On the heat of formation of NH

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Experiments giving information on the heat of formation of NH have been reanalyzed. It has been found that studies on the dissociative excitation or ionization of NH-containing species give upper limits to \( \Delta H_{f0}^{\circ}(\text{NH}) \) substantially lower than the JANAF value of 3.90 eV. The most reliable of these experiments give an upper limit of 3.63 ± 0.10 eV in agreement with recent spectroscopic studies. The experiments given most weight in the JANAF compilation have been reviewed. All have been found to be more compatible with a lower heat of formation of NH than 3.9 eV. It is recommended that a new value of 3.65 ± 0.10 eV be adopted for \( \Delta H_{f0}^{\circ}(\text{NH}) \).

The heat of formation \( \Delta H_{f0} \) of NH has never been clearly established. Early work by Pannetier and Gaydon, Franklin et al., Reed and Snedden, Clyne and Thrush, and Altshuller placed \( \Delta H_{f0}(\text{NH}) \) at about 3.5 eV. Later studies by Seal and Gaydon, Kaskan and Nadler, and Stedman disputed this value and suggested a value of 3.90 eV which was subsequently incorporated into the JANAF tables. Stedman's result was incorrect because of a mathematical error, while the work of Harrington et al. shows that Seal and Gaydon's analysis was based upon a faulty assumption. In reanalyzing Kaskan and Nadler's work, we have found that corrections made for their use of faulty input data will lower their value for \( \Delta H_{f0}(\text{NH}) \) by 0.16 eV. Any additional discrepancies between the value of \( \Delta H_{f0}(\text{NH}) \) from their work and that derived from the work discussed below can be accounted for by the ±0.17 eV uncertainty in their results. We have reanalyzed a number of experiments on dissociative excitation or ionization of NH-containing molecules. The most reliable of these give an upper limit to \( \Delta H_{f0}^{\circ}(\text{NH}) \) of 3.63 ± 0.10 eV. Recent spectroscopic analyses of predissociation in NH by Graham and Lew and by Zechsch showed the results \( \Delta H_{f0}^{\circ} \approx 3.65 \pm 0.05 \) eV and \( \Delta H_{f0} < 3.67 \) eV. These results agree excellently with the analysis of the dissociative excitation experiments given here, and indicate that \( \Delta H_{f0}^{\circ}(\text{NH}) = 3.65 \pm 0.10 \text{ eV} \).

Experiments on the dissociative excitation or ionization of NH-containing molecules can be analyzed to give upper limits to the heat of formation of NH. The processes are represented by Eq. (1):

\[
\text{RNH} + E_{in} \rightarrow \text{NH}^* + \text{R}, \tag{1a}
\]

or

\[
-\text{NH} + R^*, \tag{1b}
\]

where \( E_{in} \) represents the input energy either through electrons, photons, or electronically excited metastables and the asterisk may represent electronic excitation or ionization. Equation (2) represents the energy balance from Process (1a):

\[
E_{in} \geq \Delta H_{f0}^{\circ}(\text{NH}) + E_{R^*} - \Delta H_{f0}^{\circ}(\text{R}) - \frac{1}{2}RT, \tag{2}
\]

with a similar equation holding for Process (1b). In a process occurring at threshold, the fragments separate with zero excess energy. Thus one must use the heats of formation of the species at 0 °K. This point has been overlooked in most of the literature. The internal energy (rotational) of the parent molecule is also available to contribute to the dissociation process, hence the \( \frac{3}{2}RT \) term in Eq. (2). The upper limit to \( \Delta H_{f0}^{\circ}(\text{NH}) \) from Process (1a) is

\[
\Delta H_{f0}^{\circ}(\text{NH}) \leq E_{in} + \Delta H_{f0}^{\circ}(\text{RNH}) + \frac{3}{2}RT - E_{R^*} - \Delta H_{f0}^{\circ}(\text{R}). \tag{3}
\]

Table 1 lists the various molecules studied, the excitation source, the excited fragment observed, and the resultant upper limit for \( \Delta H_{f0}^{\circ}(\text{NH}) \). The second and fifth entries are much higher than any of the others and result from processes occurring with excess kinetic energy. There are other examples of this in the literature. Of the remaining entries, two molecules give upper limits consistent with the higher value of \( \Delta H_{f0}^{\circ}(\text{NH}) \) listed in the JANAF tables, but the others are much lower. Averaging all but entries two and five gives \( \Delta H_{f0}^{\circ}(\text{NH}) \approx 3.69 \pm 0.13 \text{ (eV)} \).

Stedman claimed his data supported the higher value of 3.90 eV, but reanalysis shows his calculation to be in error, as the reaction between metastable Kr\(^{3p_2}\) and RNH gives a value of 3.61 eV for \( \Delta H_{f0}^{\circ}(\text{NH}) \). We have shown previously that the method of formation of metastable krypton used by Stedman, i.e., energy transfer from argon metastables, will give a negligible concentration of the higher energy, Kr\(^{3p_0}\), metastable.

Okabe and Lenzi measured the threshold for formation of NH\(^{c_2^+}\) in the dissociative excitation of NH\(_2\) by UV light. Using that threshold and a value for \( \Delta H_{f0}(\text{NH}) \) of 3.51 eV, they deduced a singlet-to-triplet splitting in NH of 1.6 eV. The recent observation of the NH \(^b\Sigma^+\) → \(^X\Pi\) emission by Gilles et al., and the determination of the electron affinity of NH \((\text{a}^1\Delta)\) by Engelking and Lineberger have established the singlet-to-triplet splitting to be 1.56 eV. Thus, in Okabe and Lenzi's study, the most uncertain value in their energy-balance equation becomes the heat of formation of NH. Their data reanalyzed give \( \Delta H_{f0}^{\circ}(\text{NH}) \approx 3.62 \text{ eV} \).

The work of Reed and Snedden depends upon the ionization potential of NH which they measured to be 13.1 ± 0.05 eV. Foner and Hudson have subsequently confirmed this value.

Franklin et al. claim an uncertainty, including the effects of electron energy spread and energy-scale calibration, of ±0.1 eV in their appearance potential. A further uncertainty in the thermochemical values used to extract \( \Delta H_{f0}^{\circ}(\text{NH}) \) gives an overall uncertainty of ±0.15
TABLE I. Upper limits to $\Delta H_f$(NH) from dissociative-excitation experiments on NH-containing compounds.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{in}}$</th>
<th>Fragment excitation energy $^b$</th>
<th>$\Delta H_f$(NH)$^{c,d}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^+ + \text{HN}_2 \rightarrow \text{NH}(^2\Pi) + \text{N}_2$</td>
<td>4.3</td>
<td>3.69</td>
<td>3.79</td>
<td>14</td>
</tr>
<tr>
<td>NH($e^+$) + $\text{N}_2$</td>
<td>6.8</td>
<td>5.37</td>
<td>4.61</td>
<td>14</td>
</tr>
<tr>
<td>NH($e^+$) + $^2\text{N}_2$</td>
<td>16.0</td>
<td>15.38</td>
<td>3.60</td>
<td>2</td>
</tr>
<tr>
<td>$e^+ + \text{NH}_2 \rightarrow \text{NH}(^2\Pi) + 2\text{H}$</td>
<td>12.2</td>
<td>3.69</td>
<td>3.67</td>
<td>14</td>
</tr>
<tr>
<td>NH($e^+$) + H$_2$</td>
<td>10.1</td>
<td>5.37</td>
<td>4.37</td>
<td>14</td>
</tr>
<tr>
<td>NH + H$_2$</td>
<td>17.1</td>
<td>13.1</td>
<td>3.64</td>
<td>3</td>
</tr>
<tr>
<td>NH + 2H</td>
<td>21.6</td>
<td>13.1</td>
<td>3.66</td>
<td>14</td>
</tr>
<tr>
<td>$e^+ + \text{HNCO} \rightarrow \text{NH}(^2\Pi) + \text{CO}$</td>
<td>7.4</td>
<td>3.69</td>
<td>3.91</td>
<td>14</td>
</tr>
<tr>
<td>$e^+ + \text{CH}_2\text{CH}_2 \rightarrow \text{NH}(^2\Pi) + \text{C}_2\text{H}_4$</td>
<td>6.7</td>
<td>3.69</td>
<td>3.91</td>
<td>14</td>
</tr>
<tr>
<td>NH</td>
<td>\text{H}</td>
<td>\text{H}</td>
<td>\text{H}</td>
<td>\text{H}</td>
</tr>
<tr>
<td>$e^+ + \text{CH}_3\text{NH}_2 \rightarrow \text{NH}(^2\Pi) + \text{CH}_3 + \text{H}$</td>
<td>11.0</td>
<td>3.69</td>
<td>3.50</td>
<td>14</td>
</tr>
<tr>
<td>$e^+ + \text{NH}_3 \rightarrow \text{NH}(^2\Pi) + \text{NH}_4 + \text{H}$</td>
<td>10.4</td>
<td>3.69</td>
<td>3.64</td>
<td>14</td>
</tr>
<tr>
<td>$h\nu + \text{NH}_2 \rightarrow \text{NH}(^2\Pi) + \text{H}_2$</td>
<td>9.35</td>
<td>5.37</td>
<td>3.62</td>
<td>13</td>
</tr>
<tr>
<td>Kr($^{87}\text{Kr}$) + HN$_2 \rightarrow \text{NH}(X) + \text{N}_2(2^3\Sigma_g^+, \nu' = 11)$</td>
<td>9.91</td>
<td>9.48</td>
<td>3.61</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$Threshold energy for the reaction.
$^b$Spectroscopic values for NH calculated from data in J. M. Lents, J. Quant. Spectrosc. Radiat. Transfer 13, 297 (1976); for N$_2$ from A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977); and the ionization potentials for N$_2$ and NH from Refs. 9 and 21, respectively.
$^c$The values listed in this column are upper limits calculated from Eq. (3).
$^d$Thermochemical values from Ref. 9 except ethyleneimine and methylamine which come from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, "Energetics of Gaseous Ions," J. Phys. Chem. Ref. Data 6, Suppl. 1 (1977). And HN$_2$ which is from Ref. 22. The heats of formation for the latter three molecules were extrapolated from 298 K to 0 K by statistical mechanical techniques, considering only the translational and rotational contributions to the enthalpy.

$\text{eV}$ to their determination. Reed and Snedden$^a$ also claim their appearance potentials to be uncertain by 0.1 $\text{eV}$, but do not discuss their sources of error. Uncertainties in auxiliary thermochromy lead to an overall uncertainty of 0.15 $\text{eV}$ in Reed and Snedden’s work assuming their assessment of their threshold accuracy is valid. Okabe and Lenz$^b$ claim an uncertainty of 0.06 $\text{eV}$ based upon the uncertainty in their measured threshold and bandpass of their photolysis source. Errors in the auxiliary thermochromy used in analyzing their work are much smaller than this. The only significant uncertainty in the study of Stedman$^c$ would be in the thermochromic value for $\Delta H_f$(HN$_2$), which is $3.08 \pm 0.04 \text{ eV}$. All four of these experiments are in excellent agreement that $\Delta H_f$ = 3.69 $\pm 0.10 \text{ eV}$. Fukui$^d$ et al. fail to place error limits upon their numbers. The fairly large spread in the values of $\Delta H_f$(NH) derived from their work is suggestive of fairly large uncertainties in their experimental procedure. Some of this spread, however, may stem from poorly known thermochromy of the parent molecules, methyl amine, ethyleneimine, and HNCO.

It would appear that the most reliable values for $\Delta H_f$(NH) would come from the work of Franklin$^e$, Reed and Snedden,$^f$ Stedman,$^g$ and Okabe and Lenz.$^b$ These experiments are in excellent agreement among themselves and with the recent spectroscopic data. The study and of Fukui et al.$^d$ adds additional support to a value of $\Delta H_f$(NH) somewhat lower than that listed in the JANAF tables.

Seal and Gaydon$^h$ formed NH in a high temperature, equilibrium environment (4000–6000 K) by shock heating mixtures of N$_2$/H$_2$/Kr and NH$_3$/Kr. They measured absolute concentrations of NH by absorption on the NH $A^2\Pi$ – $X^2\Sigma^+$ transition, using published values for the transition probabilities, and assumed that there was no interference due to emission from the upper state. However, Harrington et al.$^i$ were able to observe the NH$A^2\Pi$ – $X^2\Sigma^+$ emission at 336 nm in shock heated NH$_3$/Ar mixtures in the same temperature range. They analyzed their data, using the then accepted value for $\Delta H_f$(NH) of 3.51 eV to obtain a transition probability for the observed emission which is reasonably close to the results from other, more direct studies. Correcting the observed absorption in the study of Seal and Gaydon,$^h$ for interference from emission would give a lower $\Delta H_f$(NH).

Kaskan and Nadler$^s$ value for $\Delta H_f$(NH) is derived from their measurement of the concentration ratio $[\text{NH}]/[\text{H}_2\text{O}]$. Recent work by German$^t$ and by Kinsey$^u$ group indicates that $f_0$(OH) = $1.08 \times 10^{-4}$ as opposed to the value of $7.1 \times 10^{-13}$ used by Kaskan and Nadler. Thus, they overestimated their OH concentrations by about 50%. Their experimental values for the concentration ratio need to be raised by a factor of 2.3 since
the error in [OH] will be squared. The effect of this will be to lower \( \Delta H_f'(NH) \) to explain their data. An additional 8% reduction to their value for \( \Delta H_f(NH) \) will occur by using updated values for \( \Delta G_{298}^{0} \) for NH\(_3\) and OH. With the above mentioned corrections, the Kaskan and Nadler result becomes 3.77 ± 0.17 eV.

We feel that the evidence is strongly in favor of a lower value for \( \Delta H_f^{0}(NH) \) than is currently listed in the JANAF tables. Further experiments are warranted to establish precisely \( \Delta H_f^{0}(NH) \). In the interim, we suggest a value of 3.65 ± 0.10 eV be adopted.

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\( ^{\text{JANAF Thermochromical Tables, Natl. Stand. Ref. Data Ser. }} \)
\( \text{Natl. Bur. Stand. 37 (1971), and supplements through 30 June 1977.} \)