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## The Dissociation of Ammonium Chloride\*

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Two values for the standard free energy of dissociation of ammonium chloride into ammonia and hydrogen chloride, calculated by two independent paths, are 21,860 cal. and 21,780 cal. at 298.1°K. The good agreement serves as additional evidence for the complete dissociation of ammonium chloride in the vapor phase. The corresponding values calculated for  $\Delta H$  at 298.1 are 42,160 and 42,260 cal. Two independent values for the standard entropy of the aqueous ammonium ion at 298.1°K derived from these data are 26.5 and 27.1 cal. mole<sup>-1</sup> deg.<sup>-1</sup>.

THE vapor densities and dissociation pressures of ammonium chloride have been the subject of a number of investigations;<sup>1-5</sup> the observed dissociation pressures are in good agreement, but the earlier vapor densities indicated partial dissociation of the vapor to  $\text{NH}_3$  and  $\text{HCl}$  whereas the later measurements show that the vapor is completely dissociated. An independent approach to the equilibrium  $\text{NH}_4\text{Cl}(s) = \text{NH}_3(g) + \text{HCl}(g)$  is possible from available thermal studies.

The entropies at 298.1°K of  $\text{NH}_4\text{Cl}$ ,<sup>6</sup>  $\text{NH}_3$ ,<sup>7</sup> and  $\text{HCl}$ <sup>8</sup> are 22.6, 46.03, and 44.66 units, from which  $\Delta S^\circ_{298.1} = 68.1$  for the above reaction. Thomsen<sup>9</sup> gives 41,900 cal. for  $\Delta H$ , and Berthelot<sup>10</sup> finds 42,600 cal.

The heat capacity of  $\text{NH}_4\text{Cl}$  has been measured from room temperature to 525°K by H. Klink-

hardt.<sup>11</sup> At 457.6°K a transition occurs for which  $\Delta H = 970$ .<sup>12</sup> The thermodynamic properties of  $\text{NH}_3$  and  $\text{HCl}$  at higher temperatures are given by Stephenson and McMahon and by Giauque and Overstreet. From these data and the equations  $\Delta F^\circ = -RT \ln p_2/4 = \Delta H^\circ - T\Delta S^\circ$ ,  $\Delta H^\circ = \int \Delta C_p dT$ , and  $\Delta S^\circ = \int \Delta C_p d \ln T$ , the dissociation pressures may be calculated. Within the limits of error of the experimental data the calculated pressures agree with the measured pressures, and confirm the more recent observations that the vapor is completely dissociated.

Since the greatest uncertainty lies in the value of  $\Delta H^\circ$ , it is profitable to reverse the calculations and obtain a more reliable value of  $\Delta H^\circ$  from the dissociation pressures and heat capacities. The constancy of the  $\Delta H^\circ$  values calculated from the dissociation pressures is a stringent test of the assumption of complete dissociation and of the dissociation pressure data. From the data of Rodebush and Michalek,  $\Delta H^\circ_{298.1} = 42,100 \pm 40$ ; from the data of Smits and Lange,  $\Delta H^\circ_{298.1} = 42,130 \pm 40$ ; from the data of Smith and Lombard,  $\Delta H^\circ_{298.1} = 42,090 \pm 40$ ; and from the data of Braune and Knoke,  $\Delta H^\circ_{298.1} = 42,190 \pm 10$ . Only the data of Smith and Lombard show a trend in the calculated  $\Delta H^\circ$  values, and this trend is probably caused by an incorrect temperature scale. The data of Braune and Knoke are the most consistent. The value  $\Delta H^\circ_{298.1} = 42,160$  cal. is adopted, from which  $\Delta F^\circ_{298.1} = 21,860$ .

\* Contribution No. 508 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

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<sup>10</sup> M. Berthelot, *Thermochimie* (Paris, 1897), Vol. 2, p. 221.

<sup>11</sup> H. Klinkhardt, *Ann. d. Physik* [4] **84**, 188 (1924).

<sup>12</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **52**, 138 (1916/1917).

These results may be represented to a satisfactory degree of approximation by taking  $\Delta C_p = -7.7$  from 298.1 to 457.6°K, and  $\Delta C_p = -5.5$  above the transition temperature. Then  $\Delta H^\circ = 44,460 - 7.7T$  from 298.1 to 457.6°K and  $\Delta H^\circ = 42,490 - 5.5T$  above 457.6°K. Then  $\Delta F^\circ = 44,460 + 17.7T \log T - 119.7T$  below 457.6°K, and  $\Delta F^\circ = 42,490 + 12.7T \log T - 101.9T$  above the transition temperature. The dissociation pressures above 457.6°K are then given by  $\log p_{\text{atmos}} = -4644/T - 1.38 \log T + 11.43$ .

The free energy and heat of formation of  $\text{NH}_4\text{Cl}$  from  $\text{NH}_3$  and  $\text{HCl}$  may be obtained by another path. The solubility of  $\text{NH}_4\text{Cl}$  at 25°C is 7.38*M*, and the activity coefficient, from vapor pressures of aqueous solutions, of the saturated solution is 0.611.<sup>13</sup> The free energy of solution is then  $\Delta F^\circ = -RT \ln (0.611 \times 7.38)^2 = -1780$ . A less reliable value for the free energy of solution,  $\Delta F^\circ = -1700 \pm 150$ , may be derived from cell measurements by Brönsted.<sup>14</sup> The heat of solution in 120 moles of water at 25°C is 3730 cal.,<sup>15</sup> and the heat of dilution<sup>16</sup> is -126 cal.; hence,  $\Delta H^\circ = 3600$ . These values are combined with the following reactions at 298.1°K:

	$\Delta F^\circ$	$\Delta H^\circ$
$\text{NH}_3(g) + \text{H}_2\text{O}(l) = \text{NH}_4\text{OH}(aq)$	- 2,390 <sup>17</sup>	- 8,285 <sup>18</sup>
$\text{NH}_4\text{OH}(aq) = \text{NH}_4^+ + \text{OH}^-$	6,520 <sup>19</sup>	865 <sup>20</sup>
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}(l)$	- 19,093 <sup>21</sup>	- 13,358 <sup>22</sup>
$\text{HCl}(g) = \text{H}^+ + \text{Cl}^-$	- 8,598 <sup>22</sup>	- 17,880 <sup>23</sup>
$\text{NH}_4^+ + \text{Cl}^- = \text{NH}_4\text{Cl}(s)$	+ 1,780	- 3,600
$\text{NH}_3(g) + \text{HCl}(g) = \text{NH}_4\text{Cl}(s)$	- 21,780	- 42,260.

The agreement between the two independent values of  $\Delta F^\circ$  and  $\Delta H^\circ$  is very good. Using the averages of these two values and the standard heat and free energies for  $\text{NH}_3$ <sup>7</sup> and  $\text{HCl}$ ,<sup>23</sup> the corresponding values  $\Delta F^\circ = -48,460$  and  $\Delta H^\circ = -75,200$  are obtained for  $\text{NH}_4\text{Cl}$ .

Two independent values for the entropy of the ammonium ion may be derived from these reactions. From the first three equations and the entropy of  $\text{NH}_3(g)$ ,  $S^\circ_{\text{NH}_4^+} = 26.5$ ; from the last two equations and the entropies of  $\text{HCl}(g)$  and  $\text{NH}_4\text{Cl}(s)$ ,  $S^\circ_{\text{NH}_4^+} = 27.1$ . A third value, 26.2, may be derived from the entropy of  $\text{NH}_4\text{H}_2\text{PO}_4$ . The average,  $26.6 \pm 0.5$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, is recommended for the entropy of the ammonium ion.

<sup>17</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1923), Vol. VII, p. 240.

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