The vapor phase dissociation of ammonium salts: Ammonium halides, ammonium rhodanide, ammonium nitrate, and ammonium bicarbonate

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Vapor pressures as a function of temperature of the ammonium salts are measured by means of a simultaneous torsion effusion and mass-loss effusion technique. From a theoretical analysis, which is given first, it is shown that the enthalpies of sublimation and the degree of dissociation \( b \) in the vapor phase are related to the measured quantities. The degree of dissociation appears to be a weak function of temperature and is evaluated by:

- \( b(NH_4F, 288.91 \text{ K}) = 0.97 \)
- \( b(NH_4Cl, 352.02 \text{ K}) = 0.85 \)
- \( b(NH_4Br, 380.06 \text{ K}) = 0.51 \)
- \( b(NH_4I, 385.03 \text{ K}) = 0.39 \)
- \( b(NH_4CNS, 313.78 \text{ K}) = 0.61 \)
- \( b(NH_4NO_3, 351.89 \text{ K}) = 0.66 \)
- \( b(NH_4HCO_3, 270.56 \text{ K}) = 0.85 \)

It is assumed that \( NH_4HCO_3 \) dissociates into \( NH_3, H_2O, \) and \( CO_2 \) at the given temperatures, total vapor pressure is 0.40 Pa.

I. INTRODUCTION

Of the ammonium halides, ammonium chloride (salamoniac) is the one which has been most often and thoroughly investigated. It is particularly the solid state properties which have been studied.

Callanan et al. have measured vapor pressures of \( NH_4Cl \) and of \( NH_4Br \). They made assumptions and speculations about the degree of dissociation of the salts in the vapor phase on the basis of vapor density measurements, \(^2,3\) ab initio calculations by Clementi, \(^4\) and Knudsen effusion mass spectrometry by Goldfinger, \(^5\) again for \( NH_4Cl \) only. As Callanan et al. pointed out very precisely, a correct interpretation of the excess enthalpies of mixing of the solid state based on the basis of their total vapor pressure measurements requires a knowledge of the degree of dissociation of the vapor phase molecules. For \( NH_4Cl \), this value was expected to be near unity. \(^2,3,5\) Regarding the other ammonium salts there is no information in the literature. Since we have at our disposal combined torsion effusion mass and mass-loss effusion apparatus we are in a position to solve the problem, at least in principle. We show that the "apparent enthalpy of sublimation" as derived from the temperature dependence of measured vapor pressure is not unambiguously defined but is a function of the degree of dissociation and the method used. In the following section, we shall therefore, give a derivation of the equations that are applicable to the experimental methods used and explain how the relevant thermodynamic properties are evaluated from the experimental results. In Sec. III, the experimental setup will be described and in Sec. IV the results obtained will be given.

II. THEORETICAL

In the torsion effusion experiment the recoil force exerted on the cell by the effusing molecules is proportional to their momentum. The recoil force is compensated electromagnetically \(^6\) and therefore the quantity measured corresponds to a true pressure. Hence the torsion constant \( C \) is given from

\[ p_t = C \cdot I, \]

where \( I \) is the electric current required for compensation and \( C \) is a constant depending on the geometry of the set-up only.

The mass loss effusion experiment is based on the Hertz-Knudsen equation:

\[ \frac{dm}{dt} = A p (2\pi RT)^{-1/2} m^{1/2} \]

in which \( dm/dt \) is the mass loss per unit time, \( A \) the orifice area, \( p \) is vapor pressure, and \( M \) the molecular mass of the effusing species. If the vapor consists of \( i \) different species with molecular mass \( M_i \) and partial pressure \( p_i \), Eq. (2) is written as

\[ \sum_i \frac{dm_i}{dt} = A (2\pi RT)^{-1/2} \sum_i p_i M_i^{1/2} \]

under the condition that

\[ \sum_i p_i = p_{\text{total}} = p_{\text{torsion}} = p_t. \]

In general, additional conditions are set by the stoichiometry of the vaporization process. For instance, in our case it is assumed that the ammonium salts dissociate in the vapor phase into ammonia and acid. The equilibria involved are shown schematically in Fig. 1. The gas-phase reaction

\[ NH_4X = NH_3 + HX + \Delta H_{\text{diss}} \]

is assumed to be fast and to represent the predominant

\[ \Delta H_{\text{sub}}(NH_4X) \]

\[ \Delta H_{\text{sub}}(NH_3) \]

\[ \\]

FIG. 1. Phase reactions of ammonium halides.
Substituting in Eq. (3) the pressures of Eq. (11) and weight, Eq. (13) reduces to

During the experiment we insert into Eq. (2) the molecular mass $M_{\text{form}}$ of NH$_4$X and we then calculate $p_m$ according to

$$p_m = \frac{m}{A - b} \frac{2\pi R T}{M_{\text{form}}}^{1/2} \frac{1}{T}$$

in which $p_m$ is the "apparent" vapor pressure and $m$ the time derivative of the total mass loss. Taking one mole of NH$_4$X we have from Eq. (4)

$$p(\text{NH}_4X) = (1 - b)(1 + b)^{-1} p_t$$

$$p(\text{NH}_3) = p(\text{HX}) = b(1 + b)^{-1} p_t$$

Substituting in Eq. (3) the pressures of Eq. (11) and equating $\sum dm_i/dt$ to $m$ of Eq. (10) leads to

$$p_m M_{\text{form}}^{1/2} p_t^{1/2} (1 + b)(1 - b)^{-1} = p_m M_{\text{form}}^{1/2} - p_t M_{\text{form}}^{1/2}$$

Rearranging and dividing by $M_{\text{form}}^{1/2}$ gives

$$b = (p_m p_t^{1/2} - 1) \left\{ \frac{M_{\text{form}}^{1/2} M_{\text{NH}_4X}^{1/2}}{M_{\text{NH}_3X}^{1/2} M_{\text{NH}_4X}^{1/2}} + \frac{M_{\text{NH}_3X}}{M_{\text{NH}_4X}} \right\}^{1/2} - p_m p_t^{1/2} \left( 1 + b \right)^{-1} (1 - b)^{-1}$$

If the ratio $p_m/p_t = 1$, then $b = 0$, which means that there is no dissociation in the vapor phase. For the symmetrical case, i.e., when the substance under investigation dissociates into two fragments of equal molecular weight, Eq. (13) reduces to

$$b = \frac{p_m p_t^{1/2} - 1}{\sqrt{2} - p_m p_t^{1/2} - 1}$$

and for $b = 1$, i.e., complete dissociation, the ratio $p_m/p_t = 1/\sqrt{2} = 0.71$.

The degree of dissociation can thus be evaluated from the ratio $p_m/p_t$ and from the molecular mass of the vapor species. If the composition of the vapor phase is unknown, an apparent molecular mass, defined as:

$$M_{\text{app}}^{1/2} = \sum_i X_i M_i^{1/2}$$

(where $X_i$ is the gas-phase mole fraction) can be calculated from

$$M_{\text{app}} = \frac{p_m p_t^{1/2} M_{\text{form}}^{1/2}}{2}$$

So far we have assumed a constant temperature and evaluated $b$ from $p_m$ and $p_t$ at that temperature. Additional information can be gained from the temperature dependence of $p_m$ and $p_t$. The equilibria as given in Fig. 1 obey two independent relations:

$$-R d^2 \ln \left[ \frac{p(\text{NH}_4X)}{p_t} \right]/dT = -R d^2 \ln \left[ (1 - b)(1 + b)^{-1} p_t \right]/dT$$

$$\Delta H_{\text{sub}}(\text{NH}_4X)$$

and

$$-R d \ln (K_p)/dT = \Delta H_{\text{sub}}(\text{NH}_4X)$$

and are connected through Eq. (9). Subtracting Eq. (18) from Eq. (17) leads after some rearranging to:

$$R d b/dT = -\frac{1}{2} (1 - b) b \left[ \Delta H_{\text{dis}} - \Delta H_{\text{sub}}(\text{NH}_4X) \right]$$

This equation describes the temperature dependence of the degree of dissociation in the saturated vapor phase. From literature values of $b$ and from the results obtained here it can be inferred that $[\Delta H_{\text{dis}} - \Delta H_{\text{sub}}(\text{NH}_4X)] > 0$. Therefore, with $0 < b < 1$, it follows that $d b/dT$ is negative. In other words, the degree of dissociation of NH$_4$X will increase with temperature. So although with increasing temperature the total pressure rises, which tends to diminish dissociation, it is the higher value of $\Delta H_{\text{dis}}$ which causes increased dissociation at higher temperatures.

The Clausius–Clapeyron plots (ln$p$ against $1/T$) of both $p_m$ and $p_t$ appear to be straight lines and thus have a constant slope within experimental error. Now from the torsion experiment we determined the slope

$$-R d \ln (p_i)/dT = -\Delta H_i$$

From Eq. (17) it follows that

$$-R d \ln (p_i)/dT = -R d \ln \left[ (1 - b)(1 + b)^{-1} \right] dT$$

$$+ \Delta H_{\text{sub}}(\text{NH}_4X)$$

or with Eq. (19) it follows that

$$\Delta H_i = g(b) \left[ \Delta H_{\text{dis}} - \Delta H_{\text{sub}}(\text{NH}_4X) \right] + \Delta H_{\text{sub}}(\text{NH}_4X)$$

with $g(b) = b(1 + b)^{-1}$.

Differentiating the logarithm of Eq. (12) with respect to reciprocal temperature results in:

$$\Delta H_m = f(s, b) \left[ \Delta H_{\text{dis}} - \Delta H_{\text{sub}}(\text{NH}_4X) \right] + \Delta H_i$$

with $s = (M_{\text{NH}_4X}^{1/2} + M_{\text{NH}_3X}^{1/2} - M_{\text{NH}_3X}) M_{\text{NH}_4X}^{1/2} / 2 M_{\text{NH}_4X}$ and

$$f(s, b) = (s - 1)(1 - b) g(b) (1 + b)^{-1}$$

Writing $\Delta H_{\text{dis}}$ and $\Delta H_{\text{sub}}(\text{NH}_4X)$ in Eqs. (22) and (23) explicitly leads to

$$\Delta H_{\text{dis}} = \Delta H_i + \left[ 1 - g(b) \right] f^{-1}(s, b) \cdot (\Delta H_m - \Delta H_i)$$

$$\Delta H_{\text{sub}} = \Delta H_i - g(b) \cdot f^{-1}(s, b) \cdot (\Delta H_m - \Delta H_i)$$

So, in principle, the values of $\Delta H_{\text{dis}}$ and $\Delta H_{\text{sub}}(\text{NH}_4X)$ can be calculated from $b$ obtained from Eq. (13) and $\Delta H_m - \Delta H_i$. These values are obtained as follows.

The experimental "apparent" vapor pressures $p_m$ and $p_t$ are calculated from Eqs. (1) and (10). Then these values, for each technique separately, are fitted to the following equation:

$$R \ln (p_i/p_0) = -\Delta G(\theta)/\theta + \Delta H(\theta)(1/\theta - 1/T)$$

where $p_0$ is a reference pressure (1 Pa), $\theta$ is a reference temperature usually chosen midrange and in such a way that $p_0(\theta) = 0.400$ Pa. $\Delta G(\theta)$ and $\Delta H(\theta)$ are the coefficients to be evaluated and if $p_m/p_t = 1$ they are the Gibbs energy and enthalpy of sublimation, respectively. We always made several independent measurements of $p_m$ and $p_t$ as a function of temperature, and
TABLE I. Experimental results expressed in terms of the coefficients of Eq. (26). \( \Delta G \) and \( \Delta H \) must be considered as apparent values, (see the text).

| Ammonium salt | \( M_{\text{tot}} \) gr mol\(^{-1} \) | \( T_1 \) K | \( T_2 \) K | \( \theta \) K | \( \Delta G_0(\theta) \) J mol\(^{-1} \) | \( \Delta H_0(\theta) \) J mol\(^{-1} \) | \( P_f(\theta) \) Pa | \( \Delta G_m(\theta) \) J mol\(^{-1} \) | \( \Delta H_m(\theta) \) kJ mol\(^{-1} \) | \( P_m(\theta) \) Pa | \( \rho_m/P_f(\theta) \) |
|---------------|---------------------------------|-------------|-------------|-------------|---------------------------------|---------------------------------|-----------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|
| \( \text{NH}_4\text{F} \) | 37.04 | 275 | 298 | 288.91 | 2201 | 72.3 | 0.40 | 3029 | 71.1 | 0.28 | 0.71 |
| \( \text{NH}_4\text{Cl} \) | 52.49 | 337 | 364 | 352.02 | 2682 | 86.9 | 0.40 | 3645 | 86.3 | 0.27 | 0.72 |
| \( \text{NH}_4\text{Br} \) | 97.95 | 367 | 394 | 380.06 | 2895 | 91.9 | 0.40 | 3717 | 92.5 | 0.31 | 0.77 |
| \( \text{NH}_4\text{I} \) | 144.94 | 373 | 401 | 385.03 | 2933 | 92.6 | 0.40 | 3649 | 92.8 | 0.32 | 0.80 |
| \( \text{NH}_4\text{CNS} \) | 76.12 | 302 | 326 | 313.78 | 2391 | 80.2 | 0.40 | 3121 | 79.1 | 0.30 | 0.76 |
| \( \text{NH}_4\text{NO}_3 \) | 80.04 | 336 | 364 | 351.89 | 2681 | 89.9 | 0.40 | 3559 | 89.1 | 0.30 | 0.74 |
| \( \text{NH}_4\text{HCO}_3 \) | 79.06 | 262 | 280 | 270.56 | 2061 | 68.8 | 0.40 | 3263 | 67.4 | 0.23 | 0.59 |

III. EXPERIMENTAL

The principal dimensions of the experimental set-up have been described previously. An extensive description of the fully automated measuring procedure is given in Ref. 7. The effusion cell used (resembling a garden sprinkler) has two effusion orifices of 1 mm diameter made in 6 \( \mu \)m platinum foil and placed 20 mm apart. No Clausing corrections are necessary. The cell is loaded with approximately 300 mg of sample and up to ten runs are made each consisting of 120 data points over a temperature range as indicated in Table I. Usually after a few runs \( \Delta G \) and \( \Delta H \) of Eq. (26) (apparent values in this case) become constant. Mean values are reported in Table I.

The samples were used as delivered. For the ammonium halides we found an initial mass loss already at low temperatures; this was obviously a result of adsorbed water. As measurements were not constant and reproducible, probably as a result of nonvolatile impurities accumulating on the sample surface, we purified these samples by vacuum sublimation under a continuous evacuation (\( 10^{-2} \) Pa) and at temperatures as given in Table I. The results obtained with these samples were reproducible and are reported.

IV. RESULTS AND DISCUSSION

In Table I we give the experimental results expressed in terms of the coefficients (\( \Delta G \) and \( \Delta H \)) of Eq. (26). These coefficients must be regarded as apparent values or as intercepts and slopes of the so-called Clausius–Clapeyron plots. In addition, we give \( M_{\text{tot}} \) as used in Eq. (10), and the experimental temperature range. The imprecision in the pressure measurements does not exceed 5\%, and for \( \Delta H \) it is \( \pm 1 \) kJ mol\(^{-1} \). Inaccuracy is estimated to be not more than twice these values. When measuring pure substances in our setup we always found 0.95 < \( \rho_m/P_f < 1.05 \). From this we infer that the inaccuracy in the degree of dissociation is \( \pm 0.1 \), see Table II.

One might be doubtful whether the results of Table I represent equilibrium data, as the methods used are essentially dynamic in nature. Moreover, Chalken et al.\(^5\) report an accommodation (evaporation) coefficient of \( \sim 10^{-4} \). If total vapor pressure data (\( P_\text{v} \)) are compared, one finds that the results of Callanan et al.\(^1\) at higher temperatures but obtained with a static method combine most satisfactorily both for \( \text{NH}_4\text{Cl} \) and for \( \text{NH}_4\text{Br} \). Extrapolating their vapor pressure equation over a range of 150 K we calculate at the reference temperature \( \theta \) of Table I: \( P_f(\text{NH}_4\text{Cl}, 352 \text{ K}) = 0.45 \text{ Pa} \) and \( P_f(\text{NH}_4\text{Br}, 380 \text{ K}) = 0.35 \text{ Pa} \). In view of the extrapolation range this result makes us confident that our results can be regarded as equilibrium data also. An extremely small evaporation coefficient would have led to nonreproducible results dependent on sample size. Preliminary experiments in the same setup with a Langmuir effusion cell indicated that the evaporation coefficient would probably be smaller than unity but not below 0.1. A further and extensive comparison with other literature data will not be made as this would require an elaborate discussion of results obtained at (much) higher temperatures and the recalculation and reinterpretation of these results in view of the varying degree of dissociation and methods used. Although this would be interesting we feel that it is outside the scope of this investigation.

Taking into account the indicated error ranges we can conclude that only \( \text{NH}_4\text{F} \) is completely dissociated in the vapor phase and that the other salts are not. In the literature\(^{5,4,1}\) experimental determinations of \( b \) are found only for \( \text{NH}_4\text{Cl} \). These investigators, working at (considerably) higher temperature, report values for \( b \) which are practically unity. From this we conclude that in the case of \( \text{NH}_4\text{Cl} \) the degree of dissociation is a weak function of temperature, as is described by Eq.

<table>
<thead>
<tr>
<th>Ammonium salt</th>
<th>( b(\theta) )</th>
<th>( g(b) )</th>
<th>( s )</th>
<th>( 100^\circ \text{f}(s, b) )</th>
<th>( K_f(\theta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_4\text{F} )</td>
<td>0.97</td>
<td>0.49</td>
<td>0.41</td>
<td>-0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>( \text{NH}_4\text{Cl} )</td>
<td>0.05</td>
<td>0.46</td>
<td>0.39</td>
<td>-1.57</td>
<td>1.04</td>
</tr>
<tr>
<td>( \text{NH}_4\text{Br} )</td>
<td>0.51</td>
<td>0.34</td>
<td>0.33</td>
<td>-0.47</td>
<td>0.144</td>
</tr>
<tr>
<td>( \text{NH}_4\text{I} )</td>
<td>0.39</td>
<td>0.28</td>
<td>0.28</td>
<td>-0.56</td>
<td>0.070</td>
</tr>
<tr>
<td>( \text{NH}_4\text{CNS} )</td>
<td>0.61</td>
<td>0.32</td>
<td>0.32</td>
<td>-0.37</td>
<td>0.235</td>
</tr>
<tr>
<td>( \text{NH}_4\text{NO}_3 )</td>
<td>0.66</td>
<td>0.40</td>
<td>0.35</td>
<td>-0.57</td>
<td>0.309</td>
</tr>
<tr>
<td>( \text{NH}_4\text{HCO}_3 )</td>
<td>0.85</td>
<td>0.46</td>
<td>0.69</td>
<td>-1.45</td>
<td>0.093</td>
</tr>
</tbody>
</table>
(19), and that \( \frac{db}{dT} \) is positive. It is also interesting to note that dissociation diminishes in the series from fluoride to iodide. For the calculations on ammonium bicarbonate we assumed that it dissociates into three molecules \((\text{NH}_3, \text{H}_2\text{O}, \text{CO}_2)\) and the relevant equations were adjusted accordingly.

Ammonium nitrate shows a solid phase transition at 357.4 K and connected with this there is a small enthalpy change of 1.34 kJ mol\(^{-1}\). This transition was not visible in the vapor pressure measurements.

In Table II we give the degree of dissociation \( b \) as calculated with Eq. (13) and the numerical values of \( g(b) \), \( s \), \( f(s, b) \), and \( K_i(\theta) \) as defined in Eqs. (22), (23), and (6), respectively. As can be seen from Table I the values for \( A_i \) and \( \Delta H_{\text{obs}} \) are equal within experimental error. The maximum difference, including errors, is about \( \pm 3.5 \) kJ mol\(^{-1}\). Unfortunately, this means that because of the addition of errors the calculation of \( \Delta H_{\text{obs}} \) with Eqs. (24) and (25) is not useful in this case. A possible alternative might be to use a literature value for \( \Delta H_{\text{obs}} \) or \( \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) \). As indicated above, because the dissociation is more or less complete no experimental values for \( \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) \) can be found in the literature.

For \( \Delta H_{\text{obs}} \) Clementi and Gayles calculated, using \( \text{ab initio} \) methods, that \( \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) = 67 \) kJ mol\(^{-1}\), while Goldfinger and Verhaagen found from their Knudsen mass-spectrometrical experiments that \( \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) = (42 \pm 13) \) kJ mol\(^{-1}\). Taking an average value of \( (\text{NH}_4\text{Cl}, g) = (55 \pm 15) \) kJ mol\(^{-1}\) for \( \Delta H_{\text{obs}} \) leads with Eqs. (24) and (25) to \( (\Delta H_{\text{obs}} - \Delta H_{\text{obs}}) = +0.95 \pm 0.45 \) kJ mol\(^{-1}\) and \( \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) = (114 \pm 15) \) kJ mol\(^{-1}\). Then from Eq. (9), \( \Delta H_{\text{obs}} = (169 \pm 15) \) kJ mol\(^{-1}\). Now this result contradicts the observation that \( \text{NH}_4\text{Cl} \) is completely dissociated in the gas phase at higher temperatures. Therefore, we conclude that \( \Delta H_{\text{obs}} = \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) \), which implies that [see Eq. (10)] \( b \) is only a weak function of temperature. The same phenomenon is observed for the lower carboxylic acids also. It is therefore difficult to predict in a general way the temperature dependence of \( b \). The assumption that \( b \) increases with temperatures, as is observed, implies that \( \Delta H_{\text{obs}} > \Delta H_{\text{obs}}(\text{NH}_4\text{Cl}) \). When \( (\Delta H_{\text{obs}} - \Delta H_{\text{obs}}) \) changes sign, \( b \) will start to decrease and a maximum value will be found, as with the carboxylic acid.

In conclusion, it can be said that the degree of dissociation will be a weak function of temperature and it therefore can best be determined by direct methods.

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