[CONTRIBUTION FROM THE BUTTERFIELD LABORATORY OF UNION COLLEGE]

Heats of Solution and Reaction in Anhydrous Liquid Ammonia. VI[1]

BY FREDERICK C. SCHMIDT, JOSEPH SOTTYSIAK, EDWARD TAJKOWSKI AND WALTER A. DENISON[2]

Introduction

In previous papers of this series the heat of solution–concentration curves of some of the ammonoacids have been published and have been found similar to the corresponding acids in water.[3] In this present paper the heat of solution of the ammonoacid, ammonium iodide, is reported over a fairly wide range of concentrations along with the heats of solution of sodium iodide, sodium chloride, and sodium nitrate. Some heats of solution of several alcohols are also reported.

The heats of solution of ammonium iodide, sodium iodide, sodium nitrate and sodium chloride are presented in Table I while those of the alcohols are given in Table II.

As will be noticed in Fig. 1, the curves for ammonium and sodium iodide show a similar rapid decrease in the molar heat of solution with a decrease in concentration. In the regions of small ratios of the ammonium salts to ammonia, there are, no doubt, discontinuities in the curves due to the heat effects produced by formation of salt ammoniates. Several ammoniates of both ammonium and sodium iodide are reported in the literature.[5] In Fig. 1, the curves for the ammono acids, ammonium chloride and bromide, have been repeated for contrast.[3] Both ammonium and sodium iodide show a negative heat of dilution. The molar heat of solution curve for sodium nitrate shown in Fig. 2 is normal for salts and shows a heat of solution at infinite dilution of 4000 calories.

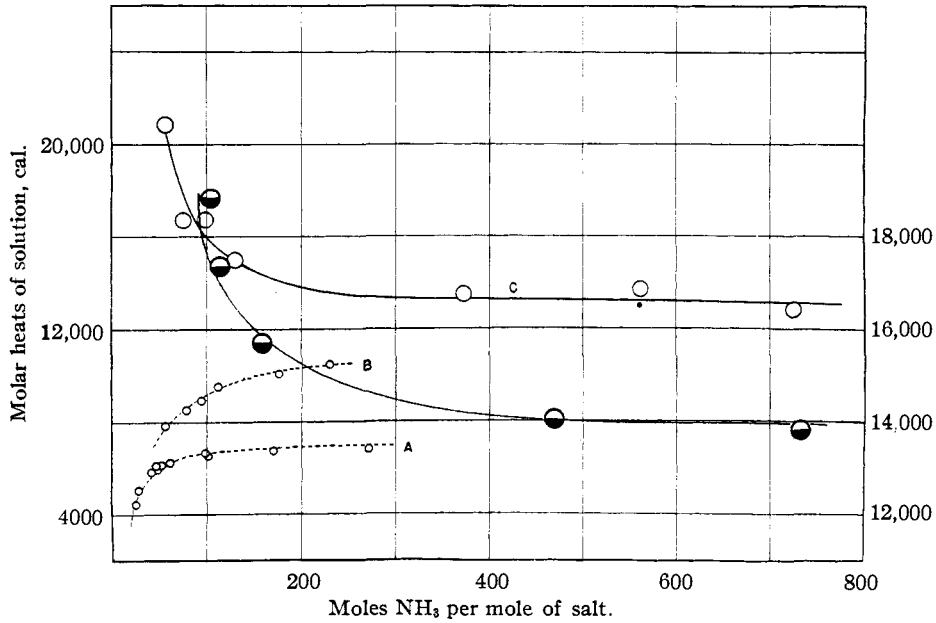

Fig. 1.—Molar heats of solution: (A) NH_4Cl; (B) NH_4Br; (C) NH_4I; and ◒, NaI. Ordinates for NaI on right.

Experimental

The calorimeter and experimental procedure were the same as used in previous measurements.[4] The experimental accuracy of the instrument is about 1%. Three-tenths to four grams of salt was used in each series of measurements. The salts were of "reagent" grade and were recrystallized once from distilled water and dried in a vacuum at 100°. The alcohols were dried over anhydrous cupric sulfate and distilled into weighed fragile glass bulbs out of contact with the air.

The heat of solution of sodium chloride was determined well within its solubility range. More

(1) This investigation was made possible by aid received from the Warren Fund of The American Academy of Arts and Sciences. Original manuscript received October 11, 1940.

(2) Present address: Carbide and Carbon Chemicals Corporation, South Charleston, W. Va.

(3) Schmidt, Sottysiak and Kluge, THIS JOURNAL, **58**, 2509 (1936).

(4) Schmidt, Studer and Sottysiak, *ibid.*, **60**, 2780 (1938).

(5) G. Spacu and P. Voichescu, *Z. anorg. allgem. Chem.*, **233**, 197 (1937).

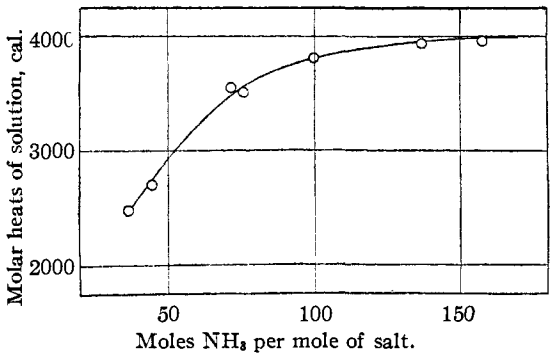

Fig. 2.—Molar heats of solution of sodium nitrate.

concentrated solutions could not be examined because of the low solubility of this salt. The heat of solution of methanol in liquid ammonia

TABLE I

MOLAR HEATS OF SOLUTION OF AMMONIUM AND SODIUM SALTS AT −33.4°

Sample, g.	Moles NH_3 per mole of salt	Molar heat effect, cal.
	Ammonium Iodide	
4.269	56.1	20860
2.764	74.0	16700
2.145	98.6	16750
1.606	129.5	14900
0.680	372.2	13450
.451	562.1	13350
.349	726.5	13000
	Sodium Iodide	
2.375	107.6	18850
2.209	116.1	17360
1.587	162.9	15700
1.290	200.9	15250
0.553	472.4	14000
.357	732.9	13900
	Sodium Nitrate	
0.942	157.5	3960
1.084	136.9	3930
1.485	99.7	3810
1.959	75.6	3510
2.068	71.3	3550
3.333	44.5	2700
4.024	36.7	2480
	Sodium Chloride	
0.589	174.5	1460
.518	197.9	1480

TABLE II

MOLAR HEATS OF SOLUTION OF SOME ALCOHOLS AT −33.4°

Alcohol	Sample, g.	Moles NH_3 per mole alcohol	Molar heat effect, cal.
Methanol	1.044	53.0	1960
Methanol	1.602	34.8	1996
n-Propanol	1.582	66.5	655
n-Butanol	1.387	93.0	− 100
Benzyl	2.214	85.6	600
Furfuryl	2.242	76.7	580

lies between that of water (3224 cal.)[6] and ethanol (1100 cal.),[4] as would be expected. Examination of Table II shows that as the number of carbon atoms in the normal alcohols increases, the molar heat of solution decreases.

Summary

The molar heats of solution of ammonium iodide and sodium iodide have been measured over a wide range of concentration and found to have a negative heat of dilution.

Heats of solution of sodium nitrate and sodium chloride, as well as those of a few alcohols, are reported.

(6) C. A. Kraus and F. C. Schmidt, THIS JOURNAL, **56**, 2297 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. II. The Stability and Activity Coefficients of the Silver-Ammonia Ion[1]

BY PAUL F. DERR, RUTH M. STOCKDALE AND W. C. VOSBURGH

Randall and Halford[2] have measured the solubility of silver chloride in ammonia solutions and have shown their results to be in good accord with those of previous workers. They have calculated the activity coefficients of the complex salt $Ag(NH_3)_2Cl$ and the dissociation constant of the complex ion. The activity coefficients are smaller than the corresponding activity coefficients of simple uni-univalent salts. Whether they are true activity coefficients or stoichiometric ones applying only to this reaction is not shown. The latter is the more probable, since the true activity coefficients of the complex ion would not be expected to differ much from those of the silver ion or other univalent ions.

In connection with another investigation it was

(1) Part of a thesis submitted by Paul F. Derr in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Randall and Halford, THIS JOURNAL, **52**, 178 (1930). References to previous work are given by Randall and Halford.