the divalent vanadous ion tends to change to a trivalent vanadic ion with evolution of hydrogen gas. However, this would not be true for solutions having a pH of about 4.3 or above at 25°, or about 4.9 or above at 0°.

The standard free energy, entropy and heat of reaction, and equilibrium constant of this reaction are given in Table VI.

In calculating the entropy and heat of reaction it has been necessary to make the assumption that the value of dE/dT at 25° is the same as the average value over the interval from 0 to 25°, but this customary assumption is probably a good approximation.

TABLE V

c_1	m_1	k	ω	E''_c obs.	$\Delta E''_c$ obs.-compt.	$\frac{f'_2}{f'_3}$ compt.
			At 25°			
1.0	1.0372	0.2082	1.0804	+0.2826	+0.0004	2.83
0.5	0.5100	.05591	0.58703	.2818	− .0013	2.94
.2	.2019	.1221	.25120	.2822	+ .0009	2.75
.1	.10061	.1916	.13917	.2795	+ .0007	2.49
.05	.05022	.2723	.07757	.2755	− .0008	2.24
0 extrapolated				.2553		
				Av. dev.	.0008	
			At 0°			
1.0	1.0372	0.00729	1.0523	0.2913	+0.0005	2.94
0.5	0.5100	.02231	0.5328	.2890	− .0018	2.94
.2	.2019	.05583	.2244	.2904	+ .0019	2.67
.1	.10061	.10278	.1213	.2861	+ .0001	2.40
.05	.05022	.1775	.06805	.2828	− .0007	2.16
0 extrapolated				.2654		
				Av. dev.	.0010	

TABLE VI

THERMODYNAMIC QUANTITIES FOR THE REACTION $V^{++} + H^+ = V^{+++} + {}^1/_2H_2$ AT UNIT ACTIVITIES OF THE IONS AND H_2 GAS AT 1 ATM.

	25°C.	0°C.
${}_{\text{H}}E^{\text{v}}_0$, v.	+ 0.255	0.265
ΔF^0 k.j.	−24.6	−25.6
ΔF^0 kcal.	− 5.89	− 6.12
ΔS^0 joules/deg.	−39	
ΔS^0 cal./deg.	− 9.3	
ΔH^0 k.j.	−36.0	
ΔH^0 kcal.	− 8.60	
$K = a_2a_{\text{H}}/a_3 =$	4.8×10^{-5}	1.3×10^{-5}

Summary

1. An improved method of making vanadous sulfate, $VSO_4 \cdot 7H_2O$, is described.

2. The oxidation–reduction potential of trivalent–divalent vanadium ions has been determined by potential measurements on cells of the type $\overset{-}{\mathrm{Pt}}$, $^1/_2V_2(SO_4)_3(c_3)$ + $VSO_4(c_2)$ + $H_2SO_4(c_1)$, $H_2SO_4(c_1)$, Hg_2SO_4, $\overset{+}{\mathrm{Hg}}$ at both 25 and 0°.

3. Combining these data with measurements by Harned and Hamer on the cell Pt, H_2, H_2SO_4, Hg_2SO_4, Hg we have estimated the standard potential of the cell dependent on the reaction $V^{++} + H^+ = V^{+++} + {}^1/_2H_2$, and the equilibrium constant of this reaction.

$$ {}_{\mathrm{H}}E_0^{\mathrm{v}} = +0.255 \text{ at } 25° $$
$$ {}_{\mathrm{H}}E_0^{\mathrm{v}} = +0.265 \text{ at } 0° $$
$$ K = \alpha_2\alpha_{\mathrm{H}}/\alpha_3 = 4.8 \times 10^{5} \text{ at } 25° $$
$$ K = \alpha_2\alpha_{\mathrm{H}}/\alpha_3 = 1.3 \times 10^{-5} \text{ at } 0° $$

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

The Light Absorption and Fluorescence of Triarylmethyl Free Radicals

BY GILBERT N. LEWIS, DAVID LIPKIN AND THEODORE T. MAGEL

The experiments here described had the double purpose (1) of seeking the relation between color and structure in odd molecules and (2) of looking for the "windmill" type of isomerism, which, however, has since been definitely established in the ions of crystal violet and malachite green.[1] Unfortunately, our experimental work was abruptly terminated some years ago so that the interpretation of some of the curves must await further study.

The Absorption and Fluorescence Spectra of Triphenylmethyl.—When the spectrum of triphenylmethyl is observed visually, two sharp absorption bands are seen. The one at higher frequency was found by Anderson[2] to have a double maximum. In order to ascertain whether the several absorption bands represent merely vibrational terms in a single electronic band, we have studied photographically, and with high dispersion, both the absorption and fluorescence of triphenylmethyl. In order to bring out structure both experiments were made at liquid air temperature in the EPA solvent (5 parts ether, 5 parts isopentane and 2 parts ethanol by volume).

When a solution of triphenylmethyl is cooled some fifty degrees below 0° it gradually becomes colorless, owing to almost complete dimerization. On the other hand, when the solution in EPA is suddenly cooled by liquid air it preserves its color indefinitely and under these conditions it is not even photosensitive. Evidently the photochemical process is at least bimolecular and bimolecular reactions cannot occur in rigid media.[3]

Figure 1 is a direct microphotometer tracing of the photograph of the absorption spectrum of triphenylmethyl. Figure 2 gives the corresponding tracing for the fluorescence spectrum. Both spectra prove to be remarkably complex. In Fig. 1 we have indicated seven and in Fig. 2 nine distinct bands which are undoubtedly real since they were confirmed by complete repetition of the photographing and microphotometer tracing.

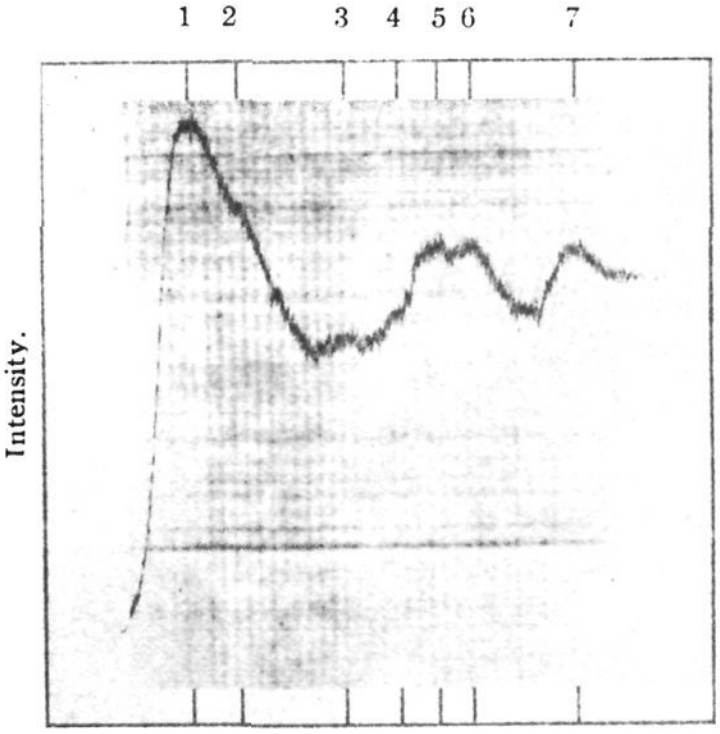

Fig. 1.—Absorption spectrum of triphenylmethyl in EPA at 90°K. There are at least 7 recognizable maxima at the positions marked. The frequencies (cm.$^{-1}$) of the numbered peaks in Figs. 1–5 are given in Table I.

In a molecule so loosely constructed it is most remarkable to find so much resolution of vibrational structure and such narrow individual vibrational bands. In molecules with an even number of electrons, such fine structure is to be found only in tightly bonded structures such as that of perylene.[4]

The extreme sharpness of the bands, especially of the first band, in triphenylmethyl and its alkyl derivatives, shown in later figures, makes it possible to recognize these radicals even in the presence of other colored substances.[3] This sharpness

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[1] Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

[2] Anderson, *ibid.*, **57**, 1673 (1935).

[3] Lewis and Lipkin, *ibid.*, **64**, 2801 (1942).

[4] Dadieu, *Z. Elektrochem.*, **35**, 283 (1929).