[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNION COLLEGE]

Heats of Solution and Heats of Reaction on Liquid Ammonia[1]

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In order to study more thoroughly the properties of electrolytes and other compounds in aqueous solution, thermochemical characteristics of these solutions have been examined. Among these, the heats of solution and dilution have been determined experimentally. Such data are scarce in the study of the properties of liquid ammonia solutions.

Kraus and Ridderhof designed a liquid ammonia calorimeter and some heats of solution and reaction were measured.[2]

In the present work the authors have made some measurements of the heats of solution of several electrolytes and non-electrolytes over a fairly wide range of concentrations with this same calorimeter. From the curves obtained the heats of dilution may be calculated.

Experimental Details

The calorimeter described by Kraus and Ridderhof[2] was used and was further improved by silvering, thus making the correction for the heat flow out of or into the instrument practically negligible. The new radiation constant was found to be 0.125 cal./deg./min. The other constants and the experimental procedure were the same as in the earlier investigation of Kraus and Schmidt.[3]

Temperatures were measured by means of a copper-constantan thermocouple (0.0385 mv./deg.) similar to that of Kraus and Prescott,[3] in conjunction with a "Queen" potentiometer and a matched sensitive galvanometer. Temperatures were read directly from the calibration curve of this thermocouple and were accurate to 0.01°; the heat capacity of the calorimeter being 6.73 cal. The error in heat measurement was 0.33 cal. The calorimeter contained 24.89 g. of liquid ammonia.

The heats of solution of ammonium bromide and ammonium chloride; lead iodide and absolute ethyl alcohol were measured over the maximum range of concentration allowed by the construction of the calorimeter. Trial heat effects were made on a few other electrolytes and on pyridine. The ammonium salts were of reagent quality and were recrystallized three times from distilled water. They were pumped and dried at 100° to constant weight. The ethanol was dried over lime and then anhydrous copper sulfate. It was then distilled into weighed bulbs out of contact with the air, and introduced directly into the calorimeter for measurement.

Experimental Results

The heats of solution of ammonium chloride and ammonium bromide are presented in Table I, those for absolute ethyl alcohol in Table II, and those of lead iodide and miscellaneous compounds in Table III.

TABLE I

MOLAR HEATS OF SOLUTION OF AMMONIUM CHLORIDE AND BROMIDE

Wt., g.	Mols NH_3 per mol salt	Obsd. heat effect	Molar heat effect
(A) AMMONIUM CHLORIDE			
0.2888	270.5	36.5	6754
.4592	169.6	57.3	6663
.7710	101.6	93.3	6475
.7773	99.8	96.6	6652
1.2599	61.2	146.9	6240
1.4486	53.1	166.9	6165
1.5547	49.4	174.3	5993
1.5559	49.3	176.9	6083
1.7948	42.7	196.9	5870
2.5665	29.6	240.4	5009
3.0565	25.4	258.9	4532
(B) AMMONIUM BROMIDE			
0.4957	228.4	52.6	10435
.8101	175.4	83.3	10066
1.2523	112.9	121.6	9512
1.4959	94.4	135.5	8873
1.8070	78.0	157.9	8560
2.4423	57.4	195.9	7858

TABLE II

MOLAR HEATS OF SOLUTION OF ABSOLUTE ETHANOL

Wt. sample, g.	Mols NH_3 per mol alcohol	Obsd. heat effect	Molar heat effect
2.3784	28.3	60.9	1180
2.1062	32.0	52.0	1137
1.8322	36.8	43.3	1086
1.7695	38.0	42.5	1160
1.6539	40.8	36.6	1020
1.4357	46.9	25.0	803
1.4327	47.0	27.0	867
1.3139	51.3	15.0	530

(1) This present investigation was made possible by a Grant-in-Aid from the Society of the Sigma Xi and by aid received from the Warren Fund of the American Academy of Arts and Sciences.

(2) C. A. Kraus and J. A. Ridderhof, THIS JOURNAL, **56**, 79 (1934).

(3) Kraus and Schmidt, *ibid.*, **56**, 2297 (1934); Kraus and Prescott, *ibid.*, **56**, 86 (1934).

TABLE III

SOME MOLAR HEATS OF SOLUTION

Subs.	Wt., g.	NH_3 vap. g.,	Obsd. heat effect	Molar heat effect
Lead iodide	2.4281	0.4077	137.0	26020
Lead iodide	2.1772	.3429	123.5	26151
Lead iodide	1.0755	.1616	63.8	27370
Lead iodide	0.7733	.1067	45.9	27360
Mercuric iodide	2.0202	.2598	97.0	20123
Lithium iodide	0.9225	.3231	124.7	18090
Lithium bromide	.5454	.3317	123.8	19715
Rb bromide	.6271	.0000	1.7	440
Pyridine	1.1150	.0000	−17.6	−1250

Discussion

As will be noted on examining Fig. 1, the heats of solution of the ammonium salts vary regularly over the range of concentration measured, increasing with decreasing concentration. These curves are similar to the heat of solution curves of the strong acids in aqueous solution. These results are in accord with the view that the ammonium salts are ammoniated acids in the nitrogen system of compounds.[4]

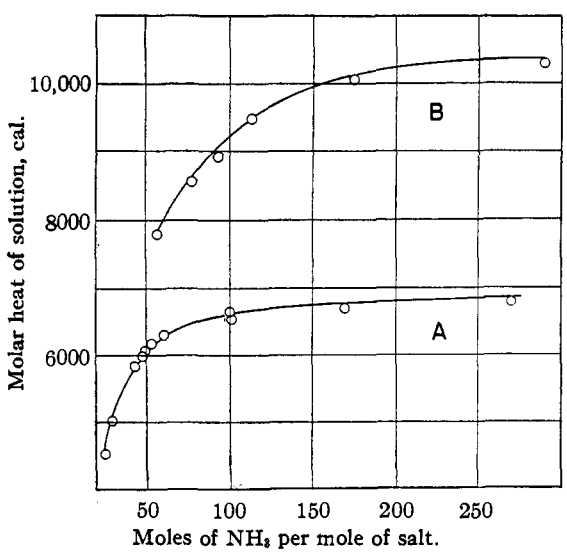

Fig. 1.—Showing variation in the molar heat of solution with concentration: (A) ammonium chloride; (B) ammonium bromide..

From these heat of solution curves it is possible to obtain the heats of dilution of these salts in liquid ammonia. The heat of solution of ammonium chloride in dilute solution is approaching 6800 calories per mole, while that of ammonium bromide at infinite dilution has a value of about 10,500 calories per mole. The absolute ethanol shows also a positive molar heat of solution which varies decidedly with the concentration. The slope of the curve for this compound, as is shown by Fig. 2, is negative. Ethanol has a negative heat of dilution in contrast with the positive dilution heat effect displayed by the ammonium salts. Apparently, energy must be supplied in order to disassociate the ethyl alcohol aggregates as the solution is diluted. The heats of solution of lead iodide, mercuric iodide and the lithium salts are high and are of the order of magnitude of heats of reaction. The lead and mercury salts are known to react with ammonia to form fairly stable ammoniates. The lithium salts, no doubt, show a high heat effect due to the solvation of the positive lithium ion with ammonia molecules. Metallic lithium itself has the highest heat of solution in liquid ammonia of all the alkali metals measured so far.[3]

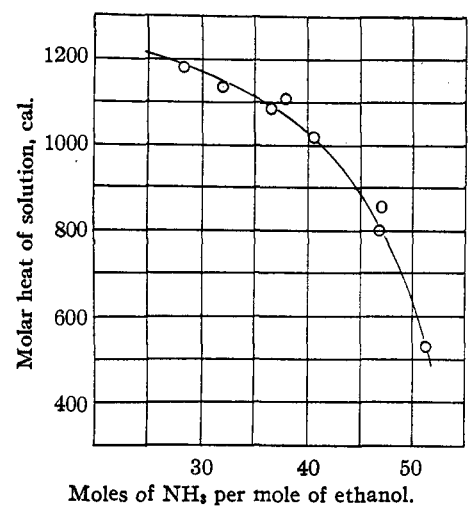

Fig. 2.—Showing variation in the heat of solution of ethanol with the concentration.

The authors wish to thank Dr. C. A. Kraus of Brown University for his kindness in the loan of the liquid ammonia calorimeter.

Summary

The molar heats of solution of ammonium chloride and ammonium bromide have been measured in liquid ammonia over a fairly wide range of concentration and show a marked heat of dilution.

The molar heat of solution of ethyl alcohol has been measured over a range of concentration and it has been shown that this compound has a decided negative heat of dilution.

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(4) Franklin, "Nitrogen System of Compounds," Reinhold Publishing Corp., New York, 1935, p. 26.