Heats of solution in liquid ammonia

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Introduction

Liquid ammonia in many of its reactions and properties simulates water. Next to water liquid ammonia is the best known electrolytic solvent. It dissolves a large number of salts to form, in general, conducting solutions, in which the ions are more mobile.

Ammonium salts in liquid ammonia solution act in a manner analogous to acids in water. They attack metals, react with metallic ammonium bases and oxides. The reaction is much slower than in water.

Ex. $\text{NH}_4\text{Cl} + \text{Na} \rightarrow \text{NaCl} + \text{NH}_3 + \text{H}$

The ammonium salts ionize to form the ammoniated hydrogen ion. $\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3\cdot\text{H}_2\text{O}$

The ammoniated hydrogen ion is similar to the solvated hydrogen ion $\text{H}_3\text{O}^+$.

Discussion of the Curves

In each case the heat evolved, in small calories, per gram mole solute is plotted against the moles of liquid ammonia per mole of solute. As the concentration decreases the curve approaches a constant value which corresponds to the differential heat solution.

The value of the ordinates $\text{NH}_3\cdot\text{H}_2\text{O}$ and $\text{MO}$ is the integral heat of solution in $N$ and $M$ moles of solvent. The difference between them, $\text{OP}$, is the
integral heat of dilution corresponding to a change in concentration from $N$ moles to $M$ moles.

Dilution Curve. The heat of dilutes is plotted against the change in the moles of ammonia. The curves approach a constant value which is the heat of dilution. These curves were plotted to compare the heat of dilution of ammonium chloride and ammonium bromide.
Discussion

The comparison between the heats of solution of inorganic salts in water and liquid ammonia, procedure and sample calculations can be found in the Journal of the American Chemical Society (cf. ref. 4). Sottysiak's Thesis contains the calorimeter constant, volume of pipette, and accompanying data.

Due to the installation of a new galvanometer and accuracy between 1% and 2% can be claimed for the above data. The method of absorbing the evolved ammonia (similar to that used by Kraus and Prescott) still causes trouble. If a new absorbing system could be installed the accuracy could be increased to less than 1%. In heats such as those obtained for lead iodide a small percentage error causes a considerable absolute error. With the present apparatus a variation of 300 calories would be within the limits of experimental error for heats of solution in lead iodide.

The values obtained for the ammonium chloride and ammonium bromide are in fair agreement with those obtained by Kraus and Ridderhof.

The rate of solution seems to be an important factor in the amount of ammonia evolved. At present there seems no way of illuminating this fault.

Note: A positive $\Delta H$ in this article denotes an exothermic heat effect. A negative $\Delta H$ an endothermic heat effect.
References.

1. The Nitrogen System of Compounds by Franklin
5. Sottsiak's Thesis (1934-1935)
Data of Heats of Solution of Ammonium Bromide in Liquid Ammonia

<table>
<thead>
<tr>
<th>Wt. of sample in grs.</th>
<th>Wt. of NH₃ in grs.</th>
<th>Grs. NH₃ evolved by sol.</th>
<th>ΔT of sol. in NH₃/mole</th>
<th>Time in Min.</th>
<th>Moles of NH₄Br total</th>
<th>ΔH(sol)</th>
<th>ΔH(sol) Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4957</td>
<td>24.81</td>
<td>08146</td>
<td>.78</td>
<td>2.5</td>
<td>288.4</td>
<td>52.649</td>
<td>10405</td>
</tr>
<tr>
<td>0.8102</td>
<td>24.66</td>
<td>.2311</td>
<td>.23</td>
<td>1.7</td>
<td>175.4</td>
<td>82.919</td>
<td>10040</td>
</tr>
<tr>
<td>1.2527</td>
<td>24.60</td>
<td>.2862</td>
<td>.84</td>
<td>5.5</td>
<td>112.9</td>
<td>121.25</td>
<td>9409</td>
</tr>
<tr>
<td>1.4959</td>
<td>24.51</td>
<td>.3836</td>
<td>.30</td>
<td>3.0</td>
<td>94.25</td>
<td>84.25</td>
<td>8825</td>
</tr>
<tr>
<td>1.8070</td>
<td>24.49</td>
<td>.4003</td>
<td>.81</td>
<td>6.0</td>
<td>77.99</td>
<td>157.91</td>
<td>8560</td>
</tr>
<tr>
<td>2.4423</td>
<td>24.36</td>
<td>.5348</td>
<td>.63</td>
<td>4.0</td>
<td>57.38</td>
<td>195.92</td>
<td>7858</td>
</tr>
</tbody>
</table>

The ammonium bromide was recrystallized from water twice, then dried in a desiccator. The pressure in the bulb was not more than fifteen microns.

Data on Heats of Solution of Ammonium Chloride in Liquid Ammonia

<table>
<thead>
<tr>
<th>Wt. of sample in grs.</th>
<th>Wt. of NH₃ in grs.</th>
<th>Grs. NH₃ evolved by sol.</th>
<th>ΔT of sol. in NH₃/mole</th>
<th>Time in Min.</th>
<th>Moles of NH₄Cl total</th>
<th>ΔH(sol)</th>
<th>ΔH(sol) Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7710</td>
<td>24.65</td>
<td>.2384</td>
<td>.27</td>
<td>2.0</td>
<td>103.20</td>
<td>92.32</td>
<td>6406</td>
</tr>
<tr>
<td>1.5547</td>
<td>24.44</td>
<td>.4462</td>
<td>.67</td>
<td>1.0</td>
<td>50.95</td>
<td>172.59</td>
<td>5939</td>
</tr>
</tbody>
</table>

Confer Sottsiak's Thesis for remaining points.
Table 3

Data of Heats of Solution of Lead Iodide in Liquid Ammonia

<table>
<thead>
<tr>
<th>Wt. of sample in g.</th>
<th>Wt. of NH₃ evolved by sol.</th>
<th>Grs. NH₃</th>
<th>ΔT of sol.</th>
<th>Time in Min.</th>
<th>Moles of NH₃/mole PbI₂</th>
<th>ΔH(sol)</th>
<th>ΔH(total)</th>
<th>Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7733</td>
<td>24.78</td>
<td>.1073</td>
<td>.33</td>
<td>8.6</td>
<td>136.1</td>
<td>46.06</td>
<td>274.60</td>
<td></td>
</tr>
<tr>
<td>1.0755</td>
<td>24.73</td>
<td>.1621</td>
<td>.32</td>
<td>5.7</td>
<td>638.2</td>
<td>63.67</td>
<td>272.95</td>
<td></td>
</tr>
<tr>
<td>2.1772</td>
<td>24.55</td>
<td>.3447</td>
<td>.36</td>
<td>3.7</td>
<td>305.8</td>
<td>124.75</td>
<td>264.20</td>
<td></td>
</tr>
<tr>
<td>2.4281</td>
<td>24.48</td>
<td>.4104</td>
<td>.38</td>
<td>4.2</td>
<td>273.4</td>
<td>136.90</td>
<td>260.25</td>
<td></td>
</tr>
</tbody>
</table>

Lead iodide had been measured. Since it had a high heat and was insoluble in water, it was decided to determine its heat. A value lower than that quoted in the reference was obtained.

The heat of solution of lead iodide represents a heat of reaction with liquid ammonia to give a colorless solution of an ammoniated lead iodide.

The lead iodide was analysed by converting to the sulfate and weighing as such. The results are given below.

<table>
<thead>
<tr>
<th>Wt. of PbI₂ in g.</th>
<th>Wt. of PbSO₄ in g.</th>
<th>Wt. of Pb in g.</th>
<th>Percent Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4559</td>
<td>.9138</td>
<td>.6244</td>
<td>42.94</td>
</tr>
<tr>
<td>.4988</td>
<td>.3176</td>
<td>.2170</td>
<td>43.50</td>
</tr>
</tbody>
</table>

The calculated percentage for lead in lead iodide is 44.93%. After washing the lead iodide twice with distilled water and drying, it was analysed again. The results were in good agreement with the theoretical percentage.
Table 4

Data on Exothermic Heats of Solution in Liquid Ammonia

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wt. of sample in grs.</th>
<th>Grs. NH₃ evolved by sol.</th>
<th>Wt. of NH₃ sol.</th>
<th>△T of sol.</th>
<th>△H(sol) total</th>
<th>△H(sol) Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>HbBr</td>
<td>.6271</td>
<td>none</td>
<td>24.89</td>
<td>.05</td>
<td>1.664</td>
<td>438.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1.1150</td>
<td>none</td>
<td>24.89</td>
<td>.53</td>
<td>-17.64</td>
<td>-1250</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.0260</td>
<td>.06652</td>
<td>24.82</td>
<td>1.31</td>
<td>65.24</td>
<td>1483</td>
</tr>
</tbody>
</table>

Since water had been measured, it was thought advisable to measure the heat of solution of the alcohols. One measurement was made on ethanol as an indicator. The ethanol was dried by refluxing over anhydrous copper sulfate and distilled out of the container.

Pyridine is a cyclic ketone in the nitrogen system. It was dried and redistilled before making a measurement.
Table 5

Data on Heats of Dilution of Ammonium Chloride in Liquid Ammonia

<table>
<thead>
<tr>
<th>Initial concentration 25 moles of NH₄⁺ mole of NH₄Cl</th>
<th>Initial concentration 60 moles of NH₄⁺ mole of NH₄Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δn</td>
<td>ΔH</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>1600</td>
</tr>
<tr>
<td>80</td>
<td>1885</td>
</tr>
<tr>
<td>120</td>
<td>2065</td>
</tr>
<tr>
<td>160</td>
<td>2165</td>
</tr>
<tr>
<td>200</td>
<td>2215</td>
</tr>
<tr>
<td>240</td>
<td>2225</td>
</tr>
</tbody>
</table>

The above values were read from the heat of solution curve of ammonium chloride.

Δn - change in moles of ammonia.

ΔH - change of heat of solution.

Table 6

Data on Heats of Dilution of Ammonium Bromide in Liquid Ammonia

<table>
<thead>
<tr>
<th>Initial Concentration 60 moles of NH₄⁺ mole of NH₄Br⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δn</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>120</td>
</tr>
<tr>
<td>160</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>240</td>
</tr>
</tbody>
</table>

The above values were read from the heat of solution curve of ammonium bromide. Δn-and ΔH have same values as above.