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Heats of solution in liquid ammonia

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Introduction

Liquid ammonia has properties which make it useful and interesting for making chemical and thermodynamic investigations, as has been pointed out by Franklin[1], and Kluge[7].

Theoretical Discussion

Lewis and Randall[8] have summarised a few of the numerous methods of utilising thermal data, such as have been compiled by the various investigators who have measured heats of solution in liquid ammonia. We find defined there (Loc. cit. Chapt8) a function called the relative heat content, denoted by L, with methods for determining its value. It can be evaluated by means of heats of solution data.

A function called the partial molal heat content, denoted $\bar{H}$, is defined thus:

$$\bar{H}_1 = \frac{\partial H}{\partial n_1} \quad ; \quad \bar{H}_2 = \frac{\partial H}{\partial n_2}$$

where n denotes the number of mols, and the subscripts 1 and 2 denote respectively solvent and solute. To obviate the necessity of knowing the absolute value of the heat content of a substance a new function called the relative heat content, denoted by L, is introduced. $\bar{L}$ then denotes relative partial molal heat content. It is the difference between the partial molal heat content of a substance, and its molal heat content in a reference state, which here is infinite dilution.

Thus $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^0$; $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0$. At infinite dilution $\bar{L}_1 = 0$; $\bar{L}_2 = 0$.

Add dn_2 mols of a substance X_2 to a solution containing n_1 mols liquid ammonia, and n_2 mols X_2:

dQ = heat absorbed, dQ/dn_2 partial molal heat of solution.

dQ = total increase in heat content.

$H_{2\,(s)}$ = molal heat content solid X_2.

$H_{2\,(s)}dn_2$ = heat content solid X_2 used.

By definition, the increase in heat content of the solution is equal to $\overline{H}_2 dn_2$.

Therefore $dQ = \overline{H}_2 dn_2 - H_{2(s)} dn_2$.

$$dQ/dn_2 = \overline{H}_2 - H_{2(s)} = \overline{L}_2 - L_{2(s)}.$$

At infinite dilution, $\overline{L}_2 = 0$,

Therefore $dQ/dn_2 = -L_{2(s)}$.

At constant pressure, $dQ = dH$.

From the existing data for, for example, ammonium chloride[5] the value of $L_{2(s)}$ is the value approached by the molar heat of solution as infinite dilution is approached. For ammonium chloride $L_{2(s)} \approx 7000$ calories. Therefore $\overline{L}_2 = dH/Dn_2 + 7000$ calories, where dH/dn_2 is the ordinate of the curve. Thus for 0.587 molal, $\overline{L}_2 = -6475 + 7000 = 525$ calories.

Knowing the values of $\overline{L}_2$, we can calculate the heat of solution of any amount of the solute in a solution containing any initial quantity of solute. The final concentration must, of course, be within the limits for which $\overline{L}_2$ is known.

Apparatus

The same apparatus was used as used by the previous investigators, except for the slight change described below.

During the condensation of ammonia in the calorimeter, the cooling liquid extends higher than the surface of the condensate. There is therefore a tendency for droplets to form on the sides of the calorimeter inside. When the cooling ammonia is pumped down to the level of the condensate, the droplets have a tendency to evaporate. This phenomenon would give results for the ammonia evolved that were too high, and results for the ammonia in the calorimeter that were correct.

To obviate this difficulty, a flask of 100 to 200 cc capacity was attached to the system near the calorimeter. The line to it contained a stop-cock. The flask was evacuated with the rest of the system, but was shut off before distillation into the calorimeter was begun. After distillation was complete, the stop-cock was opened for a short time and closed again. The pressure in the system was thus decreased momentarily, causing the ammonia to evaporate.

Weight of flask filled with mercury	1920.1 g.
Weight of empty flask	79.8
Weight of mercury	1840.3 g.
Volume of 1 g. of mercury at 25°C.	0.07382 cc.
Volume of flask	135.9 cc.

1 liter of ammonia at 1 atmosphere and 25°C. weighs 17.03/24.5 = 0.695g

Weight of ammonia withdrawn 0.1359xo.695 = 0.0944 g.

Weight of ammonia left in calorimeter 24.89-0.09 = 24.80 g.

When the bulb containing the compound whose heat of solution is to be measured is crushed beneath the surface of the liquid ammonia, splashing of the liquid sometimes occurs. When the liquid strikes the warmer part of th the calorimeter, it is vaporized and absorbed just as is the ammonia evolved from the heat of solution. This gives an abnormally large heat effect. Of coures a small amount of such splashing entails a large error in the result. The research is therefore in serious need of a method whereby the material introduced into the solution could be added slowly. This phenomenon is thought to be the cause of many of the anomolous results obtained in this research.

Discussion of Data

The data contained herein is in general not adequate to permit the construction of accurate curves; in some cases the present data, together with the recorded results of previous investigations, afford interpretation.

Table I. Discarding point A, and considering B and C, one is reminded of the behavior of ethanol[5]. Methanol appears to have a negative heat of dilution which is intermediate between that of ethanol (Loc. cit.) and ice[4].

Table II. Methyl amine hydrochloride appears to have a slight negative heat of dilution. This conclusion is surprising, because this compound is not greatly different in other properties from ammonium chloride, with the exception of the methyl group present.

Table III. The data for ammonium iodide is not sufficiently complete to permit interpretation.

Preparation of Materials

The methanol was dried by refluxing over quicklime, and distilling onto anhydrous copper sulfate. It was kept over the copper sulfate, and distilled into weighed bulbs as it was needed.

The methyl amine hydrochloride was prepared by the Hoffman-Beckman reaction from student preparation acetamide. It was purified by fractional crystallization from 95% ethanol, and pumped dry.

The ammonium iodide was of Baker and Adamson reagent purity. It was put into weighed bulbs and pumped to a pressure of 30 microns.

Physical Constants

Overstreet and Giauque[9], have made new determinations of the heat of vaporization and heat capacity of liquid ammonia.

By Overstreet and Giauque	Previously Accepted[4]
$\Delta H = 5581$ cal./mol	$\Delta H = 5570.5$ cal./mol
$C_p = 18.12$ cal./mol/deg.	$C_p = 18.17$ cal./mol

The newer values were used for the calculations here.

Data

Table I

Data on Heats of Solution of Methanol in Liquid Ammonia

Wt of Sample Grams	Ammonia Evolved Grams	Wt of Ammonia Grams	Mols Ammonia/ Mol Methanol	ΔT Deg.C	ΔP Cm.Hg	Total Heat Effect cal.	Molar Heat Effect cal.
1.0447	0.1024	24.79	44.63	0.90	0.0	63.36	1944
1.6023	0.1874	24.70	28.99	1.16	1.0	101.70	2033
0.7647	0.0776	24.81	61.02	0.93	0.0	56.24	2356

Table II

Data on Heats of Solution of Methyl Amine Hydrochloride

Wt. of Sample Grams	Ammonia Evolved Grams	Wt. of Ammonia Grams	Mols Ammonia per Mol CH_3NH_3Cl	ΔT Deg.C	ΔP Cm.Hg	Total Heat Effect cal.	Molar Heat Effect cal.
1.2820	0.2725	24.62	76.13	0.60	0.0	109.06	5743
1.0039	0.1769	24.71	97.58	0.77	0.0	83.41	5609
0.5941	0.1025	24.79	165.41	0.45	0.0	48.49	5510

Table III

Data on Heats of Solution Of Ammonium Iodide in Liquid Ammonia

Wt. of Sample Grams	Ammonia Evolved Grams	Wt. of Ammonia Grams	Mols Ammonia per Mol NH_4I	ΔT Deg.C	ΔP Cm.Hg	Total Heat Effect cal.	Molar Heat Effect
1.0264	0.2110	24.68	204.72	0.04	0.0	70.47	9954.5
2.7640	0.9173	23.97	73.84	0.56	0.2	319.1	16736
*2.1453	0.6740	23.42	96.12	0.81	1.1	249.4	16657
*0.5665	0.1092	23.98	372.42	0.05	0.0	37.45	9585

The data marked with the asterisk (*) was obtained from runs in which the previously mentioned flask was used. The appropriate correction was made.

Table IV

Data on Heats of Solution of Various Alcohols in Liquid Ammonia

Alcohol	Wt. of Sample Grams	Ammonia Evolved Grams	Wt. of Ammonia Grams	Mols Ammonia per Mol Alcohol	ΔT Deg.C	ΔP Cm.Hg	Total Heat Effect cal.	Molar Heat Effect cal.
Propyl	1.5826	0.0000	24.89	55.47	0.52	0.1	17.47	663
Butyl	1.3673	0.0000	24.89	78.04	-0.06	0.0	-1.99	-106.3
Benzyl	2.2144	0.0000	24.89	71.32	0.38	0.0	12.62	615.8

Summary

Methanol shows an exothermic heat of solution, and a negative heat of dilution intermediate between that of water and of ethanol.

Trial runs made on methyl amine hydrochloride give a heat of solution of the order of 5600 calories per mol.

Trial runs made upon ammonium iodide give a heat of solution of the order of 10,000 calories.

Measurements of the heats of solution of various alcohols indicate that the heat effect becomes less with increasing number of carbon atoms.

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