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HEATS OF SOLUTION OF SILVER HALIDES
IN LIQUID AMMONIA

A thesis presented to the Department of
Chemistry of Union College, in partial
fulfillment of the requirements for the
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Heats of Solution of Silver Halides in Liquid Ammonia

Introduction

Of the many solvents known to man, water and liquid ammonia probably are the best. Each has its advantages and disadvantages. It was the hope of the experimenters to make use of one of the advantages of liquid ammonia, that of the solubility of metallic sodium to give a free electron, to find the heat of reduction of the silver ion to the metallic state.^{1,2} The following reaction was the one to be used.



What actually might have been obtained was the energy of the first ionization of silver plus the heat of solvation of the silver ion. The heats of solution of sodium⁵ and sodium bromide⁵ were known over reasonable concentrations, but it was our first task to obtain such a curve for silver bromide. After making several determinations at different concentrations it became evident that this salt was too insoluble for the required purposes. At low concentrations calorimeter errors and other experimental errors became too large for sufficient accuracy. One value will be reported in this thesis.

As silver iodide was known to be much more soluble than silver bromide it was decided to substitute a similar reaction to obtain the desired end.



Again, the heats of solution of sodium⁵ and sodium iodide⁷ were

known, but the necessary silver salt had not as yet been investigated thoroughly. Two determinations had been reported^{3,4} but unfortunately time and circumstances did not permit the making of enough additional determinations to draw a reliable curve.

Apparatus and Procedure

The apparatus and procedure are much the same as described in the departmental theses of Sottysiak⁵ and Davison³. The actual calorimeter is described in a paper by Schmidt, Studer, and Sottysiak.⁶

The weighed sample was sealed under reduced pressure, ca. 10 microns, in a sample bulb, and the whole fused on the end of the crusher rod in the reaction flask. The system was then sealed and evacuated to a pressure of 10 microns, purged with ammonia gas, and again evacuated. The pipette end of the system was then closed off, and ammonia from a storage tank was allowed to distill into the liquid ammonia jacketed pipette. When the pipette had filled to a level indicating 29.89 grams of ammonia the source was closed off, and a jacket of liquid ammonia in a silvered Dewar was placed around the reaction flask which was itself a silvered Dewar. The pipette end of the apparatus was then opened to the rest of the system, and the ammonia jacket removed from the pipette allowing the ammonia in the pipette to vaporize and recondense in the reaction flask. When all of the solvent had boiled over, the pipette end was again closed off, the ammonia escape adjusted, and the magnetic

stirrer started. When the temperature had become constant over a period of one minute as indicated by a thermocouple, one end of which was in the reaction flask and the other in a freezing mixture of water and ice, the sample bulb was crushed against the bottom of the reaction flask. Temperature readings were taken every 15 seconds. Ammonia volatilized by the heat liberated was captured in distilled water over the ammonia escape which was transferred to a volumetric flask and diluted to five hundred milliliters. The solution was then titrated against standardized sulfuric acid and the number of grams of liberated ammonia calculated. This multiplied by the heat of vaporization of NH_3 gave the number of calories measured by the vaporized ammonia. The change in temperature in the apparatus expressed in millivolts divided by .038 millivolts per degree gave the change in temperature in the apparatus in degrees Centigrade. This multiplied by the heat constant of the apparatus, 40.95 calories per degree, gave the number of calories required to change the temperature of the apparatus. This latter quantity added to the number of calories used in vaporizing the ammonia resulted in the total number of calories liberated when the given sample dissolved in 29.89 grams of ammonia. By the method of ratios this was reduced to calories per gram mole of solute. The ratio, mols NH_3 /mol solute, was also calculated.

Preparation of Salts

The silver bromide used was prepared by mixing equivalent amounts of dissolved c.p. silver nitrate and c.p. sodium bromide

in a slightly acid solution. The mother liquor was filtered off, and the precipitate washed several times, using about three liters of distilled water. The silver bromide was then transferred to a weighing bottle and dried at 110°C . for three hours.

The silver iodide was prepared in the same manner using sodium iodide instead of sodium bromide. In each case nitric acid was used to acidify the solution.

Sample Calculation

salt	wt. of sample	EMF	ml. H_2SO_4 per 50 ml. NH_3 sol.	N. of H_2SO_4	size of aliquot portions
AgI	2.4503 g.	.004 mv.	8.05	.1186	50 ml.

$$\Delta T^{\circ} = \frac{.004}{.038} = .105^{\circ} \text{C.}$$

$$\Delta H_{\Delta T} = .105 \times 40.95 = 4.31 \text{ calories}$$

$$\begin{aligned} \text{grams of } \text{NH}_3 \text{ evolved} &= (\text{ml.})(\text{N.})(\text{no. aliquot portions in total})(\text{me. wt. of } \text{NH}_3) \\ &= (8.05)(.1186)(10)(.017) = .1623 \text{ grams of } \text{NH}_3 \text{ evolved.} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{NH}_3} &= (\text{grams of } \text{NH}_3 \text{ evolved})(\text{heat of vaporization of } \text{NH}_3) \\ &= (.1623)(327.7) = 53.19 \text{ calories.} \end{aligned}$$

$$\Delta H_s = \Delta H_{\Delta T} + \Delta H_{\text{NH}_3} = 4.31 + 53.19 = 57.50 \text{ calories } \frac{\text{cal.}}{2.4503 \text{ g.}}$$

$$Q = \Delta H_s \cdot \frac{\text{mol. wt. salt}}{\text{wt. of sample}} = \frac{57.50 \times 234.8}{2.4503} = 5510 \frac{\text{cal.}}{\text{mole}}$$

Results

salt	gms. salt	$\frac{\text{mols NH}_3}{\text{mole salt}}$	NH_3 evolved <i>grams</i>	ΔT $^{\circ}\text{C}$	ΔH <i>calories</i>	Molar ΔH <i>calories</i>
AgBr	.6260	525.7	.05363	0	17.54	5270
AgI	2.4503	168.0	.1623	.105	57.50	5510
AgI	2.0618	199.6	.1403	.184	53.53	6096
AgI	1.1025	373.2	.0768	.026	26.25	5590

Summary

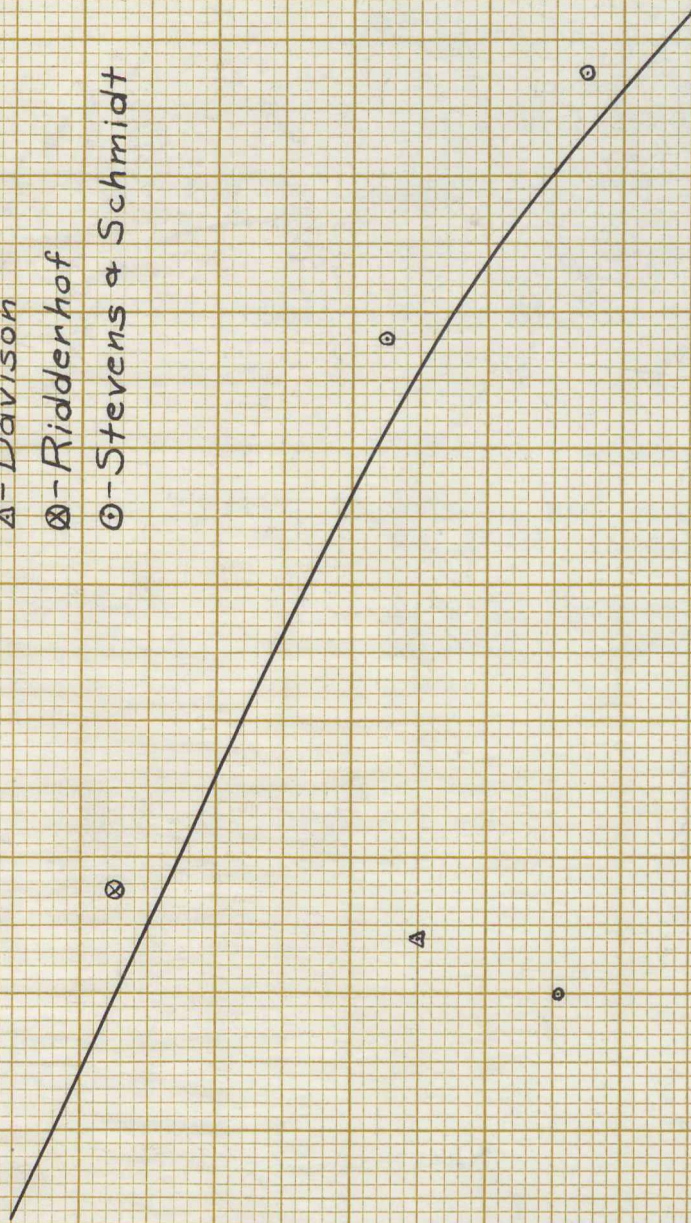
It was found that silver bromide had too low a solubility for the desired purposes. Silver iodide, which is much more soluble, is expected to have a negative heat of dilution.

The exact solubility of silver bromide and silver iodide in liquid ammonia at its boiling temperature at one atmosphere pressure (-33.4°C .) has yet to be found. The curves for the heat of solution of the same salts should be completed, and the energy of the first ionization plus the heat of ammoniation of the silver ion, using sodium as the reducing agent, should also be determined.

Heat of Solution AgI in 29.89 Gms. of Liquid Ammonia (-33.4°C.)

Δ - Davison
⊗ - Ridderhof
○ - Stevens & Schmidt

Calories/Mole



Grams of AgI

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