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The Free Energy of Ammonia

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The free energy of ammonia gas may be calculated from the moments of inertia and the fundamental frequencies, using the familiar equation

$$-(F^\circ - H_0^\circ)/T = 3/2 R \ln M + 5/2 R \ln T + R \ln Q - 7.267 \quad (1)$$

where M is the molecular weight, T the absolute temperature and Q the partition function. H_0° is used instead of E_0° in accordance with the more recent notation.¹

A very good approximation to Q at room temperature and above is obtained by regarding the partition function as the product of several separate Q 's which are characteristic of the various kinds of energy in the molecule. In this paper Q is separated into Q_E , Q_N , Q_R , Q_V and Q_D , where the subscripts refer to electronic, nuclear, rotational, vibrational and centrifugal distortion contributions, respectively. If ammonia is assumed to have a singlet electronic ground state, Q_E is unity, and it will be seen that this assumption is entirely in harmony with all equilibrium and thermal data. Q_N is the nuclear spin contribution, 24 in the case of ammonia, and in order to calculate absolute thermodynamic quantities this value would have to be used. In accordance with the usual practice, Q_N has been ignored, and for this reason the tabulated "free energies" and entropies are less than the absolute values by $R \ln 24$.

Ammonia is a symmetrical top molecule having two principal moments of inertia, $I_1 = I_2$, and I_3 , and the high temperature rotational partition function is therefore

$$Q_R = \frac{1}{\sigma} \frac{8\pi^2}{h^3} (2\pi kT)^{3/2} (I_1 I_2 I_3)^{1/2} \quad (2)$$

where σ is the classical symmetry number of which more will be said subsequently. For lower temperatures, a more nearly exact value for Q_R is obtained by using the approximation of I. E. Viney² which has been corrected by Kassel.³

$$Q_R = \frac{1}{\sigma} \frac{\pi^{1/2}}{\alpha\beta^{1/2}} \left[1 + \frac{\alpha}{\beta} \left(\frac{\alpha}{4} + \frac{\gamma}{3} \right) + \left(\frac{\alpha}{\beta} \right)^2 \left(\frac{\alpha^2}{32} + \frac{\alpha\gamma}{12} + \frac{\gamma^2}{15} \right) + \dots \right] \quad (3)$$

where

$$\alpha = \frac{h^2}{8\pi^2 I_1 kT} \quad \beta = \frac{h^2}{8\pi^2 I_3 kT} \quad \gamma = \frac{h^2}{8\pi^2 kT} \left(\frac{1}{I_3} - \frac{1}{I_1} \right)$$

This refinement introduces a correction of only 0.05% to the free energy at 300°K. and becomes completely negligible at higher temperatures.

The moments of inertia given by Wright and Randall⁴ are

$$I_1 = I_2 = 2.782 \times 10^{-40} \text{ g. cm.}^2 \\ I_3 = 4.33 \times 10^{-40} \text{ g. cm.}^2$$

Substituting these values in (3) and using values of the physical constants given by the "International Critical Tables"

$$-(F^\circ - H_0^\circ)/T = 4 R \ln T + R \ln Q_V + R \ln Q_D - R \ln \sigma - 5.159 + R \ln (1 + 2.899/T + 4.898/T^2)$$

Q_D , the contribution of centrifugal distortion caused by rotation, has been evaluated by Wilson⁵ and has the approximate form $Q_D = 1 + \rho T$, where $\rho = 1.45 \times 10^{-6}$ for ammonia. This correction affects the free energy by 0.1% at 2000°K.

The ammonia molecule has four normal vibrational frequencies, two of which are doubly degenerate: $\nu_1 = 3335 \text{ cm.}^{-1}$ (single),⁶ $\nu_3 = 948 \text{ cm.}^{-1}$ (single)⁷ and $\nu_4 = 1631 \text{ cm.}^{-1}$ (double).⁶ The value of ν_2 is in some doubt since it has not been observed spectroscopically. It is known to be large, however, and therefore of least importance to the partition function. Howard has estimated its value to be 3450 cm.^{-1} (double).⁸

The contributions of these four frequencies to $\ln Q_V$ were determined from the tables of Gordon and Barnes.⁹ Because of lack of adequate data to determine the anharmonic terms, the vibrations were regarded as being harmonic. The error incurred as a result of this neglect may become appreciable at higher temperatures; nevertheless, the tabulated values of the free energy and entropy have been given to three places of decimals in order to facilitate the application of appropriate corrections when anharmonic data become available.

(4) Wright and Randall, *Phys. Rev.*, **44**, 391 (1933).

(5) E. Bright Wilson, *J. Chem. Phys.*, **4**, 526 (1936).

(6) Shaefer and Matossi, "Das Ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 250.

(7) Barker, personal communication to Wright and Randall.

(8) Howard, *J. Chem. Phys.*, **3**, 207 (1935).

(9) Gordon and Barnes, *ibid.*, **1**, 297 (1933).

(1) See Giaque and Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

(2) Miss I. E. Viney, *Proc. Camb. Phil. Soc.*, **29**, 142 (1933).

(3) Kassel, *J. Chem. Phys.*, **1**, 576 (1933).

ν_3 is the normal vibration of the deformation-parallel type, $\delta(\pi)$, wherein the nitrogen atom approaches and recedes from the plane of the three hydrogens. This vibration is unique in that the nitrogen atom may resonate through the plane and vibrate about either of its two equilibrium positions. The nature of the energy levels for a symmetrical double minimum potential function of this type has been discussed by several authors¹⁰ and has been applied specifically to ammonia by Manning.¹¹

Whenever there are symmetrical double minima in the potential energy, the vibrational levels which are lower than the top of the dividing hill are doubled, and those above the top of the hill are spaced in a manner quite different from the levels of a simple quadratic potential function. For this reason it might be supposed that the usual Einstein function would be a poor approximation to the true partition function obtained by summing these comparatively irregular doublet levels.

Both methods of computation were employed for ν_3 , and it was found that the values from the Einstein functions of Gordon and Barnes were sensibly identical with those obtained by summing the individual vibration levels given by Manning,¹¹ provided the symmetry number σ was taken as 3 in the former case and 6 in the latter. By using the Einstein function, one ignores the doubling and therefore implicitly denies the possibility of resonance of the nitrogen atom across the plane of the hydrogen atoms, since the doubling is the direct result of this resonance. In this case the number of indistinguishable orientations obtainable by simple rotations of the molecule is three. The alternate treatment of summing both components of the split vibrational level recognizes the resonance of the nitrogen atom, and in order to be consistent the symmetry number must be taken as six.

Table I gives the calculated free energy and entropy values.

The standard free energy of formation of ammonia may be computed by combining these values of $(F^\circ - H_0^\circ)/T$ with those of hydrogen¹² and nitrogen¹³ and ΔH_0° for the reaction $3/2\text{H}_2 + 1/2\text{N}_2 = \text{NH}_3$. ΔH_0° may be obtained either

(10) Dennison and Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932); Rosen and Morse, *ibid.*, **42**, 210 (1932).

(11) Manning, *J. Chem. Phys.*, **3**, 136 (1935).

(12) Giauque, *THIS JOURNAL*, **52**, 4816 (1930).

(13) Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

TABLE I

T, °K.	$-\frac{(F^\circ - H_0^\circ)}{T}$ cal./deg./mole	S° cal./deg./mole
298.1	37.989	46.034
300	38.040	46.089
400	40.380	48.628
500	42.249	50.761
600	43.826	52.602
700	45.209	54.346
800	46.450	55.915
900	47.585	57.378
1000	48.634	58.757
1100	49.614	60.059
1200	50.535	61.296
1300	51.408	62.473
1400	52.239	63.598
1500	53.033	64.673
1600	53.792	65.704
1700	54.522	66.692
1800	55.224	67.641
1900	55.914	68.554
2000	56.559	69.434

from thermal data or by combining values of $\Delta(F^\circ/T - H_0^\circ/T)$ from spectroscopic data with $\Delta F^\circ/T$ obtained from equilibrium measurements. The results of the latter procedure are shown in Table II.

The synthesis of ammonia is a reaction for which there exists a great deal of unusually accurate equilibrium data throughout a wide range of temperatures and pressures. These data have been reviewed and corrected for gas imperfection by Gillespie and Beattie.¹⁴ Table II gives the values of ΔH_0° calculated from the equilibrium measurements of Larson and Dodge¹⁵ and Haber¹⁶ and his associates. K_p° is obtained by correcting the corresponding experimental equilibrium constant to the ideal gas state and K_p° (calcd.) is the value derived from the spectroscopic quantities $\Delta(F^\circ - H_0^\circ)/T$ and the average ΔH_0° .

ΔH_0° is very nearly constant over the entire temperature range, and it is probable that the slight trend is the result of treating the molecule as an harmonic oscillator and inadequate correction for stretching at the higher temperatures.

ΔH_0° also can be evaluated from the heat of formation of ammonia. Rossini and Bichowsky,¹⁷ who reviewed the literature up to January 1, 1934, give $\Delta H_{291.1}^\circ = -11,000$ cal. Becker and Roth¹⁸ found $\Delta H_{293.1}^\circ = -11,010 \pm 70$ cal. From either

(14) Gillespie and Beattie, *Phys. Rev.*, **36**, 743 (1930).

(15) Larson and Dodge, *THIS JOURNAL*, **45**, 2918 (1923).

(16) Haber, Tamaru and Ponnaz, *Z. Elektrochem.*, **21**, 89 (1915); Haber and Maschke, *ibid.*, **21**, 128 (1915).

(17) Rossini and Bichowsky, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(18) Becker and Roth, *Z. Elektrochem.*, **40**, 836 (1934).

TABLE II

$$K_p = (p_{\text{NH}_3}) / (p_{\text{H}_2})^{3/2} (p_{\text{N}_2})^{1/2}$$

T , °K.	p , atm.	K_p	K°	$-\Delta H_0^\circ$ cal.	K° (calcd.)
598.1	10	0.0401	0.0396	9225	0.0406
623.1	10	.0266	.0263	9227	.0269
	30	.0273	.0264	9230	.0269
	50	.0278	.0262	9223	.0269
648.1	10	.0181	.0179	9232	.0183
	30	.0184	.0178	9222	.0183
	50	.0186	.0176	9208	.0183
	100	.0202	.0180	9231	.0183
673.1	10	.0129	.0128	9260	.0128
	30	.0129	.0126	9233	.0128
	50	.0130	.0124	9215	.0128
	100	.0137	.0124	9213	.0128
698.1	10	.00919	.00912	9249	.00915
	30	.00919	.00895	9224	.00915
	50	.00932	.00892	9218	.00915
	100	.00987	.00898	9226	.00915
723.1	10	.00659	.00654	9228	.00666
	30	.00676	.00660	9240	.00666
	50	.00690	.00662	9245	.00666
	100	.00725	.00666	9253	.00666
	300	.00884	.00660	9241	.00666
	600	.01294	.00672	9266	.00666
	1000	.02328	.00690	9304	.00666
748.1	10	.00516	.00512	9309	.00496
	30	.00515	.00503	9273	.00496
	50	.00513	.00494	9247	.00496
	100	.00532	.00492	9241	.00496
	300	.00674	.00517	9315	.00496
	600	.00895	.00495	9251	.00496
	1000	.01493	.00504	9278	.00496
773.1	10	.00381	.00379	9257	.00378
	30	.00386	.00378	9255	.00378
	50	.00388	.00375	9242	.00378
	100	.00402	.00374	9236	.00378
	300	.00498	.00391	9304	.00378
	600	.00651	.00381	9265	.00378
834.1	30	.00213	.00209	9292	.00204
880.1	30	.00135	.00132	9213	.00136
893.1	30	.00126	.00124	9289	.00122
904.1	30	.00109	.00111	9261	.00111
977.1	30	.000656	.000648	9258	.000646
983.1	30	.000646	.000637	9310	.000620
995.1	30	.000582	.000574	9264	.000573
1085.1	30	.000338	.000334	9288	.000328
1187.1	30	.000199	.000197	9307	.000193
1225.1	30	.000168	.000166	9316	.000162

Average $-\Delta H_0^\circ = 9254$

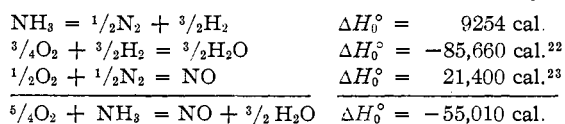
value, $\Delta H_{298.1}^\circ = -11,040$ cal. Since the entropies of ammonia, hydrogen,¹² and nitrogen¹³ at 298.1°K. are 46.03, 31.23, and 45.79, respectively, $\Delta S_{298.1}^\circ = -23.71$. Combining this with the thermal value of $\Delta H_{298.1}^\circ = -11,040$ cal., according to the relation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$; $\Delta F_{298.1}^\circ = -3972$ cal. When this is subtracted from the 298.1°K. value of $\Delta(F^\circ - H_0^\circ)$ one obtains $\Delta H_0^\circ = -9364$ cal. The value of ΔH_0° derived

from equilibrium data (-9254 cal.) is about 1% less than this thermal value. In view of the excellence of the equilibrium data and the uncertainty of the thermal measurements, it would appear that the equilibrium value is the more reliable.

ΔS° may also be determined from the third law of thermodynamics. Overstreet and Giaque¹⁹ have compared the experimental ΔS° values from third law and equilibrium measurements, and have also shown that the third law value of the entropy of ammonia agrees with the spectroscopic value.

The Oxidation of Ammonia.—The results of Table I may be used to compute the equilibrium constants for the Ostwald reaction in which ammonia is oxidized to nitric oxide and steam. This is an equilibrium which is probably impossible to measure directly due to the simultaneous oxidation of ammonia to nitrogen and steam. The formation of nitrogen is of course thermodynamically favored due to the instability of nitric oxide with respect to nitrogen and oxygen.

The values of $(F^\circ - H_0^\circ)/T$ for ammonia are combined with those of oxygen,²⁰ nitric oxide,²¹ and steam²² in accordance with the reaction $\text{NH}_3 + 3/4\text{O}_2 = \text{NO} + 3/2\text{H}_2\text{O}$. ΔH_0° is obtained for this reaction from the individual ΔH_0° 's



The equilibrium constants thus obtained are given in Table III.

TABLE III

$$K_p^\circ = (p_{\text{H}_2\text{O}})^{3/2} (p_{\text{NO}}) / (p_{\text{O}_2})^{3/4} (p_{\text{NH}_3})$$

T , °K.	K°
298.1	3.52×10^{38}
400	1.30×10^{28}
600	8.23×10^{17}
800	6.44×10^{12}
1000	5.60×10^9
1200	5.20×10^7
1500	4.92×10^5

Summary

The thermodynamic functions of ammonia have been computed from the moments of inertia and the normal modes of vibration of the molecule for the temperature range 298.1 to 2000°K. The

(19) Overstreet and Giaque, *THIS JOURNAL*, **59**, 254 (1937).(20) Johnston and Walker, *ibid.*, **55**, 172 (1933).(21) Johnston and Chapman, *ibid.*, **55**, 153 (1933).(22) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1933).(23) Giaque and Clayton, *THIS JOURNAL*, **55**, 4875 (1933).

results have been correlated with the equilibrium data of the Haber and Fixed Nitrogen Laboratories and have been used further to compute

equilibrium constants for the Ostwald reaction in which ammonia is oxidized to nitric oxide.

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Evidence Favoring the Existence of the Compound Hydrogen Perselenide¹

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While attempting to develop a method for the determination of selenium, the authors encountered what appears to be a previously undescribed compound of selenium. Mellor in his treatise on "Inorganic and Theoretical Chemistry" does not describe hydrogen perselenide, although he does discuss some of the salts of this acid. Fresenius, Fischback and Frommes³ mention that when selenium is treated with reducing agents such as zinc-hydrochloric acid mixtures, there is a compound carried over with the hydrogen. When this compound is allowed to bubble through lead acetate, a black precipitate is formed, which the authors assumed to be lead selenide. However, they do not give any quantitative results.

Experimental Part

A known solution of selenious acid was made up and standardized by reducing the selenium to the elemental state with hydroxylamine, filtering, drying and weighing. The solution was also standardized by adding potassium iodide and sulfuric acid and titrating the released iodine with standardized sodium thiosulfate.

Known quantities of the selenious acid solution were introduced into a generating flask which was connected by glass tubing to the bottom of an absorbing tube containing lead acetate solution. Five grams of 20-mesh aluminum and enough water to make about 20 ml. of solution were placed in the generator; about 3 ml. of concentrated hydrochloric acid was then added through the funnel. When the reaction was well started, the acid concentration was adjusted in such a manner that 2 or 3 bubbles passed through the absorber per second. The absorber contained 25 ml. of the following lead acetate solution: 10 g. of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ + 3 ml. of glacial acetic acid + 100 ml. of 1 *N* NH_4Ac in a total volume of 1 liter. The type of absorber used worked efficiently. A second absorber was connected to the first in several runs but there was never any precipitate formed in it. The efficient absorption is probably due to two factors: 1, the insolubility of lead diselenide; 2, the high solubility of the perselenide gas.

The selenium in the generator appeared to be reduced to elemental selenium and then the reduction proceeded further. A black precipitate was obtained in the absorber. This precipitate was filtered with suction through No. 00 Munktell filter paper in a Gooch crucible. At this point several different procedures were tried. In one of them the precipitate was dried and weighed. The composition was calculated on the assumption that all of the selenium in the generator had been converted into the lead-selenium compound. The data in Table I show that the percentage composition corresponded to PbSe_2 .

The time necessary for complete removal of the selenium from the generator varied with the amount added. Fifteen to twenty minutes was long enough for quantities around 1 mg. but one and one-half hours were necessary for 10-mg. quantities. This was shown by changing absorbers during the reaction period until a precipitate was no longer formed in the lead acetate solution. If solid material such as soil was present in the generator, much longer periods of time were necessary for complete removal of the selenium. For instance, about one hour was necessary to remove 1 mg. of selenium from 20 g. of soil.

TABLE I

RECOVERIES OF SELENIUM FROM AQUEOUS SOLUTIONS				
Se added (H_2SeO_3), mg.	PbSe_2 , mg.	Calculated wt. PbSe_2 , mg.	PbSO_4 , mg.	Calcd. wt. PbSO_4 , mg.
10.00	23.20	23.05		
10.00	22.40	23.05		
10.00	23.00	23.05	19.00	19.10
10.00	22.50	23.05	18.50	19.10

In a second procedure the lead-selenium precipitate was filtered, dried and weighed, then decomposed with nitric acid, evaporated to fumes with sulfuric acid and then diluted with alcohol and water so that the final mixture contained 10% sulfuric acid and 30% ethyl alcohol. The lead sulfate so obtained was filtered, ignited at 400°, cooled and weighed. The weight of lead sulfate obtained was compared with the theoretical yield, assuming the composition of the lead-selenium precipitate to be PbSe_2 (see Table I).

In a third procedure the lead-selenium precipitate was filtered, washed with hot, saturated ammonium acetate solution and decomposed with 1 ml. of concentrated nitric acid. The acid was neutralized with ammonia and the lead determined by the well-known Dithizone procedure of Winter, Robinson, Lamb, and Miller.⁴ Knowing the

(1) Authorized for publication, July 15, 1938.

(2) Present address: National Canners Association, San Francisco, Calif.

(3) Fresenius, Fischback and Frommes, *Z. anal. Chem.*, **96**, 447 (1934).

(4) Winter, Robinson, Lamb and Miller, *Ind. Eng. Chem., Anal. Ed.*, **7**, 265 (1935).