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 ionizaton of NH-containing species give upper limits to $\Delta H_{j0}^{o}(NH)$ 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 $\Delta H_{0}^{e}(NH)$.

The heat of formation (ΔH_f) of NH has never been clearly established. Early work by Pannetier and Gaydon,¹ Franklin et al.,² Reed and Snedden,³ Clyne and Thrush,⁴ and Altshuller⁵ placed ΔH_f (NH) at about 3.5 eV. Later studies by Seal and Gaydon,⁶ Kaskan and Nadler,⁷ and Stedman⁸ disputed this value and suggested a value of 3.90 eV which was subsequently incorporated into the JANAF tables.⁹ Stedman's result was incorrect because of a mathematical error, while the work of Harrington et al.¹⁰ 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 $\Delta H_f(NH)$ by 0.16 eV. Any additional discrepancies between the value of $\Delta H_f(NH)$ 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 $\Delta H_{f0}^{\circ}(NH)$ of 3.63 ± 0.10 eV. Recent spectroscopic analyses of predissociation in NH $c^{1}\pi$ by Graham and Lew¹¹ and by Zetzsch¹² have obtained the results $\Delta H_{f0}^{\circ} \ge 3.65 \pm 0.05$ eV¹¹ and $\Delta H_{f0}^{\circ} < 3.67$ eV.¹² These results agree excellently with the analysis of the dissociative excitation experiments given here, and indicate that $\Delta H_{f0}^{\circ}(NH) = 3.65$ ±0.10 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.^{2,3,8,13,14} The processes are represented by Eq. (1):

$$RNH + E_{in} \rightarrow NH^* + R , \qquad (1a)$$

or

$$\rightarrow$$
 NH + R^{*}, (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):

$$E_{in} \geq \Delta H_{f0}^{\circ}(\mathrm{NH}) + E_{\mathrm{NH}} * + \Delta H_{f0}^{\circ}(\mathrm{R}) - \Delta H_{f0}^{\circ}(\mathrm{RNH}) - \frac{3}{2}RT, \quad (2)$$

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. 2,3,8,14 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).¹⁵ The upper limit to $\Delta H_{f0}^{\circ}(NH)$ from Process (1a) is

 $\Delta H_{f0}^{\circ}(\mathrm{NH}) \le E_{in} + \Delta H_{f0}^{\circ}(\mathrm{RNH}) + \frac{3}{2}RT - E_{\mathrm{NH}} * - \Delta H_{f0}^{\circ}(\mathrm{R}).$ (3)

Table I lists the various molecules studied, the excitation source, the excited fragment observed, and the resultant upper limit for $\Delta H_{f0}^{\circ}(NH)$. 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.^{8,16,17} Of the remaining entries, two molecules give upper limits consistent with the higher value of $\Delta H_{f0}^{\circ}(NH)$ listed in the JANAF tables, but the others are much lower. Averaging all but entries two and five gives $\Delta H_{f0}^{\circ}(NH) \leq 3.69 \pm 0.13$ (σ) eV.

Stedman⁸ claimed his data support ed the higher value of 3.90 eV, but reanalysis shows his calculation to be in error, as the reaction between metastable $Kr({}^{3}P_{2})$ and HN_{3} gives a value of 3.61 eV for $\Delta H_{f0}^{\circ}(NH)$. We have shown previously¹⁸ 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, $Kr {}^{3}P_{0}$, metastable.

Okabe and Lenzi¹³ measured the threshold for formation of NH($c^{1}\pi$) in the dissociative excitation of NH₃ by UV light. Using that threshold and a value for ΔH_{f} (NH) of 3.51 eV, they deduced a singlet-to-triplet splitting in NH of 1.6 eV. The recent observation of the NH $b^{1}\Sigma^{*}$ - $X^{3}\Sigma^{-}$ emission by Gilles *et al.*, ¹⁹ and the determination of the electron affinity of NH($a^{1}\Delta$) by Engelking and Lineberger²⁰ 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 ΔH_{f0}° (NH) \leq 3.62 eV.

The work of Reed and Snedden³ depends upon the ionization potential of NH which they measured to be 13.1 ± 0.05 eV. Foner and Hudson²¹ have subsequently confirmed this value.

Franklin *et al.*² 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 $\Delta H_{f0}^{\circ}(NH)$ gives an overall uncertainty of ± 0.15

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Reaction	Ein²	Fragment excitation energy ^b	$\Delta H_f(\mathrm{NH})^{\mathrm{c,d}}$	Reference
e^{-} + HN ₃ \rightarrow NH($A^{3}\pi$) + N ₂	4.3	3.69	3.79	14
$NH(c^{1}\pi) + N_{2}$	6.8	5.37	4.61	14
$NH(X) + N_2^+$	16.0	15.58	3.60	2
$e^+ + \mathrm{NH}_3 \rightarrow \mathrm{NH}(A^3\pi) + 2\mathrm{H}$	12.2	3.69	3.67	14
$NH(c^{1}\pi) + H_{2}$	10.1	5.37	4,37	14
$NH^{+}+H_{2}$	17.1	13.1	3.64	3
$NH^{+}+2H$	21.6	13.1	3.66	3
e^{-} + HNCO \rightarrow NH($A^{3}\pi$) + CO	7,4	3.69	3.91	14
$e^+ + CH_2 - CH_2 - NH(A^{3}\pi) + C_2H_4$	6.7	3.69	3.91	14
Н				
e^- + CH ₃ NH ₂ \rightarrow NH($A^{3}\pi$) + CH ₃ + H	11.0	3.69	3.50	14
e^{-} + NH ₂ -NH ₂ - NH($A^{3}\pi$) + NH ₂ + H	10.4	3,69	3.64	14
$h\nu + \mathrm{NH}_3 \rightarrow \mathrm{NH}(c^{1}\pi) + \mathrm{H}_2$	9.35	5.37	3,62	13
$Kr(^{3}P_{2}) + HN_{3} \rightarrow NH(X) + N_{2}(B^{3}\pi_{g}, v' = 11)$	9.91	9.48	3.61	. 8

TABLE I. Upper limits to $\Delta H_f(NH)$ from dissociative-excitation experiments on NH-containing compounds.

^aThreshold energy for the reaction.

Spectroscopic values for NH calculated from data in J. M. Lents, J. Quant. Spectrosc.

Radiat. Transfer 13, 297 (1973); 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.

"The values listed in this column are upper limits calculated from Eq. (3).

^dThermochemical values from Ref. 9 except ethylenimene 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_3 which is from Ref. 22. The heats of formation for these 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.

eV to their determination. Reed and Snedden³ also claim their appearance potentials to be uncertain by 0.1 eV, but do not discuss their sources of error. Uncertainties in auxilliary thermochemistry lead to an overall uncertainty of 0.15 eV in Reed and Snedden's work assuming their assessment of their threshold accuracy is valid. Okabe and Lenzi¹² claim an uncertainty of 0.06 eV based upon the uncertainty in their measured threshold and bandpass of their photolysis source. Errors in the auxilliary thermochemistry used in analyzing their work are much smaller than this. The only significant uncertainty in the study of Stedman⁸ would be in the thermochemical value for $\Delta H^{\circ}_{f_{298}}(HN_3)$, which is $3.08 \pm 0.04 \text{ eV}$.²² All four of these experiments are in excellent agreement that $\Delta H_{f0}^{\circ} \leq 3.63 \pm 0.10$ eV. Fukui *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 thermochemistry of the parent molecules, methyl amine, ethylenimine, and HNCO.

It would appear that the most reliable values for ΔH_{f0}° (NH) would come from the work of Franklin *et al.*,² Reed and Snedden,³ Stedman,⁸ and Okabe and Lenzi.¹³ These experiments are in excellent agreement among them-selves and with the recent spectroscopic data. The study and of Fukui *et al.*¹⁴ adds additional support to a value

of $\Delta H^{\circ}_{f0}(NH)$ somewhat lower than that listed in the JANAF tables.

Seal and Gaydon⁶ 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 $A^{3}\pi$ - $X^{s}\Sigma^{-}$ 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.*¹⁰ were able to observe the NH(A $^{3}\pi$ - X^{Σ}) emission at 336 nm in shock heated NH₃/Ar mixtures in the same temperature range. They analyzed their data, using the then accepted value for $\Delta H_{f0}^{\circ}(NH)$ 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,⁶ for interference from emission would give a lower $\Delta H_f^{\circ}(NH)$.

Kaskan and Nadler's⁷ value for $\Delta H_f(NH)$ is derived from their measurement of the concentration ratio $[NH][H_2O]^2/[NH_3][OH]^2$. Recent work by German²³ and by Kinsey's²⁴ group indicates that $f_{00}(OH) = 1.08 \times 10^{-3}$ as opposed to the value of $7.1 \times 10^{-4.25}$ 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 ΔG_{f2000} for NH₃ and OH.⁹ 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 $\Delta H_{f0}^{\circ}(NH)$ than is currently listed in the JANAF tables. Further experiments are warranted to establish precisely $\Delta H_{f0}^{\circ}(NH)$. In the interim, we suggest a value of 3.65±0.10 eV be adopted.

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