

acteristic basic ion of the system, bisulfate ion. The simplicity of the nature of electrolyte solutions in sulfuric acid appears clearly from the fact that we are thus able to apply the solubility product principle to an electrolyte of an initial solubility of 0.8 molal and over a range of concentrations of added electrolyte from zero to nearly three molal.

Summary

Cryoscopic measurements on various ionized solutes in the solvent sulfuric acid may be simply interpreted by taking account of the large dissociation of the solvent. Within the best precision of the Beckmann method, ionic activity coefficients are constant over a wide range of concentrations.

In agreement with this it is found possible to apply the solubility product principle to the effect of water upon the solubility of barium sulfate in sulfuric acid.

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The Reduction Potential of Vanadic Acid to Vanadyl Ion in Hydrochloric Acid Solutions

BY CHARLES D. CORYELL AND DON M. YOST

Introduction

Earlier investigations of cells involving pentavalent and tetravalent vanadium gave values of -0.92 volt¹ and -1.0 volt² for the molal reduction potential in sulfuric acid solutions. Abegg, Auerbach and Luther³ base their figure of -1.20 volts on the first mentioned determination. Uncertain liquid junction potentials diminish the reliability of these determinations, and the undetermined part that the acid concentration plays in the cell reactions introduces uncertainty in the interpretation of the published values.

In this paper are presented the results of measurements on cells in which the potentials due to liquid junctions are practically eliminated. Hydrochloric acid solutions of the vanadium compounds were used rather than sulfuric acid solutions because it is in chloride solutions that a knowledge of the reduction potential is most often desired. This is, for example, the case in applications to qualitative analysis.⁴

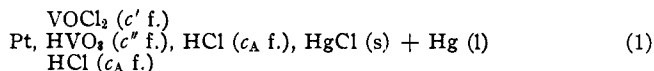
(1) Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

(2) Foerster and Böttcher, *Z. physik. Chem.*, [A] **151**, 321 (1930).

(3) Abegg, Auerbach and Luther, "Messungen elektromotorische Kräfte galvanische Ketten," Halle A.S., Wilhelm Knapp, 1911, p. 199.

(4) See, for example, Noyes and Bray, "Qualitative Analysis of the Rare Elements," Macmillan Co., New York, 1927.

The cell whose electromotive force was determined is



The concentrations of vanadic acid and vanadyl salt were kept low, and the hydrochloric acid was present at the same concentration in both half-cells in order to make the liquid junction potentials negligible.

Preparation of the Materials and Experimental Procedure

The stock solutions of vanadyl chloride were prepared by the method described by Yost and Claussen.⁵ The total chloride present was determined gravimetrically by precipitating it as silver chloride, and the vanadyl salt was determined by titration with standard permanganate.

Vanadic acid solutions were prepared by dissolving vanadium pentoxide in hydrochloric acid of known strength. The pentoxide was made from recrystallized ammonium metavanadate by carefully heating the salt in a stream of oxygen. The small amount (1%) of vanadium dioxide present as impurity was determined and allowed for in calculating the final concentration of hydrochloric acid. The method developed by Ramsay⁶ was employed for the analysis of the vanadic acid solutions.

The hydrochloric acid and mercury were carefully purified, and the calomel was prepared as described by Ellis.⁷

The densities of the solutions were determined so that the concentrations could be expressed in terms of formula weights per 1000 g. of water.

The Pyrex glass cell was a modification of the design developed in this Laboratory. The stopcocks connecting the half-cells were so surrounded by glass that no contact with the thermostat liquid was possible. The presence of three calomel half-cells and two vanadium half-cells, all interconnected, made possible various combinations and checks. Observations on the electromotive force of a cell were begun about an hour after the cell had been placed in the thermostat, and were then continued at suitable intervals for a period of about one week.

The measurements were made at 25.00 and at 33.90°. Accurately reproducible results and constancy were not attained in all cases, until a small amount of ferric chloride was added to the vanadium solutions. The quantity added was so small a fraction (0.05%) of the total vanadium concentration that it could not affect materially the concentration of the latter substance. With hydrochloric acid concentrations of 0.25 f. and lower no ferric chloride was added since constancy and reproducibility were attained without its use.

Results of the Electromotive Force Measurements at 25°

Table I contains representative results of the electromotive force measurements made at 25.00°. Each observed value \mathcal{E} is the average for two cells, in each of which equilibrium had been reached and maintained for twenty-four hours. The electromotive forces of individual cells rarely varied by more than ± 0.2 millivolt, except in those cases where the hydrochloric acid concentrations were 0.01012 f. and 2.146 f. All concentrations are given in formula weights per 1000 g. of water.

(5) Yost and Claussen, *THIS JOURNAL*, **53**, 3350 (1931).

(6) Ramsay, *ibid.*, **49**, 1138 (1927).

(7) Ellis, *ibid.*, **38**, 737 (1916).

TABLE I
RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS AT 25°

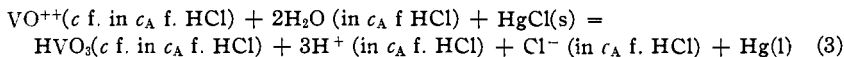
Expt.	Formal concentration		$\frac{(\text{HVO}_3)}{(\text{VOCl}_2)}$	Electromotive force		Mean
	HCl	VOCl_2		E (obs.)	E'' (calcd. by Eq. 2)	
1	2.146	0.01518	0.8090	-0.8217	-0.8272	
2		.02269	.2705	.7943	.8279	
						-0.8276
3	1.031	0.01992	1.6094	-0.7621	-0.7499	
4		.02974	0.8090	.7442	.7496	
5		.01487	.8090	.7448	.7503	
6		.01487	.8090	.7447	.7502	
7		.03954	.4054	.7276	.7508	
8		.01977	.4054	.7272	.7504	
9		.01977	.4054	.7267	.7499	
10		.04445	.2705	.7163	.7499	
						-0.7501
11	0.5106	0.00986	1.6094	-0.6985	-0.6863	
12		.01472	0.8090	.6808	.6863	
13		.01472	.8090	.6804	.6858	
14		.01472	.8090	.6805	.6859	
15		.00736	.8090	.6805	.6860	
16		.01957	.4054	.6633	.6865	
						-0.6861
17	0.2541	0.007317	0.8090	-0.6228	-0.6233	
18				.6229	.6283	
19				.6221	.6276	
20				.6222	.6277	
						-0.6280
21	0.1013	0.002917	0.8090	-0.5496	-0.5551	
22				.5485	.5540	
23				.5497	.5552	
24				.5485	.5539	
						-0.5546
25	0.05061	0.001458	0.8090	-0.4958	-0.5013	
26				.4957	.5012	
						-0.5013
27	0.01012	0.0002912	0.8090	-0.3703	-0.3758	
				.3702	.3757	
						-0.3758

In the last column of Table I are given values of the electromotive forces E'' calculated from the equation

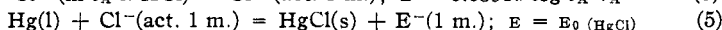
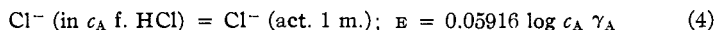
$$E'' = E + 0.05915 \log \frac{(\text{HVO}_3)}{(\text{VO}^{++})} \quad (2)$$

It will be noted that the values of E'' for different vanadium concentrations at fixed hydrochloric acid concentrations are constant within the limits of experimental error; this shows that the activity coefficients of the two vanadium compounds are constant, and both contain the same number of vanadium atom.

The mean values of E'' given in Table II represent the electromotive forces at 25° resulting from the following change in state



The vanadium half-cell potential, E' , referred to the standard hydrogen electrode is obtained by adding to E'' the electromotive forces produced by the following two reactions



The values of the mean ion activity coefficient γ_A of the hydrochloric acid at its prevailing concentration c_A formal are given by Randall and Young,⁸ and the molal electrode potential of the calomel electrode is -0.2689 volt.⁹ Thus the values of E' (equal to $E'' - 0.2689 + 0.05915 \log c_A \gamma_A$) are indicative of the oxidizing power of vanadic acid in c_A formal hydrochloric acid, and such values are the ones to be used in practical applications of the results.

If it is assumed that the activity coefficient of the hydrogen ion is equal to the mean ion activity coefficient γ_A of hydrochloric acid, the electrode potentials $E_0 = E' + 0.05915 \log c_A^3 \gamma_A^3$ may be calculated, and are presented in the fifth column of Table II. In calculating the values for E_0 no correction has been made for the activity coefficients of vanadyl ion and vanadic acid, or for the changing activity of the water.

TABLE II
REDUCTION POTENTIALS OF VANADIC ACID TO VANADYL ION IN HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS AT 25°

c_A formal	Hydrochloric acid Act. coeff. γ_A	E''	Electromotive forces E'	E_0
2.146	1.065	-0.8276	-1.0753	-1.0115
1.031	0.8147	.7501	1.0235	1.0369
0.5106	.7572	.6861	0.9794	1.0527
.2541	.7596	.6280	.9392	1.0659
.1012	.7954	.5546	.8882	1.0822
.05061	.8285	.5013	.8517	1.0962
.01012	.9037	.3758	.7653	1.1271

Discussion of the Reduction Potentials at 25°

Table II shows that the reduction potential E' for the conversion of vanadic acid to vanadyl ion in 1.031 f. hydrochloric acid solution at 25° is -1.0235 volts. This is much greater than the potential (-1.3594 volts) for the reaction $\text{Cl}^-(1 \text{ m.}) = \frac{1}{2}\text{Cl}_2(1 \text{ atm.}) + E^-$, but only a little above the potential (-1.0659 volts) for $\text{Br}^-(1 \text{ m.}) = \frac{1}{2}\text{Br}_2(1) + E^-$.

(8) Randall and Young, *THIS JOURNAL*, **50**, 989 (1928).

(9) This value of -0.2689 volt is the molal electrode potential of the calomel cell for the case in which oxygen is not excluded. A number of investigators have found this cell to be reproducible and constant (Ref. 8) and because of its practical convenience it appears to be a desirable experimental standard. The activity coefficients of Randall and Young have been used to obtain this value, -0.2689 volt, which should replace the older one, -0.2700 volt, given by Lewis and Randall ("Thermodynamics," McGraw-Hill Book Co., N. Y., 1923). Evidently the value for oxygen-free cells, -0.2676 volt, determined by Randall and Young cannot be applied to the results with cells in which air is present.

In fact, in 2.145 f. hydrochloric acid the value of -1.0753 volts is somewhat below this latter potential. In as dilute acid as 0.0101 f. the potential (-0.7653 volt) is still considerably less than that of $I^-(1 \text{ m.}) = \frac{1}{2}I_2(s) + E^-$ (-0.5357 volt), however.

The values of the standard electromotive forces E_0 given in Table II show, even though the hydrogen-ion activity has been already corrected to unit activity, that the reduction potential of vanadic acid to vanadyl ion varies greatly with the acid concentration. Any decrease in the ion activity coefficient of vanadyl ion with increasing acid concentration would increase this variation still more. The effect of acid seems then to arise principally from the effect of the hydrochloric acid on the vanadic acid. The following considerations and experiments confirm this view.

It was found that the solubility of moist vanadium pentoxide in hydrochloric acid increases rapidly with the acid concentration, and this results in a corresponding decrease in the activity coefficient of the vanadic acid.¹⁰ To correlate this fact with the results of the potential measurements, the activity coefficients of vanadyl ion were assumed equal to those of barium ion¹¹ at the same ionic strength, and the activity coefficients of the vanadic acid were then calculated from the values of E_0 . These coefficients were taken arbitrarily as unity in 0.101 m. hydrochloric acid. The results described are presented in Table III.

TABLE III

THE SOLUBILITY AND ACTIVITY COEFFICIENTS OF VANADIC ACID IN HYDROCHLORIC ACID

Formality of HCl	Act. coeff. HCl, γ_A	Act. coeff. $VO^{++}(Ba^{++})$	Solubility vanadic acid as HVO_3 , f.	Activity coefficients of vanadic acid	
				from e. m. f.'s	from solubilities
0.018	0.88	0.59	(0.0049)	5.0	(2.2)
.101	.80	.34	.0097	1.0	1.0
.254	.76	.23	.052	0.36	0.19
.503	.76	.16	.182	.15	.053
1.03	.81	.11	.220	.056	.044

As will be seen in the table the activity coefficients derived from solubility measurements are in as good agreement as could be expected with those calculated from electromotive force measurements. The rough agreement also furnished justification for the cell reaction assumed in Equation (3). It seems likely that the effect of the hydrochloric acid arises from the formation of complex ions or, as Professor Pauling has suggested, the ion $V(OH)_4^+$.¹²

(10) As a result of colloid formation the solubility of the pentoxide in 0.018 m. hydrochloric acid is too high and the corresponding activity coefficient is too low. In the table the values are placed in parentheses.

(11) The values were calculated from the data given by Scatchard and Tefft, *THIS JOURNAL*, **52**, 2270 (1930).

(12) Later experiments have shown that the solubility of vanadium pentoxide in perchloric acid varies with acid concentration in the same way as found when hydrochloric acid was used. This is good evidence for the existence of an ion of the type $V(OH)_4^+$.

Due to lack of more precise information it is not possible at this time to evaluate the conventional standard reduction potential of vanadic acid to vanadyl ion. The values of E' in Table II represent the potentials which are to be used in any applications under the conditions indicated. The value of E' at the rounded hydrochloric concentration of 1.0 molal is -1.0216 volts, which corresponds to a free energy decrease of $-23,572$ cal.

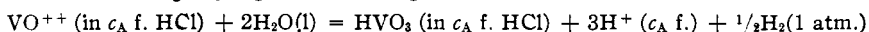
The Temperature Coefficient of Electromotive Force and the Change in Heat Content Accompanying this Reaction

In order to determine the temperature coefficient of the electromotive forces, a number of cells were measured at 33.90° as well as at 25.00° . In Table IV are presented the results of these measurements. The values are given to more significant figures in this case, since individual cells showed variations that were smaller than the variations between different cells.

TABLE IV
RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS AT TWO TEMPERATURES

Cell	Formality of HCl	Temp., °C.	E. m. f. in volts		$\Delta E'$ volts	$10^5 \frac{\Delta E'}{\Delta T}$
			E (obs.)	E' (calcd.)		
3	1.031 m.	25.00	-0.76218	-0.74995	0.00544	61.2
		33.90	.75711	.74451		
5		25.00	.74481	.75027	.00540	60.8
		33.90	.73926	.74487		
6		25.00	.74471	.75017	.00545	61.3
		33.90	.73911	.74472		
7		25.00	.72766	.75086	.00539	60.6
		33.90	.72159	.74547		
8		25.00	.72715	.75035	.00533	60.0
		33.90	.72114	.74502		
9		25.00	.72679	.74999	.00551	62.0
		33.90	.72060	.74448		
Mean						+61.0
13	0.5106	25.00	.68033	.68579	.00685	77.0
		33.90	.67333	.67894		
14		25.00	.68048	.68594	.00698	78.6
		33.90	.67335	.67896		
Mean						+77.8

By applying the Gibbs-Helmholtz equation to the values of the temperature coefficient given in Table IV, after correcting for the corresponding coefficient of the calomel electrode in the same range,⁷ the change in heat content accompanying the following reaction was calculated.

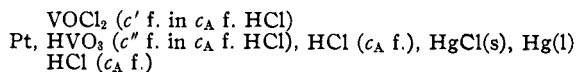


when $c_A = 1.0$, $\Delta H = 29,350$ cal. and when $c_A = 0.5$, $\Delta H = 29,220$ cal.

At present there are no heat data with which these results may be compared.

Summary

Measurements have been made on the following cell at several acid concentrations and varying concentrations of vanadic acid and vanadyl chloride.



The electromotive force of the cell varies greatly with the acid concentration, and normally with the concentration of vanadic acid and vanadyl ion. An explanation for the effect of the acid is offered.

The reduction potential E' at 25° with reference to the molal hydrogen potential as zero was found to be -1.0216 volts in molal hydrochloric acid, slightly greater than the bromine potential (-1.0659 volts) and considerably more positive than the chlorine potential (-1.3594 volts). The corresponding potentials at other acid concentrations are presented in Table II.

From the temperature coefficient of electromotive force the heat content increase accompanying the reduction by hydrogen of one mole of vanadic acid in hydrochloric acid solution to vanadyl ion and water was found to be $-29,350$ cal.

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The Nephelometric Determination of Chloride

BY I. M. KOLTHOFF AND HENRY YUTZY

Two procedures for the nephelometric determination of chloride have been described in the literature, one by T. W. Richards and R. C. Wells,¹ the other by A. B. Lamb, Carleton and Meldrum.² The former is of historical interest, since it was the first real nephelometric method described. The method of Lamb and co-workers is recommended by J. H. Yoe³ for general use. However, in its application to the chloride determination in unknowns, it should be remembered that foreign electrolytes may affect the light reflecting power of the silver chloride suspensions, whereas the method has been developed and recommended by the authors for the determination of traces of chlorine in war gases. Preliminary experiments on its application yielded many unexpected difficulties and a

(1) Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904).

(2) Lamb, Carleton and Meldrum, *THIS JOURNAL*, **42**, 251 (1920).

(3) Yoe, "Photometric Chemical Analysis," Vol. II, Nephelometry, John Wiley and Sons, New York, 1929, p. 137.