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## The Free Energy of Hydrogen Cyanide from Spectroscopic Data

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The free energy and heat content of gaseous hydrogen cyanide are computed from spectroscopic data, and the equilibrium constant for the reaction involving the formation of the gas from its elements is tabulated. The results are in good agreement with the experimental value for the free energy of formation obtained by Lewis and his associates, but are in definite disagreement with the results of Badger. The equilibrium constant for the exchange reaction with deuterium is also tabulated. From the spectroscopic entropy for the gas and the most recent density data, the entropy of liquid hydrogen cyanide is estimated.

\*HE determination of the free energy of hydrogen cyanide has been a problem that has concerned physical chemists for many years. Von Wartenberg<sup>1</sup> attempted to measure the equilibrium constant for the reaction involving the formation of the gas from its elements, but his data provide little more than an order of magnitude, while the more recent results of Lewis and his associates<sup>2</sup> and of Badger<sup>3</sup> are not in as close agreement as one could wish. Badger and Woo<sup>4</sup> have computed from spectroscopic data  $S^{\circ}_{298.1}$  for the gas, and from this, the other known entropies, and the heat of formation given in International Critical Tables, Yost and Stone<sup>5</sup> have calculated  $\Delta F^{\circ}_{298.1}$  for the formation of the gas from its elements. Recently, as an example of the use of approximation methods,<sup>6</sup> I computed the rotational-vibrational contribution to F/T for 1500°K, and the present paper gives the results of similar calculations of the free energy and heat content for the temperaturerange of greatest experimental interest.

The spectroscopic constants<sup>7</sup> are:  $\epsilon_V = 2037.0v_1$  $+52.0v_{1}^{2}+712.1v_{2}-2.9v_{2}^{2}+3364.2v_{3}-51.3v_{3}^{2}$  $+3.1l^2-0.2v_1v_2-15.1v_1v_3-19.6v_2v_3$ ;  $B_v = 1.47890$  $\times (1 - 0.00625v_1 - 0.00726v_3); D = -3.63 \times 10^{-6}.$ The rotational-vibrational interaction term for  $\nu_2$ has not been determined, but from Choi and Barker's work it is evidently small. The resulting  $(F^{\circ}-E_0^{\circ})/T$  and  $(H^{\circ}-E_0^{\circ})$  are listed in Table I;<sup>8</sup> the reader is referred to example 2 of reference 6, for details of the calculation.

There has been no recent determination of the heat of combustion of hydrogen cyanide; Thomsen<sup>9</sup> gives 158,600 cal. Von Wartenberg and Schutza<sup>10</sup> have recently pointed out in connection with their measurement of the heat of combustion of cyanogen, that about three and a half percent of the nitrogen is converted to nitric oxide; if a correction be made for this, Thomsen's value for cyanogen is raised by 1500 cal. to 261,100 cal., in excellent agreement with their result 261,300 cal. Since Thomsen carried out his

TABLE I.  $K_1 = (P_{HCN})/(P_{H_2})^{\frac{1}{2}}(P_{N_2})^{\frac{1}{2}};$  $K_2 = (P_{HCN})(P_{HD})/(P_{DCN})(P_{H_2}).$ 

T⁰K	$-(F^{\circ}-E_{0}^{\circ})/T$ cal./deg.	$(H^{\circ} - E_0^{\circ})$ kcal.	$-\log K_1$	K2
250	39.537	1.807		0.65
298.1	40.824	2.210	20.91	0.84
300	40.871	2.225	20.76	0.84
350	42.029	2.666	17.54	1.01
400	43.060	3.127	15.12	1.15
500	44.846	4.099	11.74	1.36
600	46.371	5.125	9.49	1.52
700	47.712	6.199	7.89	1.63
800	48.913	7.314	6.68	1.71
900	50.005	8.469	5.75	1.77
1000	51.010	9.658	5.01	1.81
1200	52.811	12.12	3.90	1.87
1400	54.399	14.69	3.10	1.91
1600	55.823	17.34	2.51	1.93
1800	57.117	20.06	2.06	1.95
2000	58.306	22.83	1.69	1.96
$S^{\circ}_{298,1}$	48.238			

<sup>8</sup> The natural constants used were: hc/k = 1.4324, R = 1.9869, additive constant for the translational free energy = -7.267. None of the entries in Table I includes the nuclear-spin contribution.

<sup>&</sup>lt;sup>1</sup> Von Wartenberg, Zeits. f. anorg. allgem. Chemie 52, 299 (1907).

<sup>&</sup>lt;sup>2</sup> Lewis and Randall, Thermodynamics (1923), p. 584 et

<sup>Badger, J. Am. Chem. Soc. 46, 2166 (1924).
<sup>3</sup> Badger, J. Am. Chem. Soc. 46, 2166 (1924).
<sup>4</sup> Badger and Woo, J. Am. Chem. Soc. 54, 3523 (1932).
<sup>5</sup> Yost and Stone, J. Am. Chem. Soc. 55, 1889 (1933).
<sup>6</sup> Gordon, J. Chem. Phys. 3, 260 (1935).
<sup>7</sup> Choi and Barker, Phys. Rev. 42, 777 (1932); Herzberg and Spinks, Proc. Roy. Soc. A147, 434 (1934); Adel and Barker, Phys. Rev. 45, 277 (1934).</sup> 

Thomsen, Thermisch-chemische Untersuchungen, Vol. II, p. 387. <sup>10</sup> Von Wartenberg and Schütza, Zeits. f. physik. Chemie

A164, 386 (1933).

hydrogen cyanide and cyanogen combustions under comparable conditions, it is evident that his hydrogen cyanide value should be increased by roughly half the correction for cyanogen, giving a heat of combustion of 159,400 cal. per mole. Combining this with the heats of combusion of graphite<sup>11</sup> and hydrogen,<sup>12</sup> 94,240 and 68,313 cal., respectively,  $\Delta H_{298}$  for the reaction  $C_{\beta \text{graph.}} + \frac{1}{2}N_2 + \frac{1}{2}H_2 = \text{HCN}(g) \text{ is } 31,000 \text{ cal. From}$ this and the thermodynamic data for graphite,<sup>13</sup> hydrogen<sup>14</sup> and nitrogen,<sup>15</sup>  $\Delta F^{\circ}_{298.1}$  for the reaction is 28.510 cal. and  $\Delta E_0^{\circ}$  is 31,090 cal. The resulting log  $K_1 = \log (P_{\rm HCN}) / (P_{\rm H_*})^{\frac{1}{2}} (P_{\rm N_*})^{\frac{1}{2}}$  are listed in the fourth column of the table.

A repetition of Lewis and Randall's calculation<sup>2</sup> for the free energy of hydrogen cyanide but using spectroscopic free energies of formation for water, carbon monoxide, carbon dioxide and ammonia<sup>16</sup> leads to a standard free energy of formation at 298.1° of 28,520 cal., some 350 cal. less than the result they obtained by using the older free energy data, and in fortuitously close agreement with the value obtained in this paper. Badger<sup>3</sup> used the equilibrium  $NH_3+C=HCN+H_2$ , and found for 800°,  $K = 5.8 \times 10^{-6}$ , leading to a  $\Delta F^{\circ}_{800}$  of 19,200 cal.; from a slight extrapolation of Haber's data.<sup>17</sup> the standard free energy of formation of ammonia at this temperature is 9200 cal., so that the free energy of formation of hydrogen cyanide at 800° would be 28,400 cal.,

nearly 4000 cal. greater than the result from Table I, viz. 24,470 cal. The discrepancy is most puzzling, as Badger approached equilibrium from both sides, and his apparent experimental error is much less than 4000 cal. Von Wartenberg's averaged result for log  $K_1$  at 2000° (quoted by Lewis and Randall), log  $K_1 = -1.24$ , probably agrees as closely as can be expected with the value in the table.

Recently Bartunek and Barker<sup>18</sup> have determined the moment of inertia and fundamental frequencies of DCN,  $I = 22.92 \times 10^{-40}$ ;  $\omega_1 = 1897$ ,  $\omega_2 = 569.1, \omega_3 = 2630 \text{ cm}^{-1}$ . The second- and thirdorder terms in the expression for the energy levels are not known, but to a good approximation the difference between the rotationalvibrational contributions for HCN and DCN may be obtained by using the harmonic oscillator-rigid rotator approximation for both molecules, i.e., for HCN,  $I = 18.72 \times 10^{-40}$ ;  $\omega_1 = 2089$ ,  $\omega_2 = 712.1$ ,  $\omega_3 = 3313$  cm<sup>-1</sup>. The respective zeropoint energies for the two molecules (one-half unit of vibrational energy for the valence frequencies  $\nu_1$  and  $\nu_3$ , and one unit<sup>19</sup> for the degenerate deformation frequency  $\nu_2$ ) are 9718 and 8062 cal. per mole, respectively; thus from Johnston and Long's data<sup>20</sup> for HD and Giauque's for H<sub>2</sub>,  $\Delta E_0^{\circ}$  for the reaction H<sub>2</sub>+DCN=HD +HCN is 837 cal. The resulting  $K_2 = (P_{\text{HCN}})$  $\times (P_{\rm HD})/(P_{\rm DCN})(P_{\rm H_{*}})$  for the exchange reaction are listed in the last column of Table I.

While the calculation of  $S^{\circ}_{298,1}$  for HCN(g) is perfectly straightforward, the calculation of the entropy of HCN(l) is a matter of some uncertainty. Perry and Porter's measurements of the vapor pressure<sup>21</sup> can be represented by the equation

$$\log p_{mm} = 7.44558 - (1453.063/T) + 2.1052 \times 10^{-3}T - 3.716 \times 10^{-6}T^2 \quad (1)$$

<sup>19</sup> Dennison, Rev. Mod. Phys. 3, 280 (1931).

<sup>20</sup> Johnston and Long, J. Chem. Phys. 2, 389 (1934). There are obviously some serious misprints in their approximation equations which are intended to represent the entries in their Table IV between 1000° and 3000°. The following equations agree with their tabulated values for this range within  $\pm 0.001$  cal./deg. For HD,

 $-(F^{\circ} - E_{0}^{\circ})/T = -8.597 + 3.5R \ln T - R \ln [1 - \exp(-5199.1/T)] - 1.25 \times 10^{-5}T + 1.15 \times 10^{-8}T^{2}.$ For D<sub>2</sub>,

<sup>&</sup>lt;sup>11</sup> Roth and Naeser, Zeits. f. Elektrochem. 31, 461 (1925), as corrected by Clayton and Giauque, reference 13.

<sup>&</sup>lt;sup>12</sup> Rossini, Nat. Bur. Stand. J. Research **6**, 1 (1931). <sup>13</sup> Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932). Their table of  $(F^{\circ} - E_{0}^{\circ})/T$  and the calculations of this paper both are based on the assumption that there is no zero-point entropy for graphite. It has been pointed out by the author (J. Chem. Phys. 1, 308 (1933)) and by Kassel (J. Am. Chem. Soc. 56, 1838 (1934)) that there is some evidence from the experimental results for the producer gas equilibrium that there may be a zero-point entropy for graphite of 0.5 cal./deg. Had such a zero-point entropy been assumed, the standard free energy of formation at 298° would have been 28,660 cal., and all the entries in the fourth column of Table I would have been increased numerically by 0.11.

<sup>14</sup> Giauque, J. Am. Chem. Soc. 52, 4816 (1930).

<sup>&</sup>lt;sup>15</sup> Giauque and Clayton, J. Am. Chem. Soc. 55, 4875 (1933).

<sup>(193).</sup> <sup>16</sup> For water, -56,690 cal. (Gordon, J. Chem. Phys. 2, 65 (1934)); for CO, -33,000 cal. (Clayton and Giauque, reference 13); for CO<sub>2</sub>, -94,440 cal. (Kassel, J. Am. Chem. Soc. 56, 1838 (1934)); for NH<sub>3</sub>, -3935 cal. The value for ammonia was obtained from Haber's direct measurement of the heat of formation at room temperature (reference 17), -11,075 cal. at 298°, and the entropies of hydrogen, 31.23 (reference 14), of nitrogen, 45.79 (reference 15), and of am-monia, 45.79 (Kassel, Chem. Rev. 18, 277 (1936)).

<sup>&</sup>lt;sup>17</sup> Haber, Zeits. f. Elektrochem. 20, 597 (1914).

 $<sup>-(</sup>F^{\circ}-E_{0}^{\circ})/T = -7.541 + 3.5R \ln T - R \ln$ 

 $<sup>[1 - \</sup>exp(-4288.7/T)] + 1.00 \times 10^{-6}T + 1.10 \times 10^{-8}T^{2}.$ 

<sup>&</sup>lt;sup>21</sup> Perry and Porter, J. Am. Chem. Soc. 48, 299 (1926).

which fits their experimental results somewhat more closely than does the equation they employ. If hydrogen cyanide were a perfect gas, this would correspond to a heat of vaporization at 298.1°K of 6603 cal. Actually, as Usherwood<sup>22</sup> and Felsing and Drake<sup>23</sup> have shown, the gas deviates very markedly from ideality. Felsing and Drake find for P=1 atm. that the ratio (density of actual gas)/(density of ideal gas) is 1.0705 at 30°C, 1.0301 at 70°C and 1.0170 at 110°C, results which are in agreement with Usherwood's less precise measurements. Bredig and Teichmann<sup>24</sup> find that the critical pressure and temperature are 53.2 atm. and 456.7°K, respectively, which would correspond (assuming a Berthelot equation) to a density ratio of 1.025 at 30°C and 1 atm.; thus there must be considerable association. Even in the absence of complete P - V - Tdata, however, it is still possible to make a plausible estimate of the necessary corrections to the calculated thermodynamic quantities.

Assume that the actual gas consists of unassociated molecules obeying the Berthelot equation (partial pressure P') and of double molecules which behave ideally (partial pressure P''). Then if  $\alpha$  be the degree of association,

$$PV = (P' + P'')V = RT[1 - \alpha/2 + \beta(1 - \alpha)], \quad (2)$$

where  $\beta$  is the Berthelot term  $(9p_r/128t_r)$ . $(1-6/t_r^2)$ ,  $t_r = T/T_c$ ,  $p_r = P'/P_c$ , and  $T_c$  and  $P_c$ are the critical temperature and pressure, respectively. Eq. (2) can then be solved for P' at Felsing and Drake's three temperatures, giving P' = 0.953, 0.987 and 0.995 atm., respectively, with corresponding fugacities for the single molecules of 0.930, 0.970 and 0.983 atm. The fugacity of the double molecules is equal to their partial pressure, so that log  $K_a$  for the reaction (HCN)<sub>2</sub>=2 HCN is 1.263 at 303.2°, 1.850 at 343.2° and 2.278 at 383.2°K. When these values of log  $K_a$  are graphed against 1/T, they lie quite closely on a line whose slope corresponds to a heat of association,  $\Delta H_a$ , of 6780 cal. per mole (HCN)<sub>2</sub>. To a good enough approximation P'can be replaced by P in the definition of  $\beta$  in Eq. (2) and  $\alpha$  can be replaced by  $2P/(K_a+4P)$ , since even with these simplifying assumptions Eq. (2) (with the values of  $K_a$  obtained above) predicts densities which agree with Felsing and Drake's data within their limit of error. V can thus be written explicitly as a function of T, Pand  $K_a$ , and thus by means of the relation  $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ , an expression for the entropy of the nonideal saturated vapor can be obtained by conventional methods:

$$S_{\text{actual gas}} = S_{\text{ideal gas}} + (R/4). \ln (K_a + 4P)/K_a$$
$$-R\beta' - P.\Delta H_a/T(K_a + 4P)$$
$$+ (P/K_a).(R\beta' - \beta.\Delta H_a/T), \quad (3)$$

where  $R\beta'$  is the Berthelot correction to the entropy  $R(27p_r/32t_r^3)$  and  $\Delta H_a = 6780$  cal. Eq. (1) predicts for 298.1° a vapor pressure of 738.8 mm,<sup>25</sup> so that the entropy of the saturated vapor as an ideal gas is 48.294; from the value of  $K_a$  at 303.2° and the heat of association,  $K_a$  at 298.1° is 15.1, so that the entropy of the actual saturated vapor is 47.17 cal./deg. From Eq. (2), the density ratio at this temperature is 1.080 for the saturated vapor so that the heat of vaporization is 6112 cal. and the  $\Delta S$  of vaporization 20.50 cal./deg. Thus  $S^{\circ}_{298,1}$  for HCN(l) is 26.67 cal./deg.; had ideality of the gas been assumed throughout, the result would have been 26.14 cal./deg. One would expect, however, that the third law entropy of liquid hydrogen cyanide would be definitely less that 26.67 in view of the results that have been obtained for other unsymmetrical molecules such as nitric oxide,<sup>26</sup> carbon monoxide13 and nitrous oxide.27

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<sup>&</sup>lt;sup>22</sup> Usherwood, J. Chem. Soc. 121, 1604 (1922).

 <sup>&</sup>lt;sup>23</sup> Felsing and Drake, J. Am. Chem. Soc. 58, 1714 (1936).
 <sup>24</sup> Bredig and Teichmann, Zeits. f. Elektrochem. 31, 449 (1925).

<sup>&</sup>lt;sup>25</sup> The normal boiling point according to Eq. (1) is 298.86°K.

<sup>&</sup>lt;sup>26</sup> Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).

<sup>&</sup>lt;sup>27</sup> Blue and Giauque, J. Am. Chem. Soc. 57, 991 (1935).