

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.

### 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.

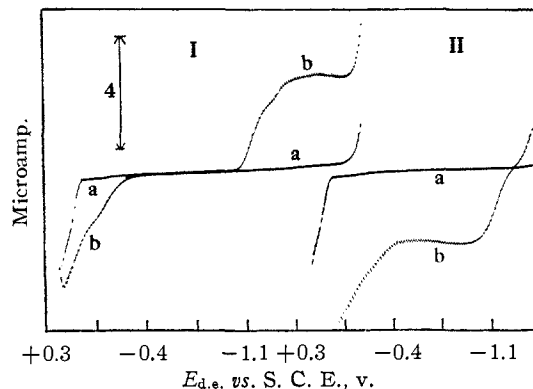


Fig. 7.—(I) Polarograms of (a) 0 and (b) 1.83 millimolar  $+3$  vanadium in 1  $M$  potassium oxalate at  $pH$  10.0. (II) Polarograms of (a) 0 and (b) 2.30 millimolar  $+2$  vanadium in the same medium.

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.

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

BY E. HENNELLY, D. K. STEVENS, M. WARREN, H. ZUHR AND J. SOTTYSIAK<sup>1</sup> WITH FREDERIC C. SCHMIDT

### 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.<sup>2</sup>

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  $80^{\circ}$ . 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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(2) Schmidt, Studer and Sottysiak, *THIS JOURNAL*, **60**, 2780 (1938).

were washed several times with distilled water. After drying in the dark, an analysis for silver showed these salts to be pure. The metallic potassium used in the reduction was filtered under a pressure of nitrogen according to the method of Kraus and Schmidt.<sup>3</sup> In carrying out the reduction of the silver ion by the electron, one component (silver iodide) was introduced into the calorimeter, and the other (K) was put into a fragile bulb. When the calorimeter reached a steady state, this bulb was crushed under the solution of silver iodide in liquid ammonia.

### III. Heats of Solution

Below in Tables I and II are given the molar heats of solution of the amine hydrochlorides and the two silver salts measured over a wide range of concentrations. As will be noticed in Fig. 1, the curves for the change in the molar heat of solution of the amine salts with the concentration are analogous in both curvature and slope to those of the strong ammonio acids in liquid ammonia. The curve for ammonium chloride has been repeated for comparison. Figure 2 shows the heat of solution-concentration curves for the silver salts. It is interesting to note that the curve for the bromide shows a decrease in the molar heat effect with a decrease in concentration. This phenomenon is similar to that shown by the

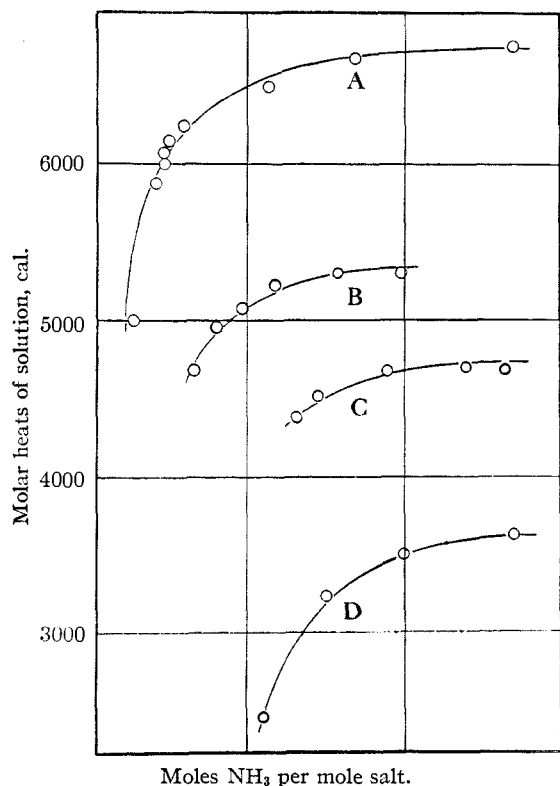


Fig. 1.—Molar heats of solution: A,  $\text{NH}_4\text{Cl}$ ; B,  $\text{CH}_3\text{-NH}_2\text{Cl}$ ; C,  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ ; D,  $\text{CH}_3\text{CH}_2\text{NH}_2\text{Cl}$ .

(3) Kraus and Schmidt, *ibid.*, 56, 2297 (1934).

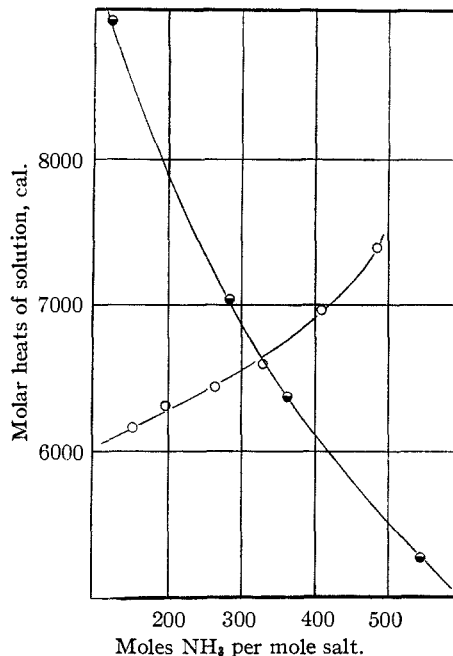


Fig. 2.—Molar heats of solution of silver halides:  $\text{AgI}$ ,  $\circ$ ;  $\text{AgBr}$ ,  $\bullet$ .

curves for the atomic heats of solution of those heavily solvated elements, lithium, calcium, barium and strontium.<sup>2</sup>

TABLE I  
MOLAR HEATS OF SOLUTION OF ALKYL SUBSTITUTED AMMONIUM CHLORIDES AT  $-33.4^\circ$

Sample, g.	Moles $\text{NH}_3$ per mole salt	Molar heat of solution, cal.
Monomethylammonium chloride		
0.5907	199.5	5320
.7335	159.6	5300
.9989	118.4	5246
1.1835	99.4	5090
1.4709	80.2	4956
1.7501	66.8	4678
Dimethylammonium chloride		
0.8731	265.0	4679
.9625	240.0	4702
1.2256	190.0	4700
1.5759	146.0	4525
1.7623	131.0	4390
Monoethylammonium chloride		
0.8663	270.3	3620
1.1600	200.0	3500
1.5316	152.0	3232
2.4350	113.0	2435

### IV. Heats of Reaction

In Table III are given the data pertaining to the complete ammonolysis of aniline hydrochloride, or the heat of transfer of the proton from the phenylammonium ion to the ammonia molecule. Data for the reduction of silver iodide by metallic potassium in liquid ammonia are also represented.

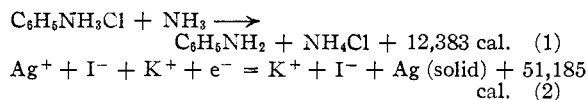
TABLE II  
MOLAR HEATS OF SOLUTION OF SOME SILVER HALIDES AT  
-33.4°

Sample, g.	Moles NH <sub>3</sub> per mole salt	Molar heat of solution, cal.
Silver bromide		
2.6578	123.8	8931
1.1493	285.0	7044
0.8958	367.5	6370
.6260	525.7	5270
Silver iodide		
2.1615	156.2	6150
2.0618	199.6	6300
1.5235	268.7	6420
1.2294	332.8	6570
1.0004	411.0	6930
0.8493	484.2	7400

TABLE III  
HEATS OF REACTION IN LIQUID AMMONIA

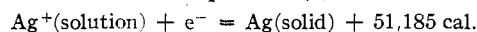
Subst. (1)	Wt. (1)	Subst. (2)	Wt. (2)	Heat of reaction, calories	Mean
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> Cl	1.0936	NH <sub>3</sub>	Excess	12,336	12,383
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> Cl	1.1780	NH <sub>3</sub>	Excess	12,431	
Aniline	1.4740	NH <sub>4</sub> Cl <sub>am.</sub>	Equiv.	3170	51,185
Aniline	1.4743	NH <sub>3</sub>	Excess	3220	
AgI <sub>am.</sub>	3.0020	K	Equiv.	51,353	
AgI <sub>am.</sub>	1.4350	K	Equiv.	51,017	

The energies of the above reactions are represented by the equations



Combining the heat of mixing of the aniline with liquid ammonia (3221 cal.) (Table III) and the heat of solution of ammonium chloride<sup>4</sup> (6700 cal.) with the heat of reaction of equation 1, we obtain as a heat of solution and ammonolysis of aniline hydrochloride 2405 cal. This small heat effect indicates that phenylammonium ion is quite unstable and easily loses the proton to ammonia.

The net result of equation (2) would be



This heat represents the heat of reduction of the silver ion as it exists in liquid ammonia solution.

## V. Summary

The heats of solution of the hydrochloride of methylamine, dimethylamine, ethylamine, silver bromide, and silver iodide have been determined over a range of concentrations in anhydrous liquid ammonia.

The heat of ammonolysis of aniline hydrochloride and the heat of reduction of the silver ion as it exists in liquid ammonia solution by the electron in liquid ammonia are reported.

(4) Schmidt, Sottysiak and Kluge, *ibid.*, **58**, 2509 (1936).

SCHENECTADY, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## Photochemical Investigations. VIII. The Photolysis of Solutions of Ethylene Iodide<sup>1</sup>

BY ROBERT J. GRABENSTETTER<sup>2</sup> AND EDWIN O. WIIG

The thermal decomposition of ethylene iodide in carbon tetrachloride solution has been shown by Polissar<sup>3</sup> to proceed simultaneously by a unimolecular decomposition and an iodine catalyzed decomposition. Arnold and Kistiakowsky<sup>4</sup> found a similar behavior in the gas phase which Ogg<sup>5</sup> has shown can be explained by a chain mechanism similar to the one suggested by Schumacher<sup>6</sup> for the decomposition in carbon tetrachloride solution. Both Ogg and Schumacher suggested that such a chain mechanism would explain the addition of halogen to ethylenic linkages as well as the decomposition of such halogen compounds.

For the iodine photosensitized decomposition

(1) Presented at the Atlantic City, New Jersey, meeting of the American Chemical Society, September 10, 1941.

(2) Abstract from part of a thesis submitted in 1941 to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy. Present address: Proctor and Gamble Co., Ivorydale, Ohio.

(3) Polissar, *THIS JOURNAL*, **52**, 956 (1930).

(4) Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(5) Ogg, *THIS JOURNAL*, **58**, 607 (1936).

(6) Schumacher, *ibid.*, **52**, 3132 (1930).

of ethylene iodide in carbon tetrachloride solution at 4360 and 4050 Å. a quantum yield of 25 was found,<sup>7</sup> in agreement with the suggested chain mechanism. At longer wave lengths Schumacher and Stieger<sup>8</sup> found a smaller quantum yield for this sensitized reaction. This was subsequently shown by Dickinson and Nies<sup>9</sup> to be due to the smaller absorption coefficient of iodine at the longer wave lengths. These workers also demonstrated that the regions of continuous absorption by iodine were only slightly more effective than the regions of discontinuous absorption. The direct photolysis and the iodine photosensitized decomposition of gaseous ethylene iodide also probably proceed by the same chain mechanism.<sup>10</sup>

In a previous investigation<sup>11</sup> of the photolysis of ethylene iodide in carbon tetrachloride solution, using light absorbed only by ethylene iodide, it

(7) Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

(8) Schumacher and Stieger, *ibid.*, **12B**, 348 (1931).

(9) Dickinson and Nies, *THIS JOURNAL*, **57**, 2382 (1935).

(10) Janneck and Wiig, *ibid.*, **62**, 1877 (1940).

(11) DeRight and Wiig, *ibid.*, **57**, 2411 (1935).