286. *Vanadium Ion Oxidation–Reduction Potentials.*

By A. B. Hart and J. R. Partington.

The electromotive forces of cells containing 4- and 5-valent vanadium ions in solutions of hydrochloric and sulphuric acids have been measured and the standard potentials calculated. The formulæ of the 4- and the 5-valent vanadium ions are discussed, and it is shown that their electrochemical behaviour in acid solutions is best explained on the assumption that they exist as $VO^{\cdot\cdot}$ and $VO_2^{\cdot}$, respectively.

The red vanadium pentoxide is more soluble in strong acids than in water, forming feebly coloured solutions, usually greenish-yellow, which contain 5-valent vanadium in a state usually described as vanadic acid and formulated as HVO_3, since the simple salts formed with bases are MVO_3. On reducing this solution with sulphur dioxide, etc., a more intensely coloured blue solution is obtained which contains 4-valent vanadium in a form described as a vanadyl salt, *e.g.*, $VOSO_4$, yielding the vanadyl ion $VO^{\cdot\cdot}$. Rutter (*Z. anorg. Chem.*, 1907, **52**, 368) showed that the electrochemical reaction between vanadic acid and vanadyl sulphate was reversible, and obtained a comparative value of the normal reduction potential of vanadic acid in 0·5N-sulphuric acid. Foerster and Böttcher (*Z. physikal. Chem.*, 1930, **151**, 321), in a more comprehensive investigation of the electrolytic reduction of vanadium solutions, suggested the electrode reaction

$$VO_2^{\cdot} + 2H^{\cdot} = VO^{\cdot\cdot} + H_2O + \boldsymbol{F} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with the following equation representing the formation of the 5-valent ion in acid solution :

$$V_2O_5 + H_2SO_4 = (VO_2)_2SO_4 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is equivalent to an amphoteric function of vanadic acid :

$$HVO_3 + H^{\cdot} = VO_2^{\cdot} + H_2O$$

The cells used by Foerster and Böttcher were of the type

$$\mathrm{Hg}\left|\mathrm{Hg_2SO_4},\ (a)\ 2\text{N-}\mathrm{H_2SO_4},\ (b)\ \text{N-}\mathrm{H_2SO_4}\right|\begin{array}{l} \left.\begin{array}{l}\text{(i) } 3\text{N-}\mathrm{H_2SO_4} \\ \text{(ii) } 1{\cdot}5\text{N-}\mathrm{H_2SO_4}\end{array}\right\}[\mathrm{VO_2^{\cdot}}] \\ \quad 0{\cdot}75\text{N-}\mathrm{H_2SO_4}\ \ [\mathrm{VO^{\cdot\cdot}}] \end{array}\Bigg|\,\mathrm{Pt}$$

and all involved a liquid contact potential which was not allowed for. The vanadium-ion concentrations were kept equal, the solution being prepared by the electrolytic reduction of a solution of the pentoxide in sulphuric acid until half the vanadium was in the 4-valent state. From the initial concentration of acid, and equations (1) and (2), the acid concentration in the cell was calculated. The assumed reaction scheme leads to the following equation for the E.M.F. of the half-cell :*

$$E = E_0 + \phi \ln (VO_2^{\cdot})(H^{\cdot})^2/(VO^{\cdot\cdot}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and hence for two different acid concentrations :

$$\Delta E = 2\phi \ln (H^{\cdot})_1/(H^{\cdot})_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

if the activity ratio of the vanadium ions is unaltered by change of acid concentration. Values of ΔE were calculated on the assumption that $(H^{\cdot}) = a_{\pm}$ for sulphuric acid (Lewis and Randall, " Thermodynamics," 1923, 357). There was only approximate agreement between the observed and calculated values of ΔE, especially at the lowest vanadium concentration of 0·03, but the results provide a general indication that the 5-valent vanadium ion exists in acid solutions mainly as $VO_2^{\cdot}$.

Coryell and Yost (*J. Amer. Chem. Soc.*, 1933, **55**, 1909) measured the E.M.F. of the cell

$$Pt|HVO_3,VOCl_2,HCl|HCl,Hg_2Cl_2|Hg$$

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* The following notation is used : (A) = activity of species A, [A] = concentration of A in mole/l. ; f_A = activity coefficient of A defined by $(A) = f_A[A]$, with the special values $f_1 = f_{VO^{\cdot\cdot}}$, $f_2 = f_{VO_2^{\cdot}}$; $\phi = \boldsymbol{RT/F}$.

in which the liquid contact potential was practically eliminated by having the hydrochloric acid concentrations on both sides very approximately equal, and the vanadium concentration small as compared with that of the acid. The 5-valent vanadium was now supposed to exist as HVO_3 and the cell reaction was formulated as

$$HVO_3 + 3H^{\cdot} + Cl' + Hg = VO^{\cdot\cdot} + 2H_2O + HgCl \quad . \quad . \quad . \quad (5)$$

The authors did not explain the dependence of the E.M.F. on the acid concentration, but for each acid concentration they calculated a standard potential

$$E'' = E' - \phi \ln [HVO_3]/[VOCl_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

E' being the observed E.M.F. It was found that E'' was practically constant at a fixed acid concentration when the concentration ratio of the vanadium species was varied, thus indicating that the vanadium ions both contained the same number of vanadium atoms and that their activity coefficients were constant between the concentration limits used.

A standard potential for the vanadium electrode follows from (5):

$$E_0 = E'' - \phi \ln (H^{\cdot})^3(Cl') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To evaluate this, Coryell and Yost used activity coefficients of hydrochloric acid (Randall and Young, *J. Amer. Chem. Soc.*, 1928, **50**, 989), and to refer E_0 to the standard hydrogen electrode they added the potential of the electrode $Hg|Hg_2Cl_2$, $(Cl') = 1$, which was taken as 0·2689 on the hydrogen scale. The values found were:

Moles HCl/1000 g. of H_2O	2·146	0·5106	0·1012	0·01012
E_0, volts	1·0115	1·0527	1·0822	1·1271

The change of E_0 was attributed to the decrease in activity of the vanadic acid with rising acid concentration, and the solubility of vanadic acid was found to increase rapidly with increase in acid concentration, which would agree with this assumption. The activity coefficients calculated from the solubilities were also shown to be in approximate agreement with the values from E.M.F. measurements when the activity coefficients of $VO^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$ were assumed to be equal at the same ionic strength.

From electrometric titrations of solutions of vanadium pentoxide in acid solutions with ferrous sulphate, and from the oxidation of vanadyl salt solutions with permanganate, Britton (J., 1934, 1842) estimated the effect of the acid on the oxidation–reduction potential and the approximate calculations are held to agree with reaction (5).

The work so far described did not completely solve the problem of the formula of the 5-valent vanadium ion and was followed by the more systematic investigation of Carpenter (*J. Amer. Chem. Soc.*, 1934, **56**, 1847). In this, perchloric acid was used and the E.M.F. of the cell

$$Pt|VO_2ClO_4,VO(ClO_4)_2,HClO_4|HClO_4|H_2,Pt$$

was measured under conditions in which the concentration either of vanadium ions or of acid was altered whilst the remaining concentrations were kept constant. From the results, the nature of the cell reaction and hence the formulæ of the vanadium ions could be derived. The single assumption made was that the vanadyl ion is $V_zO_z^{2z+}$. Then if the 5-valent ion is written $V_xO_y^{(5x-2y)+}$, the cell reaction is

$$V_xO_y^{(5x-2y)+} + \frac{x}{2} H_2 + (2y - 3x)H^{\cdot} = \frac{x}{z} V_zO_z^{2z+} + (y - x)H_2O \quad . \quad . \quad (8)$$

The E.M.F. of the cell, with $p_{H_2} = 1$ atm., could then be written:

$$E = E_0 + \frac{1}{x}\phi \ln (V_xO_y^{(5x-2y)+})(H^{\cdot})^{(2y-3x)}/(V_zO_z^{2z+})^{x/z} \quad . \quad . \quad . \quad (9)$$

If now the concentrations of any two solutions are kept constant whilst that of a third is varied, three relations are obtained (activities replaced by concentrations):

$$\left.\begin{array}{l} \text{(i) } E = E_1 + \phi/x \,.\, \ln [V^{V}] \\ \text{(ii) } E = E_2 + \phi/x \,.\, (2y - 3x) \ln [H^{\cdot}] \\ \text{(iii) } E = E_3 - \phi/z \,.\, \ln [V^{IV}] \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and by plotting E against the logarithm of the variable concentration all the unknowns are found. The plots were approximately straight lines, the slopes of which gave $x = 1{\cdot}09$ from (10, i), and by assuming $x = 1$ it was found from (10, ii) that $y = 2{\cdot}08$, thus indicating that the V^{V} ion is $VO_2^{\cdot}$ or possibly $V(OH)_4^{\cdot}$. On the assumption that the ion is $VO_2^{\cdot}$, Carpenter showed that Coryell and Yost's acid molalities were greater than the actual values owing to the reaction $HVO_3 + H^{\cdot} = VO_2^{\cdot} + H_2O$. This was corrected by the equation :

$$E_{\text{corr.}} = \mathrm{E}_{\text{C. \& Y.}} + 2\phi \ln [H^{\cdot}]_{\text{C.}\quad\text{Y.}}/[H^{\cdot}]_{\text{act.}}$$

and the corrected values were used to obtain E_0, the standard potential of the electrode. The cell reaction giving rise to the E.M.F. became in place of (5) :

$$VO_2^{\cdot} + 2H^{\cdot} + Cl' + Hg = VO^{\cdot\cdot} + H_2O + HgCl \quad . \quad . \quad . \quad . \quad (11)$$

and the E.M.F. was represented by an equation :

$$E_0 = E - \phi \ln [VO_2^{\cdot}][H^{\cdot}]^2[Cl']/[VO^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which all activity coefficients are assumed equal to unity; E_0 is the normal potential referred to the calomel electrode in hydrochloric acid, $(Cl') = 1$, as zero. Extrapolation of (12) against the square root of the ionic strength should give a limiting value of E_0 when the activity coefficients are unity. Carpenter found this to be 0·7307 volt, or 0·9996 volt on the hydrogen scale.

EXPERIMENTAL.

(1) *Preparation of Materials.—Vanadium pentoxide.* Hydrated vanadic acid (B.D.H.) was converted into ammonium metavanadate by warming it with a large volume of ammonia solution, filtering the solution hot, and saturating it with ammonium chloride, a white precipitate of NH_4VO_3 being obtained. It was found that addition of excess of ammonia to an acid solution of the vanadium pentoxide resulted in a discoloured product. The ammonium vanadate was fractionally crystallised three times from water and finally from conductivity water, the solutions not being heated above 70°, as this caused decomposition. The final product was dried and converted into vanadium pentoxide by careful heating in a current of pure oxygen in a platinum boat in a combustion tube. The solid became uniformly black and finally dark red, and at this point the temperature was raised to just below the fusion point for 15 minutes. Fusion was avoided as it gives rise to a crystalline product almost insoluble in acids even after prolonged boiling. When cold, the pentoxide was light orange in colour, and analysis by Ramsey's method (*J. Amer. Chem. Soc.*, 1927, **49**, 1138), and by reduction with sulphur dioxide and permanganate titration, gave agreement with theory if a small amount (0·5—1%) of V_2O_4 was allowed for. This probably originated from contamination of the ammonium vanadate with small fibres of filter paper. Solutions of vanadic acid were made in the pure acid of appropriate concentration by boiling and filtering.

Vanadyl solutions. The sulphate solution was made by reducing a suspension of the pentoxide in dilute sulphuric acid with sulphur dioxide, the excess of the latter being removed by boiling. A trace of residual sulphur dioxide would not affect the measurements, since on adding vanadic acid it would be removed. Vanadyl chloride solution was made by the method of Yost and Claussen (*J. Amer. Chem. Soc.*, 1931, **53**, 3349) by boiling a suspension of the pentoxide in just less than the theoretical amount of pure dilute hydrochloric acid and reducing it with hydrogen sulphide gas, filtering off the sulphur after adding sufficient acid to dissolve the black precipitate of V_2O_4, and removing the excess of hydrogen sulphide by boiling and filtering.

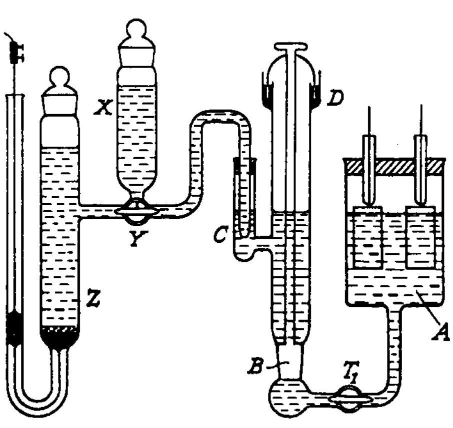
The concentration of the vanadic acid solution was determined by reducing it with sulphur dioxide, expelling the excess of the latter with a current of carbon dioxide, boiling, and finally titrating with permanganate. The method used was that recommended by Cain and Hostetter (*J. Amer. Chem. Soc.*, 1912, **34**, 274), *viz.*, reduction in solutions dilute with respect to vanadium and with sulphuric acid present to about 2N-concentration. The presence of hydrochloric acid did not affect the end-point.

Mercurous sulphate was prepared electrolytically by Hulett's method (*Physical Rev.*, 1911, **32**, 257, and was kept and used as described by Partington and Stonehill (*Trans. Faraday Soc.*, 1935, **31**, 1357). The product was slightly grey owing to finely divided mercury, but much less so than the calomel. Mercurous chloride was also prepared by the usual electrolytic method (Ellis, *J. Amer. Chem. Soc.*, **1916**, **38**, 737). The uniformly grey product was washed with water, dried at 100°, and kept in a calcium chloride desiccator in the dark. Before use it was allowed to stand in some of the appropriate acid.

The hydrochloric and sulphuric acid stock solutions were analysed both volumetrically and gravimetrically by the usual methods.

The mixed stock solutions for the cells were made by mixing the required volumes of vanadyl and vanadic solutions so as to give the 4- and the 5-valent ions in equivalent amounts. Allowance was made for a trace of V_2O_4 in the latter solution, especially in the case of hydrochloric acid solutions, where some reduction had occurred on boiling. The mixed solution was then completely analysed. The vanadyl salt was titrated and the total vanadium determined by sulphur dioxide reduction and titration, the 5-valent vanadium being determined by difference. The acid was determined gravimetrically, hydrochloric by precipitation of silver chloride and sulphuric by precipitation of the total sulphate as barium sulphate. The free acid present could then be calculated by allowing for the acid radical present as vanadium salts. The cell solutions were made by diluting with conductivity water.

(2) *Apparatus and Experimental Method.*—The cells used, shown in the figure, were of Pyrex glass. The right-hand side was the vanadium electrode. Solution was added to compartment A with the tap T_1 closed. The tap was then opened and the liquid allowed to run as far as the top of the ground glass plug B fitting into a ground socket. When the vessel was filled with vanadium solution as far as the plug, sulphuric acid was added to the other side through C. The two electrodes were then inserted into A, sealed in with paraffin wax, and the trap D closed with mercury or by pouring in a little melted paraffin wax. The reference electrode vessel was constructed with an acid reservoir X connected with the side tube by a three-way tap Y. This enabled the side tube to be freed from air bubbles, and acid to be added to the compartment above the plug. No attempt was made to exclude air, since it was found by special experiments, in agreement with Carpenter (*loc. cit.*), that with the acid concentrations used the substitution of air by nitrogen did not produce any change in the E.M.F. With very small acid concentrations the exclusion of oxygen would probably be necessary.



Bright platinum electrodes were used. The effect of previous polarisation by electrolysis in dilute sulphuric acid was not marked, the same equilibrium value being found with and without this treatment, and the time for attaining equilibrium was not appreciably shortened. The electrodes were arranged so that the strained part of the foil to which the platinum conducting wire was attached by welding did not come in contact with the liquid. The reference electrodes Z were made up with acid which had stood with some depolariser for some hours. At each concentration two reference electrodes and three vanadium electrodes were made up and measured against one another, and differences of more than 0·01 mv. were rare. Mercurous sulphate electrodes were easier to prepare than calomel electrodes, which occasionally differed by 0·2 mv. and were then discarded.

The cells were placed in a well-stirred air thermostat controlled to 25° ± 0·02°, as measured by a standard thermometer in a vessel of water of approximately the same heat capacity as the cells. Readings were usually taken during 2 days, although in a few cases cells were observed over a period of 8—14 days. After the second day, variations more than 0·2—0·3 mv. did not occur. The equilibrium value was reached after 2—4 hours except with more dilute solutions, for which satisfactory results were not obtained until the second day. Reproducible results were obtained without the use of a potential mediator, *e.g.*, ferric chloride. E.M.F. measurements were made to 0·1 mv. by a Tinsley ionisation potentiometer, Weston standard cell calibrated by the N.P.L., and a sensitive D'Arsonval galvanometer. All apparatus (cells, galvanometer, and potentiometer) was earthed on metal foil, and the leads were in an earthed metal casing.

Results.

Table I gives the experimental results for the cell $\overset{+}{\mathrm{Pt}}|\mathrm{VO_2Cl},\mathrm{VOCl_2},\mathrm{HCl}|\mathrm{HCl},\mathrm{Hg_2Cl_2}|\overset{-}{\mathrm{Hg}}$. The mercury electrode was negative, and by convention the sign of the E.M.F. was positive

(positive electricity flowing through the cell inside from right to left). The stock solution analysis was : $[\mathrm{HCl}] = 0{\cdot}5758$, $[\mathrm{VO_2Cl}] = 0{\cdot}01694$, $[\mathrm{VOCl_2}] = 0{\cdot}01694$, hence $[\mathrm{VO_2^{\cdot}}]/[\mathrm{VO^{\cdot\cdot}}] = 1$ and only $[\mathrm{VO^{\cdot\cdot}}]$ is given in the table.

TABLE I.

$[\mathrm{HCl}] \times 10^4$	5758	3791	3033	1011	551·5	124·7
$[\mathrm{VO^{\cdot\cdot}}] \times 10^5$	1694	1115	892·5	297·5	162·3	36·91
E, volt	0·6980	0·6612	0·6408	0·5547	0·5077	0·3926

Table II gives the results for the cell $\overset{+}{\mathrm{Pt}}|(\mathrm{VO_2})_2\mathrm{SO_4},\mathrm{VOSO_4},\mathrm{H_2SO_4}|\mathrm{H_2SO_4},\mathrm{Hg_2SO_4}|\overset{-}{\mathrm{Hg}}$. The stock solution analysis was : $[\mathrm{H_2SO_4}] = 0{\cdot}5428$, $[\mathrm{VOSO_4}] = 0{\cdot}01228$, $[(\mathrm{VO_2})_2\mathrm{SO_4}] = 0{\cdot}01232$, so the ratio $[\mathrm{VO_2^{\cdot}}]/[\mathrm{VO^{\cdot\cdot}}]$ is 1·0031. The E.M.F. values should be corrected by the addition of $\Delta E = -\phi \ln 1{\cdot}0031 = -0{\cdot}00007$ volt, and thus 0·1 mv. should be subtracted from the observed E.M.F. in each case. This has not been done with the figures in the table, the correction being made on the final value of E_0. Every value in Table II is the average of at least three measurements with completely different cells against two different reference electrodes which could be regarded as identical. Thus six platinum electrodes could be used for measurement. The two electrodes in one half-cell gave identical values, and with different cells agreement to 0·1 mv. was attained in most cases. With the last two cells in the table the possible error was 0·2 mv.

TABLE II.

$[\mathrm{H_2SO_4}] \times 10^4$	4794	2714	1357	1086	977·0	814·1
$[\mathrm{VO_2^{\cdot}}] \times 10^5$	1088	616·0	308·0	246·4	221·8	184·8
$[\mathrm{VO^{\cdot\cdot}}] \times 10^5$	1084	614·0	307·0	245·6	221·0	184·2
E, volt	0·3558	0·2859	0·2494	0·2377	0·2321	0·2225
$[\mathrm{H_2SO_4}] \times 10^4$	651·4	542·1	355·0	271·4	217·1	81·30
$[\mathrm{VO_2^{\cdot}}] \times 10^5$	147·8	123·1	80·60	61·60	49·28	18·47
$[\mathrm{VO^{\cdot\cdot}}] \times 10^5$	147·4	122·7	80·33	61·40	49·12	18·42
E, volt	0·2108	0·2021	0·1792	0·1652	0·1538	0·0980

DISCUSSION OF RESULTS.

(*a*) *The Chloride Cells.*—The method used by Carpenter in finding E_0 from the corrected results of Coryell and Yost, explained above, may be applied to the present results. The E.M.F. of the cell reaction (11) is

$$E = E_0' + \phi \ln (\mathrm{VO_2^{\cdot}})(\mathrm{H^{\cdot}})^2(\mathrm{Cl'})/(\mathrm{VO^{\cdot\cdot}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$E_0' = E_0 - E_{0\,\mathrm{Hg}}$$

where $E_{0\,\mathrm{Hg}}$ is the standard potential of the calomel electrode $\mathrm{Hg}|\mathrm{Hg_2Cl_2},(\mathrm{Cl'}) = 1$, and E_0 is the required standard potential of the vanadium ion electrode referred to the standard hydrogen electrode. This is related to the equilibrium constant for the solution by the equation

$$E_0 = \phi \ln K$$

where

$$K = (\mathrm{VO^{\cdot\cdot}})/(\mathrm{VO_2^{\cdot}})(\mathrm{H^{\cdot}})$$

Equation (12) may be rearranged as follows :

$$E - \phi \ln (\mathrm{H^{\cdot}})^2(\mathrm{Cl'}) - \phi \ln [\mathrm{VO_2^{\cdot}}]/[\mathrm{VO^{\cdot\cdot}}]$$
$$= E_0' + \phi \ln f_2/f_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and since $[\mathrm{VO_2^{\cdot}}] = [\mathrm{VO^{\cdot\cdot}}]$ and $(\mathrm{H^{\cdot}})^2(\mathrm{Cl'}) = [\mathrm{HCl}]^3 f^3_{\mathrm{HCl}}$, this equation may also be written:

$$E - 3\phi \ln [\mathrm{HCl}] = E_0' + \phi \ln f_2 f^3_{\mathrm{HCl}}/f_1 \quad . \quad . \quad . \quad . \quad (13a)$$

Extrapolation of the left-hand side against a suitable function of the ionic strength I to $I = 0$ should yield E_0', since at infinite dilution the activity coefficients all become unity. The points follow a curve very similar to that found by Carpenter, and lead to a limiting value of $E_0' = 0{\cdot}7303$ volt. This gives $E_0 = E_0' + 0{\cdot}2689 = 0{\cdot}9992$ volt, which compares very well with Carpenter's value of 0·9996 volt, so that the standard potential of this system may be considered to be well established.

If in (13) we write $(\mathrm{H^{\cdot}})^2(\mathrm{Cl'}) = (\mathrm{H^{\cdot}})a^2_{\pm}$ and then assume $(\mathrm{H^{\cdot}}) = a_{\pm}$ we find :

$$E - 3\phi \ln a_{\pm} - \phi \ln [\mathrm{VO_2^{\cdot}}]/[\mathrm{VO^{\cdot\cdot}}] = E_0' + \phi \ln f_2/f_1 \quad . \quad . \quad . \quad (14)$$

and extrapolation of the left-hand side against $I^{\frac{1}{2}}$ to $I = 0$ should yield E_0'. The values of $a_{\pm}$ are obtained from $f_{\pm \mathrm{HCl}}$, which at the concentrations used does not differ appreciably from the activity coefficient referred to molalities, for which Randall and Young's values (*loc. cit.*) may be used. The plot of the left-hand side of (14) against $I^{\frac{1}{2}}$ to zero ionic strength gives a steep, almost straight line leading to a rather uncertain extrapolation to $E_0' = 0{\cdot}7305 \pm 0{\cdot}001$, in good agreement with the value previously obtained, 0·7303.

If we put $E - 3\phi \ln a_{\pm} = E_x$, then from (14) :

$$E_x - E_0' = \phi \ln f_2/f_1$$

$$(E_x - E_0')/0{\cdot}05915 = \log_{10} f_2/f_1 \quad . \; . \; . \; . \; . \; . \; . \quad (15)$$

This enables us to find the activity ratio of the vanadium ions. Since this value is not otherwise known, it cannot be used as a check on the results unless it is assumed that f_2 and f_1 are the same as for a univalent and a bivalent ion, respectively, as given by the Debye and Hückel values. It is known, however, that over the range of concentrations dealt with, $\ln f_{\mathrm{I}}/f_{\mathrm{II}}$, where the subscripts refer to uni- and bi-valent ions, is positive and increases with the ionic strength I. This is in agreement with the present results, since in (15), E_x increases with I. The Debye and Hückel equation for a single ion (see Partington, " Chemical Thermodynamics," 1940, p. 143) gives

$$\log_{10} f_2/f_1 = (4 - 1)h\sqrt{I}/(1 + Aa\sqrt{I}) = 3h\sqrt{I}/(1 + Aa\sqrt{I})$$

where it is assumed that the ionic diameter a is a mean value for both ions. The value 3·64 A. for a gives the following values of $\log_{10} f_2/f_1$, which are compared with the experimental values of $(E_x - E_0')/0{\cdot}05915$:

[HCl]	0·5758	0·3791	0·3033	0·1011	0·05515	0·01247
$\log_{10} f_2/f_1$	0·6099	0·5532	0·5121	0·3570	0·2847	0·1556
$(E_x - E_0')/0{\cdot}05915$	0·5224	0·4648	0·4057	0·3145	0·2592	0·1572

The calculated and observed values show the same kind of agreement as is usually obtained with the Debye and Hückel theory at the lower concentrations, and it may be said that, although the rise in E_x with concentration is due mainly to the effect of a rise in I on the value of $\log_{10} f_2/f_1$, there may also be a smaller effect which decreases more slowly with concentration than the first.

(*b*) *The Sulphate Cells.*—The cell reaction in the sulphuric acid solutions, where the reference electrode is mercurous sulphate|mercury, is $VO_2^{\cdot} + 2H^{\cdot} + Hg + \frac{1}{2}SO_4'' = VO^{\cdot\cdot} + H_2O + \frac{1}{2}Hg_2SO_4$, which gives for the E.M.F. :

$$E = E_0'' + \phi \ln(VO_2^{\cdot})(H^{\cdot})^2(SO_4'')^{1/2}/(VO^{\cdot\cdot}) \quad . \; . \; . \; . \; . \quad (16)$$

and $E_0'' = E_0 - E_0'{}_{\mathrm{Hg}}$, where $E_0'{}_{\mathrm{Hg}}$ is the standard potential of the electrode $Hg|Hg_2SO_4,H_2SO_4$ $(SO_4'') = 1$, referred to the standard hydrogen electrode as zero. A difficulty arises here in that $E_0'{}_{\mathrm{Hg}}$ is not known, and hence if E_0'' is found by suitable extrapolation, E_0 cannot be calculated from the above equation. The value for the electrode $Hg|Hg_2SO_4,H_2SO_4$ $(H_2SO_4) = 1$ is 0·6231 volt (Randall and Cushman, *J. Amer. Chem. Soc.*, 1918, **40**, 393). E_0'' is found as follows. Equation (16) is rearranged :

$$E - \phi \ln (H^{\cdot})^2(SO_4'')^{\frac{1}{2}} - \phi \ln [VO_2^{\cdot}]/[VO^{\cdot\cdot}] = E_0 + \phi \ln f_2/f_1 \quad . \; . \quad (17)$$

Also $(H^{\cdot})^2(SO_4'') = a^3{}_{\pm}$, so that by replacing (SO_4'') in (17) and putting $[VO_2^{\cdot}] = [VO^{\cdot\cdot}]$ we find

$$E - \phi \ln (H^{\cdot})a^{\frac{3}{2}}{}_{\pm} = E_0'' + \phi \ln f_2/f_1 \quad . \; . \; . \; . \; . \quad (18)$$

The value of $a_{\pm}$ in (18) may readily be found, since the activity coefficient is known, but the value of $(H^{\cdot})$ is not so easily obtained. The following method gives values of $(H^{\cdot})$ which may be expected to lie close to the actual ones, especially at the lower concentrations.

Sulphuric acid exists in solution as $H^{\cdot}$ and partly dissociated HSO_4' ions. The dissociation constant of the HSO_4' ion at 25° is 0·0120 (Hamer, *J. Amer. Chem. Soc.*, 1934, **56**, 860), and from this the degree of dissociation may be calculated by the method of Schrawder and Cowperthwaite (*ibid.*, p. 2340). The value of $(H^{\cdot})$ can be found and H may be assumed to have the same activity coefficient as HCl at the same concentration, or as a uni-univalent electrolyte as calculated from the equation of LaMer, Gronwall, and Sandved (*Physikal. Z.*, 1928, **29**, 358). This calculation is dealt with below.

The left-hand side of (18) was plotted against $c^{\frac{1}{2}}$ and also $I^{\frac{1}{2}}$, and extrapolation gave $E_0'' = 0{\cdot}3977$ and $0{\cdot}3956$, respectively. The second value is probably superior, since it was found by prolonging a straight line through the last five points. E_0'' is the standard potential but, as is explained above, it is not readily converted into the standard potential of the vanadium half-cell, E_0. The most direct method for finding this would be from the cell

$$(\alpha)\ \mathrm{Pt}|\mathrm{VO}_2^{\cdot},\mathrm{VO}^{\cdot\cdot},\mathrm{H}_2\mathrm{SO}_4|\mathrm{H}_2\mathrm{SO}_4|\mathrm{H}_2,\mathrm{Pt}$$

The present results may be used in conjunction with the values for the cell

$$(\beta)\ \overset{-}{\mathrm{P}}\mathrm{t},\ \mathrm{H}_2|\mathrm{H}_2\mathrm{SO}_4,\mathrm{Hg}_2\mathrm{SO}_4|\overset{+}{\mathrm{H}}\mathrm{g},$$

which have been measured by Partington and Stonehill (*loc. cit.*), to give the E.M.F. of the cell

$$(\gamma)\ \mathrm{Pt}|\mathrm{VO}_2^{\cdot},\mathrm{VO}^{\cdot\cdot},\mathrm{H}_2\mathrm{SO}_4|\mathrm{H}_2\mathrm{SO}_4,\mathrm{Hg}_2\mathrm{SO}_4|\mathrm{Hg}|\mathrm{Hg}_2\mathrm{SO}_4,\mathrm{H}_2\mathrm{SO}_4|\mathrm{H}_2,\mathrm{Pt}$$

which is equivalent to cell (α). The E.M.F. of this is given by $E_\alpha = E - E_\beta$, where E is the observed E.M.F. of the present cells, and E_α and E_β are the E.M.F.'s of the cells (α) and (β) as written above.

The E.M.F. of cell (α) is given by $E_\alpha = E_0 + \phi \ln (\mathrm{VO}_2^{\cdot})(\mathrm{H}^{\cdot})/(\mathrm{VO}^{\cdot\cdot})$, which gives as before:

$$E_\alpha - \phi \ln (\mathrm{H}^{\cdot}) = E_0 + \phi \ln f_2/f_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Extrapolation of the left-hand side against $I^{\frac{1}{2}}$ gives $E_0 = 1{\cdot}0119$, which is the standard oxidation–reduction potential in sulphuric acid solution. This value is 12 mv. higher than the value in hydrochloric acid solution.

The method of calculation of I and $\phi \ln (\mathrm{H}^{\cdot})$ may now be explained. It was assumed (i) that dissociation of sulphuric acid into $\mathrm{H}^{\cdot}$ and HSO_4' was complete, although Noyes and Stewart (*J. Amer. Chem. Soc.*, 1910, **32**, 1133) found by transport measurements that there is only partial dissociation even at this stage, and (ii) that the HSO_4' ion was partly dissociated. The relevant dissociation constant (Hamer. *loc. cit.*) is

$$0{\cdot}0120 = K = (\mathrm{H}^{\cdot})(\mathrm{SO}_4'')/(\mathrm{HSO}_4') \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$= [\mathrm{H}^{\cdot}]f_{\mathrm{H}^{\cdot}}[\mathrm{SO}_4'']f_{\mathrm{SO}_4''}/[\mathrm{HSO}_4']f_{\mathrm{HSO}_4'} \quad . \quad . \quad . \quad . \quad (22)$$

If the activity coefficients of the univalent ions are assumed to be equal, and if the total acid concentration is c and $[\mathrm{HSO}_4'] = x$, then

$$f_{\mathrm{SO}_4''} = Kx/(2c - x)(c - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The values of $f_{\mathrm{SO}_4''}$ were calculated by the equation of LaMer, Gronwall, and Sandved for a bi-bivalent electrolyte with $a = 3{\cdot}64$ A. Equation (23) holds for the pure acid and requires slight modification to apply to the vanadium half-cell. If c' is the concentration of sulphate ion resulting from the complete dissociation of the vanadium sulphates, then

$$f_{\mathrm{SO}_4''} = Kx/(2c - x)(c + c' - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

from which the ion concentrations and hence I and $\phi \ln (\mathrm{H}^{\cdot})$ were calculated, while (23) gave $\phi \ln (\mathrm{H}^{\cdot})$ for the pure acid in the reference electrode. The two sets of values of $\phi \ln (\mathrm{H}^{\cdot})$ differed by 0·5 mv. at the higher concentrations and by 0·1 mv. for the more dilute solutions.

The values of $a_\pm$ for sulphuric acid calculated from the present values of $(\mathrm{H}^{\cdot})$ and (SO_4'') agree fairly well with the experimental values found by Harned and Hamer (*J. Amer. Chem. Soc.*, 1935, **57**, 27) at lower concentrations, but differ from the values at higher concentrations by increasing amounts.

Doubt still exists as to the state of vanadium in the vanadic acid solutions, containing 5-valent vanadium. Britton (*loc. cit.*), from an electrometric study of the oxidation of

4-valent vanadium by permanganate and the reduction of 5-valent vanadium by ferrous sulphate, and from the solubilities of the pentoxide in acids (Meyer and Aulich, *Z. anorg. Chem.*, 1930, **194**, 278), concluded that in the solutions of 5-valent vanadium the vanadium existed as HVO_3. A saturated solution of the pentoxide in water (0·304 g./l.) had a p_H of 3 as measured by the glass electrode, which points to an ionisation into $H^{\cdot}$ and VO_3' of 30%. In 2N-sulphuric acid solution the solubility of V_2O_5 is 18·7 g./l., and as this increases only to 26·2 g./l. in 64% sulphuric acid, the conclusion was reached that no salts of 5-valent vanadium with the acids were formed. This is difficult to reconcile with the increased solubility in 2N-acid. More recently, Britton and Welford (this vol., p. 895) have measured the solubilities of vanadium pentoxide in solutions of acids of various strengths and conclude that the oxide is amphoteric. It is, however, regarded as a very weak base, and even in the presence of excess of acid the basic function does not extend much beyond the formation of the ion $VO_2^{\cdot}$. This conclusion is in general agreement with the results of the present research. Some salts corresponding with the basic function of vanadium pentoxide are described in the older literature (see, *e.g.*, Abegg, " Handbuch," III, iii, 745) but their identity is very doubtful. Lanford and Kiehl (*J. Amer. Chem. Soc.*, 1940, **62**, 1660) in a phase-rule study found $V_2O_5,4SO_3,4H_2O$, $V_2O_5,2SO_3,3H_2O$, and $V_2O_5,2SO_3,8H_2O$, but failed to find in the conditions in which they worked any evidence of other reported sulphates. A revision of this field is called for. It seems that the electrochemical behaviour of solutions of 5-valent vanadium compounds in acids can be explained on the assumption that the ion is $VO_2^{\cdot}$. It cannot be said, however, that the constitution of such solutions has yet been completely elucidated from all points of view. Further work in this direction is planned.

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