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

The Constitution of the Pentavalent Vanadium Ion in Acid Solution

BY JOSEPH E. CARPENTER

Of the more recent investigations of cells containing tetravalent and pentavalent vanadium are those of Foerster and Böttcher,[1] and Coryell and Yost.[2] The former authors give evidence for a half-cell reaction

$$VO_2^+ + 2H^+ + e = VO^{++} + H_2O \qquad (1)$$

but the latter (whose article was published at the time the present work was nearing completion), although postulating an ion $V(OH)_4^+$ on the basis of measurements of the solubility of vanadium pentoxide in acid, regarded the pentavalent vanadium as existing predominantly as HVO_3, and employed this formula in all their calculations. As a result, they were unable satisfactorily to account for the dependence of the electromotive force on acid concentration, or to determine E^0, the standard electrode potential, for the reaction.

In this paper are presented the results of measurements which confirm the correctness of the cell reaction proposed by Foerster and Böttcher. The data of Coryell and Yost are also recalculated and shown to lead to the same conclusion.

Materials.—Starting materials were Eimer and Amend C. P. hydrous vanadium pentoxide, and G. F. Smith Chemical Co. 60% perchloric acid, vacuum distilled. Both were used without further purification.

The stock solution of vanidol perchlorate, VO_2ClO_4, was prepared by dissolving vanadium pentoxide in a measured quantity of perchloric acid of known concentration. The solution was analyzed for pentavalent vanadium by the iodimetric method of Ramsey.[3] It contained a negligible amount of tetravalent vanadium.

The stock solution of vanadyl perchlorate, $VO(ClO_4)_2$, was prepared by reducing a suspension of vanadium pentoxide in a known quantity of standard perchloric acid by the method of Yost and Claussen.[4] It was analyzed for unreduced pentavalent vanadium by the method of Ramsey, and for total vanadium by the same method after first oxidizing by evaporating with concentrated nitric acid. Samples were adequately diluted before adding potassium iodide to prevent reaction with excess nitric acid.

Measurements.—The cell employed was

$$\begin{array}{c|c|c|c|c} & VO_2^+ & & & \\ Pt & VO^{++} & H^+ & H_2 & Pt \\ & H^+ & ClO_4^- & & \\ & ClO_4^- & & & \end{array}$$

Acid concentration was high relative to the vanadium concentrations, and was the same in each half-cell, thus practically eliminating the liquid junction potential. The cell consisted of two identical parts, each of which could be used as a gas electrode, being provided with a bubbling tube for washing the gas before it is introduced into the cell chamber proper. One was so used as a hydrogen electrode; through the other it was intended to pass an inert gas to exclude oxygen from the vanadium solution. It was found, however, that this precaution was unnecessary at the acid concentrations employed, although it would be essential at very low concentrations. Temperature was maintained at 25.0° by means of an oil thermostat. Hydrogen was provided by an electrolytic generator employing potassium hydroxide. The electrodes were of iridium plated on gold on platinum, as recommended by Lewis, Brighton and Sebastian.[5] They were mounted in removable caps which fitted into the cell proper by ground glass connections. These, like the ungreased two-way stopcock connecting the two parts of the cell, protruded above the thermostat liquid Measurements were made by means of a Leeds and Northrup Type K potentiometer, individual measurements being found constant and reproducible to about 0.2 millivolt.

Determination of the Vanadium Half-Cell Reaction.—The equation for the vanadium half-cell reaction may be determined, and the most probable formula for the pentavalent vanadium ion established, by observing the variation of the electromotive force of the cell with changes in the concentrations of acid and of tetra- and pentavalent vanadium. Given only the fact that tetravalent vanadium forms a series of salts of the type $VOSO_4$, so that the vanadyl ion—commonly considered to be VO^{++}—contains vanadium and oxygen atoms in equal number, we may set

x = number of atoms of vanadium in the pentavalent vanadium ion
y = number of atoms of oxygen in the pentavalent vanadium ion
z = number of atoms of vanadium in the vanadyl ion

and write the general equation

$$V_xO_y^{5x-2y} + x/2H_2 + (2y - 3x)\ H^+ = x/z\ V_zO_z^{2z} + (y - x)\ H_2O$$

The reaction proceeds spontaneously in the direction written; the corresponding electromotive force is accordingly positive, and may be represented as

$$E = E^0 - \frac{RT}{NF} \ln \frac{(V_zO_z^{2z})^{x/z}}{(V_xO_y^{5x-2y})(H^+)^{2y-3x}}$$

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(1) Foerster and Böttcher, *Z. physik. Chem.*, **A151, 321** (1930).

(2) Coryell and Yost, THIS JOURNAL, **55**, 1909 (1933).

(3) Ramsey, *ibid.*, **49, 1138** (1927).

(4) Yost and Claussen, *ibid.*, **53**, 3350 (1931).

(5) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2249 (1917).

the parentheses representing activities, and the expressions for water and hydrogen gas regarded as constant terms combined in E^0.

The reaction for the vanadium half-cell is

$$V_xO_y^{5x-2y} + 2\,(y - x)\,H^+ + xe = x/z\,V_zO_z^{2z} + (y - x)\,H_2O$$

from which it is apparent that $N = x$, giving

$$E = E^0 - \frac{RT}{F}\ln\frac{(V_zO_z^{2z})^{1/z}}{(V_xO_y^{5x-2y})^{1/x}\,(H^+)^{(2y-3x)1/x}}$$

Approximately, the activity of any solute may be replaced by its concentration. Then if the concentrations of any two solutes are held constant and that of the third varied in a series of cells, the contributions of the former to the electromotive force may be included in the E^0 term, giving

Case I $E = E_1 + (0.05915/x)\log c_{VO_2^+}$ (2)
Case II $E = E_2 + 0.05915(2y - 3x)/x\log c_{H^+}$ (3)
Case III $E = E_3 - (0.05915/z)\log c_{VO^{++}}$ (4)

In every case, if E is plotted as a function of log c, lines approximately straight should result, from the slopes of which x, y and z may be determined.

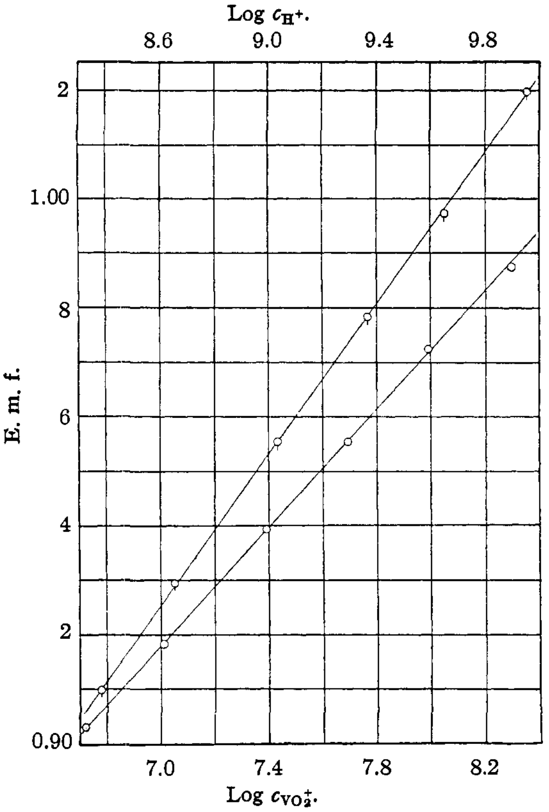

Fig. 1.—Variation of e. m. f. with: O, concn. of pentavalent vanadium; ⚲, concn. of acid (upper scale).

Results.—Measurements were made, corresponding to the three cases above, in three series, the results of which are given in Table I and plotted in Fig. 1. Straight lines are produced, the slopes of which, when equated to the equivalent expressions in equations (2) and (3) give

Case I $x = 1.09$
Case II Using $x = 1$, y is found to be 2.08

TABLE I

RESULTS OF E. M. F. MEASUREMENTS

Series 1. Concentration (in moles per liter) of $HClO_4$: 0.1077. Concentration of $VO(ClO_4)_2$: 0.004420. Slope of graph (Fig. 1): 0.0544

Cell	VO_2^+ concn.	E. m. f.
A-1	0.0005293	0.9031
2	.001017	.9182
3	.002489	.9395
4	.004947	.9554
5	.009855	.9723
6	.01967	.9875

Series 2. Concentration of VO_2ClO_4: 0.004947. Concentration of $VO(ClO_4)_2$: 0.004420. Slope of graph (Fig. 1): 0.0694

Cell	H^+ concn.	E. m. f.
B-1	0.02398	0.9098
2	.04484	.9294
3	.1077	.9554
4	.2338	.9783
5	.4442	.9974
6	.9000	1.0198

Series 3. Concentration of VO_2ClO_4: 0.004947. Concentration of $HClO_4$: 0.1077

Cell	VO^{++} concn.	0.05915 log $c_{VO^{++}}$	E. m. f.
C-1	0.004420	−0.1393	0.9554
2	.03511	− .0860	.9048
	Difference	− .0533	.0506

Thus the formula of the pentavalent vanadium ion in acid solution is proved to be VO_2^+.

Case III. Without plotting, z is found to be 1.05

This confirms the customary representation of the vanadyl ion, VO^{++}, and the cell reaction becomes

$$VO_2^+ + {}^1/_2H_2 + H^+ = VO^{++} + H_2O$$

corresponding to the half-cell reaction of equation (1).

The Data of Coryell and Yost.—These experimenters measured the electromotive force at 25° of the cell

Pt	VO_2^+ VO^{++} H^+ Cl^-	H^+ Cl^-	$HgCl_{(s)}$ $Hg_{(l)}$

for which the cell reaction is

$$VO_2^+ + 2H^+ + Cl^- + Hg_{(l)} = VO^{++} + H_2O + HgCl_{(s)}$$

However, they calculated their acid molalities on the assumption

$$V_2O_5 + H_2O = 2HVO_3$$

instead of

$$V_2O_5 + 2H^+ = 2VO_2^+ + H_2O$$

so that the reported acid molalities in their vanadium half-cells are in error by an amount equal to the respective molalities of pentavalent vanadium. In Table II, column 3, these acid molalities have been corrected; and in column 4 the electromotive forces are corrected to correspond to the reported acid molalities,[6] by means of the formula

$$E_{\text{corrected}} = E_{\text{reported}} + 0.05915 \log \frac{(m_{\text{H}^+\text{reported}})^2}{(m_{\text{H}^+\text{actual}})^2}$$

TABLE II

RECALCULATED DATA OF CORYELL AND YOST

Expt.	Reported H^+ molality	Actual H^+ molality	Corrected e. m. f.	E. m. f. of V half-cell	E. m. f. for $m_{VO^{++}} = 0.02$
1	2.146	2.134	0.8220	1.0698	1.0627
2		2.140	.7944	1.0421	1.0453
3	1.031	0.999	.7638	1.0372	1.0371
4		1.007	.7455	1.0189	1.0291
5–6		1.019	.7454	1.0188	1.0112
7		1.015	.7284	1.0018	1.0193
8–9		1.023	.7274	1.0008	1.0005
10		1.019	.7169	0.9904	1.0109
11	0.5106	0.4947	.7001	.9934	0.9752
12–14		.4987	.6817	.9750	.9671
15		.5046	.6811	.9744	.9487
16		.5027	.6641	.9574	.9568
17–20	.2541	.2482	.6237	.9349	
21–24	.1013	.0989	.5503	.8839	
25–26	.05061	.04943	.4970	.8474	
27–28	.01012	.00988	.3715	.7610	

In column 5, the potentials of the vanadium half-cells are calculated, following Coryell and Yost.[7] Now, at any fixed acid molality, we may employ the equation

$$E = E_{\text{experimental}} + 0.05915 \log \frac{m_{\text{VO}^{++}\text{experimental}}}{m_{\text{VO}^{++}\text{reference}}}$$

to calculate the electromotive force corresponding to some fixed reference molality of VO^{++}. The results of this calculation, employing a reference molality of 0.02000, are tabulated in the final column. The electromotive force thus calculated is a function of the molality of pentavalent vanadium alone, and may be plotted against log $m_{VO_2^+}$ as was done with the perchlorate data. Similarly, in a series of cells with molalities of tetra- and pentavalent vanadium in constant ratio, we may plot E as a function of log m_{H^+}. In each case, when this is done, straight lines result whose slopes are those required by equation (1), thereby again verifying the formula VO_2^+ for the pentavalent vanadium ion. Had no corrections for acid molality been applied, the data would still have remained sufficiently accurate to substantiate this conclusion.

Of course, as Coryell and Yost themselves note, the formula of the pentavalent vanadium ion might also be $V(OH)_4^+$, which differs by two molecules of water from VO_2^+. Which is correct, cannot be determined from the present data.

The Standard Electrode Potential at 25°.—The recalculated data of Coryell and Yost may be used to determine the standard electrode potential. If the quantity

$$E^{0\prime} = E + 0.05915 \log \frac{m_{\text{VO}^{++}}}{(m_{\text{VO}_2^+})\,(m_{\text{Cl}^-})\,(m_{\text{H}^+})^2}$$

be calculated for each of a series of cells in which the molalities of tetra- and pentavalent vanadium and of acid are maintained in constant ratio to one another, but each cell solution more dilute than the preceding; and if this quantity be plotted as a function of the square root of the ionic strength, a curve should result which should approach a horizontal tangent at $\sqrt{\mu} = 0$, the intercept being the standard potential, E^0, for the cell. The necessary calculations have been recorded in Table III and plotted in Fig. 2. All points but one lie on a smooth curve, which on extrapolation gives $E^0 = 0.7307$ volt, or possibly a value slightly higher. The standard electrode potential for the vanadium half-cell is found by adding that of the calomel half-cell, 0.2689 volt, obtaining 0.9996 volt.

A similar extrapolation may be made with the perchlorate data, Series 2, giving a result substantially in agreement with this. The cells

TABLE III

DETERMINATION OF THE STANDARD ELECTRODE POTENTIAL

Expt.	H^+ molality	Corrected e. m. f.	$E^{0\prime}$	$\sqrt{\mu}$
4	1.031	0.7455	0.7486	1.070
12–14	0.5106	.6818	.7390	0.7528
15	.5106	.6811	.7383	.7339
17–20	.2541	.6237	.7346	.5310
21–24	.1013	.5503	.7322	.3353
25–26	.05061	.4970	.7324	.2370
27–28	.01012	.3715	.7309	.1060
Extrapolation (Fig. 2)			.7307	0

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[6] Through the error noted, acid molalities in each half-cell were not identical as intended. A small liquid junction potential was thereby introduced, which, however, has been calculated to amount to only 0.1 millivolt in the worst cases (Experiments 3 and 4) by means of the formula of Lewis and Sargent [THIS JOURNAL, 31, 363 (1909)].

[7] Reference 2, page 1912.

were designed, however, for a different purpose, and are not as well adapted for extrapolation, which requires systematic dilution from cell to cell of all solutes present, whereas in these, vanadium concentrations were held constant. The value given above is therefore the better.

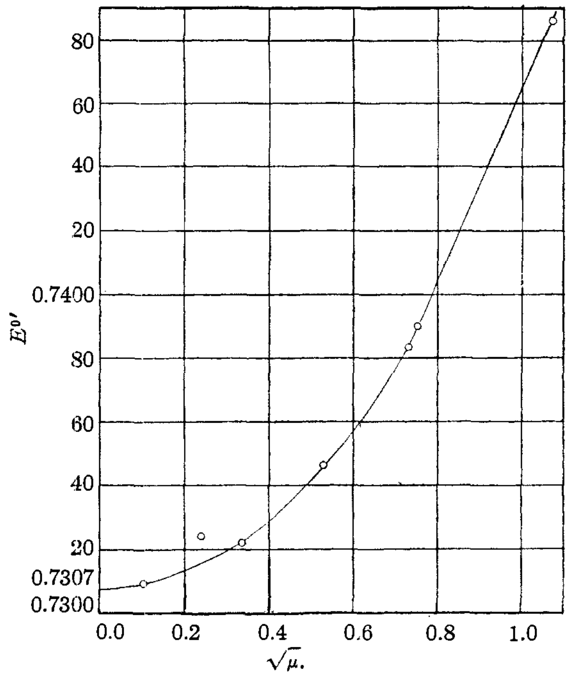


Fig. 2.—Extrapolation of E^0,

I wish to express my appreciation to Professor William C. Bray, to whom I am indebted for suggesting the problem and for valuable assistance from time to time during its completion.

Summary

1. By observation of the variation of the electromotive force of the cell

$$\mathrm{Pt}\;\left|\;\begin{matrix}\mathrm{VO_2^+}\\ \mathrm{VO^{++}}\\ \mathrm{H^+}\\ \mathrm{ClO_4^-}\end{matrix}\;\right|\;\begin{matrix}\mathrm{H^+}\\ \mathrm{ClO_4^-}\end{matrix}\;\left|\;\mathrm{H_2}\;\right|\;\mathrm{Pt}$$

with acid concentration and with concentration of pentavalent vanadium, the formula of the pentavalent vanadium ion has been shown to be VO_2^+ in acid solution.

2. The data of Coryell and Yost[2] for a similar cell have been recalculated, correcting for a small error in acid molality, and shown to be in complete agreement with this result.

3. From the recalculated data of Coryell and Yost, the standard electrode potential for the reaction

$$VO_2^+ + 2H^+ + e = VO^{++} + H_2O$$

has been determined as 0.9996 volt.

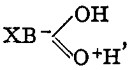
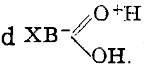
BERKELEY, CALIF. RECEIVED APRIL 30, 1934

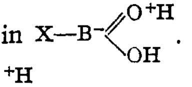
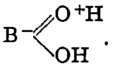
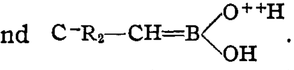
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Relative Strengths of Some Hydrocarbon Derivatives of Boric Acid

BY DAVID L. YABROFF, G. E. K. BRANCH AND BERNARD BETTMAN

Introduction

Resonance.—If the group X may act as a donor of electrons in an acid of the type $XB(OH)_2$, then the structure $X^+{=}B^-(OH)_2$ will be in resonance with the forms $XB(OH)_2$,  $XB^{-}{<}^{OH}_{O^{+}H}$, and  $XB^{-}{<}^{O^{+}H}_{OH}$. Since the negative part of the dipole in the structure $X^+{=}B^-(OH)_2$ is nearer the dissociating hydrogen atom than is the positive pole, the effect of this structure is to decrease the strength of the acid. The extent of the contribution of $X^+{=}B^-(OH)_2$ to the structure of the molecule depends on its stability with respect to $XB(OH)_2$ and on the number of structures represented by $X^+{=}B^-(OH)_2$ relative to the number represented by $XB(OH)_2$. The importance of $X^+{=}B^-(OH)_2$ becomes greater, then, as its stability increases relative to $XB(OH)_2$ and as the number of forms represented by $X^+{=}B^-(OH)_2$ increases relative to the number of structures represented by $XB(OH)_2$.

There is another type of molecular resonance introduced when X has a double bond so situated that it forms a conjugate system with the double bond in  $X{-}B^{-}{<}^{O^{+}H}_{OH}$. An example is $CR_2{=}CH{-}$ $B^{-}{<}^{O^{+}H}_{OH}$. In general, a conjugate system may have two internally ionized resonating forms. In this case they would be $C^+R_2{-}CH{=}B^-(OH)_2$ and  $C^-R_2{-}CH{=}B{<}^{O^{++}H}_{OH}$. The first of these forms is of the type $X^+{=}B^-(OH)_2$ which has