[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Characteristics of Vanadium in Oxalate Solutions

BY JAMES J. LINGANE AND LOUIS MEITES, JR.

Although the polarographic characteristics of vanadium in non-complexing solutions have been described,[1] there has been no study of the behaviors of the various oxidation states of this element in solutions containing complex forming anions. The present study was undertaken in order to secure information about the polarography of the several oxidation states of vanadium in oxalate solutions under various conditions.

Evidence has been found for the existence of previously unreported oxalate complexes of the +4, +3 and +2 states of vanadium. This paper describes the polarographic characteristics of each of these complexes, as well as of +5 vanadium in oxalate solutions. A newly discovered reduction of hydrogen oxalate ion at the dropping electrode is also described.

Experimental

The preparation and standardization of the vanadyl and vanadate solutions used in this work have been detailed elsewhere.[2] Solutions of +3 vanadium in air-free 0.02 *N* sulfuric acid were prepared from weighed quantities of a sample of vanadic sulfate decahydrate kindly furnished by Professor Grinnell Jones.[3] Solutions of +2 vanadium were prepared by reduction of vanadyl solutions with amalgamated zinc, and the reduced solutions were caught under hydrogen in a calibrated buret from which accurately known volumes could be delivered under the surface of the air-free supporting electrolyte.

Polarograms were recorded with a Sargent–Heyrovsky Model XI Polarograph, whose galvanometer was calibrated periodically. Diffusion current constants were measured with a manual apparatus employing a Leeds and Northrup Type HS galvanometer. An H-cell[4] with a saturated calomel anode, and a vertical stand-tube provided with a set of contacts leading to an automatic *m*-measuring device[5] and connected to a mercury reservoir through a lightly greased stopcock, completed the polarographic assembly.

All *p*H measurements were made with a Beckman glass electrode *p*H meter.

A water thermostat was used to maintain solutions at 25.00 ± 0.01°, and air was removed from solutions by hydrogen which had been purified by passage over copper gauze at about 500°.

Data and Discussion

+4 Vanadium.—In 0.1 *N* sulfuric acid vanadyl ion is reduced to the +2 state and gives a single well-defined wave, with a half-wave potential of −0.85 v. *vs.* the S. C. E. As the acidity is reduced the wave shifts to more negative potentials and, if the solution is unbuffered, a pre-wave develops at about −0.8 v. (see Fig. 1). The shape of this pre-wave indicates that it is due to the rate-controlled reduction of a species, possibly $VOOH^+$,[6] formed by hydrolysis of VO^{++}. This interpretation is supported by the fact that solutions of +4 vanadium buffered (*e. g.*, with acetic acid and sodium acetate) at *p*H 6.1 show only the second wave, nor is the pre-wave observed with unbuffered solutions of +5 vanadium at the same *p*H.

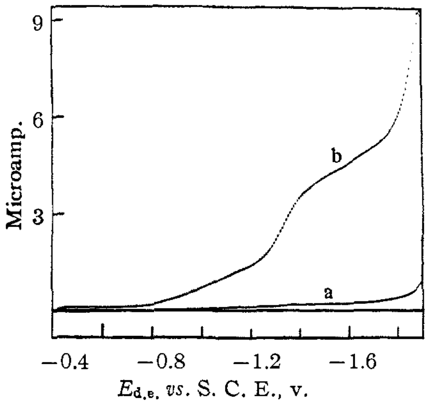

Fig. 1.—Polarograms of (a) 0 and (b) 0.97 millimolar +4 vanadium in unbuffered 1 *M* potassium sulfate, *p*H 6.1.

The half-wave potential of the main wave of +4 vanadium in unbuffered 1 *M* potassium sulfate at *p*H 6.1 is −1.290 v. *vs.* the saturated calomel electrode. Replacing the potassium sulfate in these solutions by 1 *M* potassium oxalate displaces the main wave to −1.307 ± 0.002 v. and completely eradicates the pre-wave (see Fig. 2). This shift in the half-wave potential, although small, definitely indicates the formation of an oxalato vanadyl complex.

In oxalate solutions of *p*H less than 5.4 no cathodic wave is observed, since hydrogen ion is reduced at less negative potentials than the oxalato vanadyl complex, but in solutions more basic than *p*H 6.6 the characteristic anodic wave representing oxidation of the +4 vanadium to the +5 state appears.

Table I summarizes data on the variation with *p*H of the half-wave potentials of these waves in

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[1] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[2] J. J. Lingane and L. Meites, Jr., *ibid.*, **68**, 2443 (1946).

[3] G. Jones and J. H. Colvin, *ibid.*, **66**, 1563 (1944).

[4] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

[5] J. J. Lingane, *ibid.*, **16**, 329 (1944).

[6] G. Jones and W. A. Ray, THIS JOURNAL, **66**, 1571 (1944).

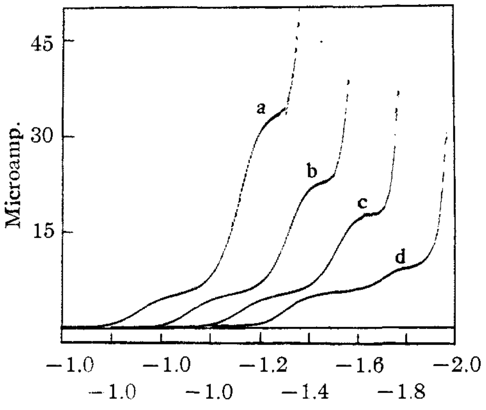

Fig. 2.—Polarograms of 0.97 millimolar +4 vanadium in 1 *M* potassium oxalate containing +0.005% gelatin, at *p*H (a) 5.50, (b) 5.70, (c) 5.90 and (d) 6.10.

the *p*H ranges in which they appear, as well as the diffusion current constants, where these have been determined. The half-wave potentials were measured from large-scale plots of $E_{d.e.}$ against log (i/i_d-i),[7] and we believe them to be precise to ±3 mv. Each diffusion current constant is the mean of ten independent measurements.

All solutions of *p*H 8.2 or less contained 1 *M* potassium oxalate; the others were saturated with the salt, whose solubility decreases rapidly with increasing *p*H. Solutions of *p*H 6.6 or higher were buffered with either the carbon dioxide–bicarbonate or the bicarbonate–carbonate system, and the solutions of *p*H 8.2 and greater were protected against air-oxidation by the addition of 0.1 *M* sodium sulfite. Neither carbonate nor sulfite causes any detectable change of the half-wave potential at any *p*H in the range in which they were used.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS OF +4 VANADIUM IN OXALATE SOLUTIONS OF VARIOUS *p*H

Half-wave potentials are referred to the saturated calomel electrode.

	Cathodic wave		Anodic wave	
*p*H	$E_{1/2}$, volts	$i_d/cm^{2/3}t^{1/6}$	$E_{1/2}$, volts	$i_d/cm^{2/3}t^{1/6}$
5.71	−1.309		.....	
5.81	−1.300		.....	
5.91	−1.307		.....	
6.02	−1.307		.....	
6.11	−1.309	4.32 ± 0.00	.....	
6.60	−1.336		+0.10	
6.79	−1.316		+ .073	
7.61	−1.290	3.93 ± 0.03	+ .051	−1.35 ± 0.03[a]
8.2	−1.314		− .126	
8.8	−1.438	3.37 ± 0.03	− .281	−1.30 ± 0.02
9.4	−1.500	3.32 ± 0.03	− .328	−1.30 ± 0.01
11.7	.....		− .453	
13	.....		− .46	

[a] In accordance with the common sign convention, a negative sign is prefixed to anodic diffusion current constants.

The concentration of vanadium used in the experiments was uniformly 0.885 millimolar.

The half-wave potential data are presented graphically in Fig. 3. Note that different ordinate scales are used for the two curves. It is seen that both half-wave potentials begin rapid shifts to more negative values at a *p*H near 7.6. Calculations of the concentrations of the various ions in the solutions, using the value 5.18×10^{-5} for the ionization constant of hydrogen oxalate ion,[8] show that at *p*H 7.4 the hydrogen oxalate ion concentration becomes equal to the concentration of +4 vanadium used in these experiments. We infer from this that the complex probably involves the hydrogen oxalate ion.

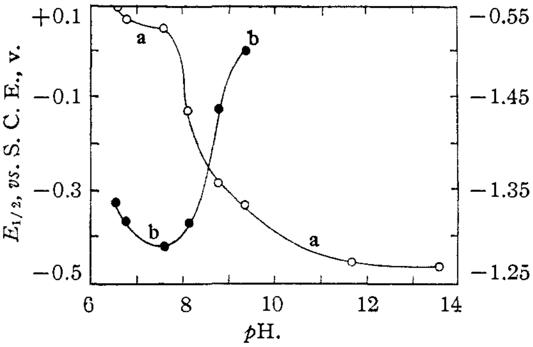

Fig. 3.—Effect of *p*H on half-wave potentials of (a) the anodic wave (left ordinate), and (b) the cathodic wave (right ordinate) of 0.885 millimolar +4 vanadium in potassium oxalate solutions.

The values of the diffusion current constants in Table I indicate that the electrode processes are not simply reduction and oxidation of the +4 vanadium contained in the complex ion, because the ratios of the cathodic to anodic diffusion current constants at any *p*H are not simple whole numbers. The diffusion current constants of the anodic wave are close to those found[9] for the anodic waves in other media, which correspond to a 1-electron oxidation of +4 vanadium. Since the reduction of the vanadium can proceed only to the +2 state, the excessively large cathodic diffusion current must be attributed to a catalytic reduction of the hydrogen oxalate ion of the complex (the normal reduction of hydrogen oxalate ion is discussed below), a view which is supported by the decrease in the cathodic diffusion current constant with increasing *p*H.

The second wave, at −1.77 v., in each of the polarograms of Fig. 2 is due to the reduction of hydrogen oxalate ion. The height of this wave was measured in solutions of varying *p*H containing 1.00 *M* total oxalate, with the results quoted in Table II. The concentrations of hydrogen

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(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

(8) H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 3111 (1939).

(9) L. Meites, Jr., Ph.D. Thesis, Harvard University, 1947.

oxalate ion were computed from the measured *p*H and the second ionization constant of oxalic acid,[8] neglecting activity coefficients. Diffusion currents have been corrected for the residual current.

TABLE II

POLAROGRAPHIC REDUCTION OF HYDROGEN OXALATE ION

*p*H	($HC_2O_4^-$), millimolar	i_d, microamperes	i_d/($HC_2O_4^-$)(microamp./millimole/liter)
5.45	55.0	35.9	0.653
5.53	46.1	30.3	.657
5.63	37.0	25.4	.686
5.78	26.4	18.1	.686
5.88	21.2	14.3	.673
6.10	12.8	8.7	.679
			Mean $0.67_2 \pm 0.01_1$

The diffusion current was also found to be directly proportional to the hydrogen oxalate ion concentration in an experiment in which a solution of sodium oxalate was added to an acetic acid–sodium acetate buffer of the same *p*H. Since care was taken to maintain the ionic strength reasonably constant in these experiments, the uncertainty due to variations of the activity coefficients with the ionic strength should have been small.

Herasymenko[10] concluded that oxalic acid was reducible at the dropping electrode according to the equation

$$H_2C_2O_4 + 2H^+ + 2e^- \longrightarrow CHOCOOH + H_2O$$

but he did not study the behavior of the reduction wave at any *p*H higher than about 3.3, and hence this reduction of hydrogen oxalate ion has been hitherto unknown. The fact that the half-wave potential is −1.77 v. independent of variations in *p*H suggests that hydrogen ion is not involved in the rate determining step in the electrode reaction, but further study is needed before this conclusion can be definitely affirmed.

+5 Vanadium.—Pervanadyl ion in strongly acid solutions gives two cathodic waves: the first, representing reduction to the +4 state, starts at the most positive obtainable e. m. f., and the second, caused by reduction to the +2 state, has a half-wave potential of −0.85 v.[1] In strongly alkaline solutions +5 vanadium produces only a single reduction wave at about −1.7 v.[11]

Figure 4 contains polarograms of +5 vanadium in 1 *M* potassium oxalate solutions. At *p*H 4.6 (curves I) the first wave exhibits its diffusion current plateau from the beginning of the polarograms, while the half-wave potential of the second is the same, −1.33 v., as that of +4 vanadium in the same medium. The respective diffusion current constants are 1.862 ± 0.003 and 5.60 ± 0.02, and the electrode processes are the successive reductions of the +5 vanadium to the +4 and +2 states.

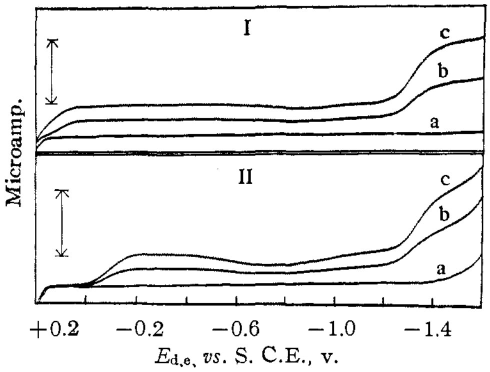

Fig. 4.—Polarograms of (a) 0, (b) 0.52, and (c) 0.98 millimolar +5 vanadium in 1 *M* potassium oxalate, at *p*H (I) 4.8, (II) 7.6.

In a 1 *M* potassium oxalate solution of *p*H 7.6, in the presence of a 1 *M* potassium bicarbonate–saturated carbon dioxide buffer, the half-wave potentials are −0.05 and −1.32 v. (curves II). The peculiar shape of the first wave, with its flat minimum several tenths of a volt after the plateau has been reached, is reminiscent of a similar wave form observed[7] with solutions of chloroindic ion in potassium chloride. An attempt was made to utilize this wave for the determination of vanadium in the presence of excess ferric iron which in oxalate solutions of *p*H about 7 gives a cathodic wave at −0.25 v.[12] However, the reduction of +5 vanadium proceeds so irreversibly in this medium that its diffusion current plateau is completely masked by even as little as a tenfold excess of ferric iron.

+3 Vanadium.—Lingane[1] found for +3 vanadium in 1 *N* sulfuric acid containing 0.005% gelatin a single well-defined cathodic wave with a half-wave potential of −0.55 v., due to reduction to the +2 state. Without gelatin present the half-wave potential of this wave in 1 *N* sulfuric acid is −0.508 ± 0.002 v., in excellent agreement with the potentiometrically determined standard potential of the vanadic–vanadous couple.[13] Without gelatin the reduction of vanadic ion proceeds reversibly, but even 0.005% gelatin leads to distinct irreversibility. No maximum is observed in the absence of gelatin, and hence the use of gelatin or other maximum suppressor is unnecessary in practical analysis.

The half-wave potential of the single cathodic wave of the intensely green solutions of +3 vanadium in 1.00 *M* potassium oxalate at *p*H 3.5 to 6.5 is −1.136 ± 0.002 v. *vs.* the saturated calomel electrode (see Fig. 5). Since this is the same as the half-wave potential of the anodic wave produced by the oxidation of the vanadous complex in the same solutions at a *p*H of 4.5, the couple is

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(10) P. Herasymenko, *Z. Elektrochem.*, **34**, 129 (1928).

(11) G. Thanheiser and J. Willems, *Arch. Eisenhuttenw.*, **13**, 73 (1939).

(12) J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

(13) G. Jones and J. H. Colvin, THIS JOURNAL, **66**, 1573 (1944).

thermodynamically reversible in these media. This question is further discussed in the following section devoted to +2 vanadium. The cathodic diffusion current constant of +3 vanadium in these solutions is 1.95 ± 0.01.

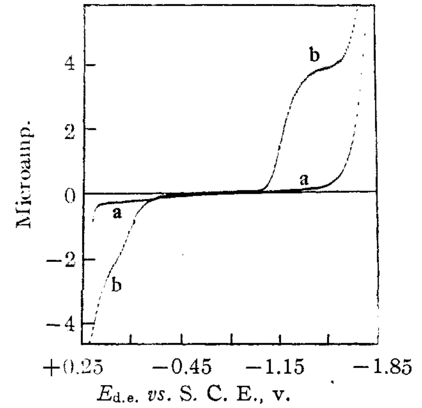

Fig. 5.—Polarograms of (a) 0 and (b) 0.71 millimolar +3 vanadium in 1 *M* potassium oxalate at *p*H 4.5.

In acidic oxalate solutions +3 vanadium also gives an anodic wave at about −0.05 v. (see Fig. 5), which appears to be nearly equal in height to the cathodic wave, and which, therefore, must represent oxidation of the vanadium to the +4 state. This wave is so ill-defined at all oxalate- and hydrogen-ion concentrations that it has no analytical applications.

+2 Vanadium.—The half-wave potential of the single anodic wave of +2 vanadium in 1 *N* sulfuric acid is −0.50 v.[1] The oxidation proceeds reversibly to the +3 state.

Solutions of +2 vanadium in potassium oxalate are colored an extremely intense reddish-brown, and yield polarograms as in Fig. 6.

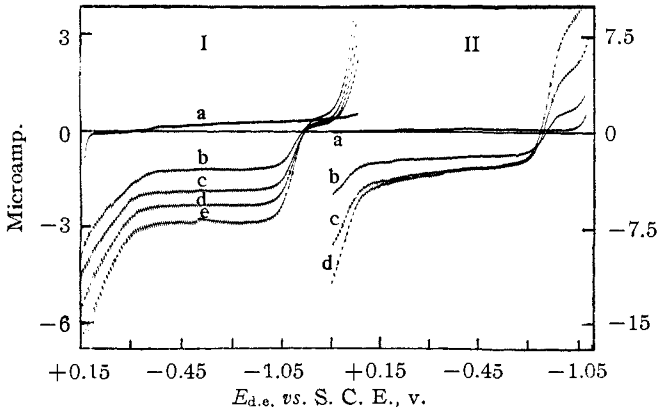

Fig. 6.—(I) Polarograms of (a) 0, (b) 0.625, (c) 0.920, (d) 1.122 and (e) 1.362 millimolar +2 vanadium in 1 *M* potassium oxalate at *p*H 6.5. (II) Polarograms of (a) 0, (b) 1.50, (c) 3.26 and (d) 4.80 millimolar +2 vanadium in 1 *M* potassium oxalate at *p*H 4.5.

In 1 *M* potassium oxalate at *p*H 6.5 (curves I, Fig. 6), the half-wave potential of the single excellently developed anodic wave is −1.091 ± 0.002 v. *vs.* the saturated calomel electrode. In the absence of air, these solutions retain their characteristic color for about a week, showing that they are comparatively stable in the presence of this low concentration of hydrogen ion. The ion of +2 vanadium in these solutions is much larger than simple vanadous ion; the respective diffusion current constants are −1.43 ± 0.03 and −1.74 ± 0.01.

The half-wave potential of +2 vanadium in 1 *M* potassium oxalate at *p*H 4.5 is −1.136 ± 0.003 v., which is exactly equal to that of the cathodic wave of +3 vanadium in the same medium (*vide supra*). At *p*H 4.5 the +2 vanadium complex is so rapidly oxidized by hydrogen ion that the diffusion current constant cannot be measured. For example, see curves c and d of curves II, Fig. 6, which represent two different concentrations of +2 vanadium: the initially higher diffusion current of curve d decreases as the vanadium is oxidized to the +3 state, and simultaneously a cathodic wave (reduction of +3 vanadium) develops just before the final current rise. The character of the anodic-cathodic wave thus produced (absence of an inflection at zero current) indicates that the electrode reactions are reversible.

A partial identification of the species involved in this couple is made possible by the data of Table III on the variations of the half-wave potentials with oxalate concentrations.

Substituting these data into the equation[12] $\Delta E^{1/2} = -0.0591\ (\Delta p)\ (\Delta \log C_{\text{ox}})$, where C_{ox} is the molar concentration of oxalate, and Δp is the difference in the number of oxalate ions coördinated with +3 and +2 vanadium, we calculate a mean of 1.98 for Δp. Therefore, we write the following schematic equation

$$\mathrm{V(C_2O_4)}_p^{(3-2p)} + \mathrm{e}^- = 2\mathrm{C_2O_4}^= + \mathrm{V(C_2O_4)}_{p-2}^{6-2p}$$

and, from the observed reversible half-wave potential and the known potential of the saturated calomel electrode, we assign the value −0.89 v. *vs.* N. H. E. to its standard potential.

TABLE III

VARIATION OF HALF-WAVE POTENTIALS OF +2 AND +3 VANADIUM WAVES WITH OXALATE CONCENTRATION AT *p*H 4.5

$K_2C_2O_4$, molar	$E^{1/2}$ of cathode +3 vanadium wave, *vs.* S. C. E., v.	$E^{1/2}$ of anodic +2 vanadium wave, *vs.* S.C.E., v.
1.00	−1.136	−1.136
0.50	−1.176	−1.101
.10	.....	−1.033

The diffusion current constant of this anodic wave at *p*H 6.5 decreases from −1.43 ± 0.03 in 1 *M* potassium oxalate to −1.40 ± 0.07 in 0.5 *M* and −1.34 ± 0.04 in 0.1 *M* potassium oxalate.

Figure 6 shows indication of a second anodic wave with a half-wave potential of about −0.05 v., which must represent oxidation to the +4 state. This half-wave potential is the same as that of the ill-defined anodic wave observed with solutions of +3 vanadium in the same media.

As the pH of the supporting electrolyte is increased above 6.5, the vanadous–vanadic oxalate couple becomes irreversible at the dropping electrode. At pH 10 (Fig. 7) the half-wave potential of the reduction wave is −1.22 v., while the anodic half-wave potential is −1.14 v. The wave given by +3 vanadium in this solution is complex in character: since its half-wave potential is close to that characteristic of the ion VO$^+$,[9] we believe that at this pH +3 vanadium divides between this ion and an oxalate complex.

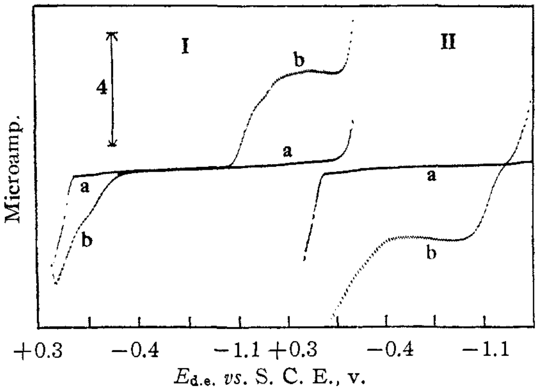

Fig. 7.—(I) Polarograms of (a) 0 and (b) 1.83 millimolar +3 vanadium in 1 M potassium oxalate at pH 10.0. (II) Polarograms of (a) 0 and (b) 2.30 millimolar +2 vanadium in the same medium.

Summary

1. +4 Vanadium has been found to form a complex hydrogen oxalate ion, which at all pH values below about 11 produces a cathodic wave corresponding to reduction of the +4 vanadium to the +2 state. Reduction of the hydrogen oxalate ion in the complex also contributes to the diffusion current of this wave.
2. In addition to the wave representing reduction to the +2 state, +5 vanadium in oxalate solutions gives a wave at more positive potentials which corresponds to reduction to the +4 state.
3. The vanadic–vanadous oxalate couple is shown to have a standard potential of −0.89 v. *vs.* the normal hydrogen electrode in solutions of pH about 4.5. In basic solutions the couple becomes irreversible, due to partial hydrolysis of the vanadic complex.
4. Half-wave potentials and diffusion current constants have been determined for all the oxidation states of vanadium in oxalate solutions of a wide variety of oxalate concentrations and pH values.
5. A previously undiscovered polarographic reduction of hydrogen oxalate ion is reported.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE BUTTERFIELD LABORATORY OF UNION COLLEGE]

Heats of Solution and Heats of Reaction in Liquid Ammonia. VII

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I. Introduction

A measurement of the heats of solution of the hydrochlorides of methylamine, dimethylamine, ethylamine and aniline would be a measurement of the competition of the base in question and the ammonia molecule itself for the proton, as indicated by the ionization constants of these same bases in water solution. Such was found to be the case. The aliphatic amine hydrochlorides showed heats of solution of the order of magnitude of normal salts. On the other hand, the heat evolved upon solution of aniline hydrochloride was of the magnitude of a heat of reaction. Subsequent measurement of the heat effect upon solution of purified aniline in liquid ammonia and in a solution of an equivalent amount of its hydrochloride in liquid ammonia indicated complete ammonolysis of this salt. Such experiments were not possible in the case of the amines, other than aniline, due to the low boiling points of these substances.

In this paper, the heat of reduction of the silver ion as it exists in liquid ammonia solution is reported.

II. Experimental

The calorimeter and procedure were the same as used in previous measurements.[2]

The amine hydrochlorides were purchased from the Eastman Corporation, Rochester, New York. These salts were recrystallized three times from absolute alcohol and dried in the fragile sample bulbs to a pressure of 10 microns at a temperature of 80°. Analysis for chlorine showed these salts to be pure. The silver halides were made from a solution of silver nitrate by the addition of a solution of Reagent Grade sodium bromide or iodide. The resulting precipitates

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[1] Present address: Ansco, Binghamton, N. Y.

[2] Schmidt, Studer and Sottysiak, THIS JOURNAL, **60**, 2780 (1938).