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The Heat of Formation of CN and the Dissociation Energies of N_2 and C_2N_2

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The heat of formation of CN has been determined by using the 0,1 emission band head of CN. $C(gr) + {}^1/_2N_2(g) = CN(g)$; $\Delta H_0^0 = 94 \pm 6$ kcal. Using this value, one obtains $C_2N_2(g) = 2CN(g)$; $\Delta H_0^0 = 114 \pm 12$ kcal. = 4.95 e.v. These new data do not yet allow a unique determination of the D_0 of N_2 due to uncertainty in the D_0 value for CN.

The heats of dissociation of N_2, CN, CO and many other important molecules have not been unambiguously determined. The available data are principally the result of spectroscopic and electron impact experiments, where usually some assumption as to the state of the dissociation products has been made.

The heats of dissociation of several of these molecules can be related. In this work we are trying to obtain data to help complete the cycle involving N_2 and CN.

$$2C(gr) + N_2(g) = 2CN(g) \quad \Delta H = a \qquad \text{I}$$

$$2C(g) = 2C(gr) \quad \Delta H = -2\Delta H_S \qquad \text{II}$$

$$2CN(g) = 2C(g) + 2N(g) \quad \Delta H = 2D_{CN} \qquad \text{III}$$

Adding I + II + III

$$N_2(g) = 2N(g) \quad \Delta H = a - 2\Delta H_S + 2D_{CN} = D_{N_2} \qquad (1)$$

The heat of sublimation of graphite (ΔH_S) has been the subject of much controversy. Direct experimental determinations have been made by Brewer, Gilles and Jenkins[1a] and Marshall and Norton.[2] The dissociation limit for reaction III has been determined by Schmid, Gerö and Zemplén.[3] The heat of reaction I was determined in the present research by measuring the variation of the equilibrium constant with temperature.

Discussion of the Method.—The heat of formation of CN gas can be calculated from the well known van't Hoff equation for the variation of equilibrium constant with temperature. The equilibrium constants are derived from the nitrogen pressure, measured directly with a mercury manometer, and the CN pressure calculated from the intensity of the CN emission spectrum. The assumption was made that the intensity of a particular emission band head (here the 0, 1 band) is proportional to the concentration of CN molecules in that particular excited state. This means we are assuming that the transition probability is independent of temperature and concentration. The CN pressures are computed from the concentrations obtained by using the ideal gas law.

Experimental.—The CN was produced by resistance heating of a graphite tube in an atmosphere of nitrogen in a King type furnace. This furnace had been constructed by Brewer, Gilles and Jenkins[1a] for their C_2 work. The graphite tube (National Carbon Co. C-18) was 12 inches long, and about 0.75 inch in diameter with a 0.5 inch hole. Its wall thickness varied in such a way that there was a uniform temperature zone for about 6 inches in the center, with the ends about 10° higher. After two runs the end zones were about 50° higher than the center.

In the first experiments, the optical train consisted of the furnace, a diaphragm with a $^1/_{16}$ inch hole, a moving holder for wire screens, and the Hilger glass prism spectrograph. Later the screens were replaced by filters consisting of glass plates on which were deposited metal films of chromel A of varying densities. These filters were made and calibrated for us by Dr. Harold Weaver at Lick Observatory. A second diaphragm immediately preceding the filters decreased the background caused by scattered light. We recalibrated the filters with a photomultiplier tube with the same arrangement of diaphragms.

Furnace temperatures were observed with a Leeds and Northrup pyrometer, previously calibrated by the National Bureau of Standards. The pyrometer telescope was clamped rigidly in place to ensure that the lens was filled with light.

All spectrograms were taken with Eastman Kodak IIa-O plates.

Starting with a new tube it was first degassed in vacuum by heating to about 2600° before it was used in an experiment. A run was made as follows: the tube was evacuated and subsequently heated in a quarter atmosphere of N_2. Five-minute exposures were taken at 50° intervals between 2200° and 2600°. The nitrogen pressure was read before and after each exposure. The temperatures of the uniform temperature region were read at the beginning and end and during each exposure. For each exposure at least one reading was made of the hotter end region to get an idea of the temperature gradient involved. At high temperatures the intensities were cut down with the filters or screens. Then a set of calibration marks was put on the same plate by running the tungsten bulb at constant current from two storage batteries and cutting down the intensity of the beam with filters ranging from about 10 to 100% transmission. These calibration marks were put on after cooling the furnace and removing the window facing the optical pyrometer, so that the optical system traversed by the beam of light would be the same as that traversed by the CN beam. The plate was then developed for five minutes with D-19 developer. It was brushed with a cotton wad during development so as to reduce the Eberhard effect. The densities of the CN spectra and calibration marks were traced with a Zeiss recording microphotometer.

To use this procedure for a heat measurement one must ascertain that one has equilibrium. To check for equilibrium, two exposures were taken at the same temperature, but changing the nitrogen pressure a factor of 5 (0.2 to 1 atm.). The same K_p was obtained within experimental error.

The linear dispersion of the apparatus is about 30 Å./mm. around 4200 Å. A line due to an impurity which would fall within several ångstroms of the band head could not be distinguished from the band head in an experiment. Thus the intensity we would measure would not be only that due to CN, but also that due to the impurity. Using Moore's multiplet tables[4] the positions of all lines of observed impurities were determined. A check was made to be sure that no line due to an impurity would fall on the band head chosen. The 0–0 band head of CN at λ 3883 has a line due to TiI on it and cannot be used for the heat determination. The 0–1 band head at λ4216 was found to be free from impurities and was used in the heat determination.

The King furnace should cause only thermal excitation at our high pressures and low voltages. Excitation due to electron collisions can occur at very low pressures where the electrons have a long mean free path, but should be of no importance under our conditions and we should have complete thermal equilibrium. However we wished to check this experimentally.

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[1] From the Ph.D. thesis of Lieselotte K. Templeton, January, 1950. This paper was presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City Meeting, September, 1949.

[1a] L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

[2] A. L. Marshall and F. J. Norton, THIS JOURNAL, **55**, 431 (1933); **72**, 2166 (1950).

[3] R. Schmid, L. Gerö and J. Zemplén, *Proc. Phys. Soc.*, **50**, 283 (1938).

[4] Charlotte E. Moore, "A Multiplet Table of Astrophysical Interest," Revised Edition, Contributions from the Princeton University Observatory, No. 20, 1945.

We compared the vibrational temperatures determined as described by Ornstein and Brinkman,[5] with that read with the pyrometer at two temperatures (2555°K. and 2633°K.). The vibrational temperatures agreed within 1% with those read with the optical pyrometer and corrected for the window absorption. This agreement is better than the experimental accuracy of the vibrational temperature determinations.

Since we have equilibrium and have no line due to an impurity nor any excitation due to electron collisions we can use the intensity of the 0, 1 band head to get the heat of formation of CN.

Computations.—As mentioned above, the intensity of the emission band was assumed to be proportional to the concentration of CN molecules, which is in turn proportional to P/T. By setting

$$\Delta H_{\mathrm{T}} = \Delta H_{2750} + \Delta C_{\mathrm{p}2750}\,(T - 2750) \qquad (2)$$

and integrating the van't Hoff isochore, one obtains

$$-R \ln kTI + R/2 \ln P_{\mathrm{N}_2} = -2720\,\frac{\Delta C_{\mathrm{p}2750}}{T} - \Delta C_{\mathrm{p}2750} \ln T + \Delta H_{2750}/T + M \qquad (3)$$

where k is a proportionality constant, I is the intensity of the band head, and M is a constant of integration. A plot of Σ, defined by the relation

$$\Sigma = -(R - \Delta C_{\mathrm{p}2750}) \ln T + R/2 \ln P_{\mathrm{N}_2} + 2750\,\frac{\Delta C_{\mathrm{p}2750}}{T} - R \ln I = \Delta H_{2750}/T + R \ln k + M \qquad (4)$$

against $1/T$ must be a straight line of slope ΔH_{2750}.

$$\Delta C_{\mathrm{p}} = C_{\mathrm{p}}(\mathrm{CN}) - {}^1\!/_2 C_{\mathrm{p}}(\mathrm{N}_2) - C_{\mathrm{p}}(\text{graphite}) = 4.97 - 4.41^{6} - 6.34^{6} = -5.78 \text{ cal./deg. mole} \qquad (5)$$

All these values are for 2750°K. $C_{\mathrm{p}}(\mathrm{CN})$ was taken as 2.5 R since we made the assumption that CN was in a single "average" quantum state. The resolution of the apparatus was not good enough to use just one line of the band head. A single average state was assigned to the band head with rotational energy between the limits of energy of the lines contributing to the most intense part of the band head. A calculation of the line of maximum intensity at the extreme temperatures indicated that there was a change of only 2 in the rotational quantum number J. This energy difference is so small that our average state will have a heat capacity of 2.5 R.

The Σ plot for one run is shown in Fig. 1 and the data are listed in chronological order in Table I. The radius of the circles represents a 5° error in the temperature readings. This error is also of the same order of magnitude as the error in the intensity. The straight line in the Σ plot was computed by least squares.

TABLE I

T, °K.	P_{N_2}, atm.	I	Σ	$1/T$
2520	0.2855	5.4	−71.756	3.968 × 10^{-4}
2597	.2901	13.0	−73.533	3.851
2659	.2934	28.0	−75.086	3.761
2669	.2954	33.7	−75.455	3.747
2733	.2980	70.7	−76.963	3.659
2793	.3007	104.5	−77.775	3.580
2851	.3033	174.0	−78.823	3.508
2901	.3063	282.0	−79.814	3.447
2749	.3059	74.3	−77.048	3.638

Before giving the results of several runs made, let us examine the sources of error. It had been found that the wire screens do not give smooth calibration curves. There was always a scattering of points and for different plates different screens seemed to scatter. Diffraction of the screens was suspected, but had been believed to be compensated for by calibrating the screens in the experimental set up used.

To see if the scattering of points of the calibration curve is due to the screens or the rest of the procedure and also to see if they gave the right calibration curve the following experiment was devised. We took a tungsten bulb, used to calibrate pyrometers, and by varying the current through it a set of calibration marks was made. Then we ran the bulb at constant current (the current used as 100% intensity) and cut down the intensity with the wire screens and made another set of calibration marks on the same plate. Relative intensities corresponding to the different currents are, from Wien's law

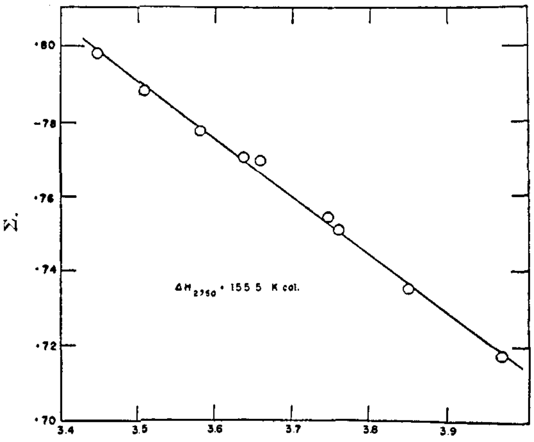

Fig. 1.—Σ plot for the formation of excited CN gas.

$$I = KE_{4216}e^{-c_2/T}$$

where E_{4216} = emissivity of tungsten at 4216A; $c_2 = hc/k$; λ = 4216 Å.; T = true temperature of the filament; and K normalizes the arbitrary scale. The emissivities used were taken from Forsythe and Adams.[7]

The calibration curve obtained by varying the current and calculating the intensities from Wien's law was very nice and smooth. The calibration curve obtained by cutting down the intensity with screens always showed scattering of the points. The two curves did not coincide, but were within experimental accuracy. It is obvious then that the scattering of points was due to the screens and not to the photometric procedure.

At first the filters also gave a scattering of points for the calibration curve. But after designing a holder for the filters so that the position of the filters is exactly reproducible the

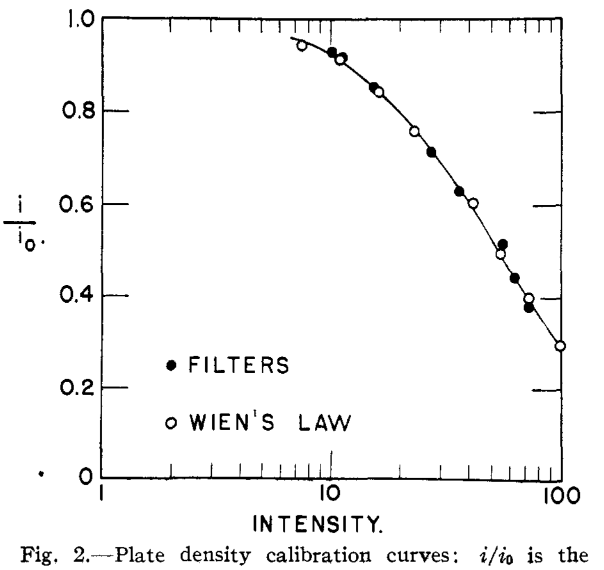

Fig. 2.—Plate density calibration curves: i/i_0 is the transmission of the calibration streak as measured with the microphotometer.

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(5) L. S. Ornstein and H. Brinkman, *Proc. Acad. Sci. Amsterdam*, **34**, 1, 33 (1931).

(6) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Series 3, June 30, 1948.

(7) W. Forsythe and E. Adams, *J. Opt. Soc.*, **35**, 108 (1945).

calibration curves obtained were nice and smooth. A curve obtained with the filters coincided with another made on the same plate by the variable-current technique described above (Fig. 2). The curve is drawn through the points calculated from Wien's law and it is seen that all the points except one obtained with the filters lie on that curve. That filter was not used in the subsequent experiments. The error for each intensity when using the filters is about 5%, which introduces an uncertainty of about 3 kcal. into the heat. This same error was also checked by retracing on the microphotometer one of the plates and the heat obtained differed by 3 kcal. To lessen the error due to intensity measurements the CN spectra were taken through appropriate filters so that each produced approximately the same density on the plate.

Checks were made on several plates to see if the sensitivity of the plate is the same in different parts of the plate. No difference in sensitivity was found outside the precision of the measurements.

To compensate for microphotometer drift and fogging of the plate, the "clear plate" reading was made just above and below each band head.

The "uniform" center region of the tube had about a 5 to 10° gradient. It is also difficult to read temperatures above 2500° to better than 5° accuracy. If we assume an error of 5° at each end of the slope and in opposite direction, it would introduce an error of 5 kcal. into the heat.

The next question is, does the temperature gradient at the end of the uniform temperature zone introduce an error? Data for two runs made with the filters are given below.

ΔH_{2750}, kcal.	Temp. gradient
160	35–50
161	10–30

It is clear from the above that the temperature gradient is not a source of error. The reproducibility of the furnace was checked in each run. After taking a series of exposures in which the temperature was gradually increased, one or two exposures were made at some of the lower temperatures. The points obtained this way fell right in line with the other points.

Thus the total probable error is ±6 kcal. for the filters and about ±8 kcal. for the wire screens.

The ΔH_{2750} for two runs made with the wire screens and computed by least squares is 156 ± 8 and 169 ± 8 kcal. The results obtained with filters are given above. Since the filters are more nearly reproducible, we take as our best value the average of the two filter results.

The C-18 graphite used in all these runs contained small amounts of V and Ti as impurities. In addition to choosing a CN head that did not lie near any impurity lines one run was made with the filters and National Carbon Co. best grade spectroscopic graphite which contained no V or Ti. The ΔH_{2750} was 153 ± 7 kcal. The uncertainty here is greater than for the other filter runs, because the temperature range used was smaller. Also the spectroscopic graphite has a lower preparation temperature and contains tars which deposited during the run on the window, which would tend to give lower intensities than the true intensities at the higher temperatures and thus would lower the ΔH. However, the results confirm that impurity lines are not affecting the C-18 runs.

Results.—The ΔH obtained experimentally is for the reaction

$$\mathrm{C(gr)} + {}^1/_2\mathrm{N_2(g)} = \mathrm{CN^*(excited\ state)\ at\ 2750\,°K.}$$

$$\Delta H^*_{2750} = 160 \pm 6\ \text{kcal.}$$

To get the ΔH for the above reaction with CN gas in the ground state, the electronic, vibrational and rotational excitation have to be subtracted from the experimental ΔH. The electronic and vibrational excitation is 25,797.85 cm.$^{-1}$ which is 73.7 kcal. The rotational energy was obtained as previously mentioned by assigning a single "average" state to the CN with rotational energy between the limits of energy of the lines ($J = 16$ to $J = 26$) contributing to the most intense part of the band head. The rotational energy thus evaluated amounted to 2.8 kcal. $\Delta H^{\text{ground}}_{2750} = 160 - 73.7 - 2.8 = 83.5$ kcal.

To get the heat of formation of CN at 0°K. one has to subtract the heat content of the substances involved in the reaction. The $H^0_{2750} - H^0_0$ for C(gr) and 1/2 $\mathrm{N_2(g)}$ were taken from the National Bureau of Standards tables.[6] The heat content of CN ground state is merely the translational energy and is therefore 5/2 RT.

$$\Delta(H_{2750} - H^0_0) = -10.8\ \text{kcal.}$$

so

$$\Delta H^0_0 = 83.5 + 10.8 = 94.3 \pm 6\ \text{kcal.}$$

Long[8] calculated this ΔH^0_0 indirectly from three different reactions. He concluded that $\Delta H^0_0 = 92.5$ kcal. was the best value. Using the National Bureau of Standards data[6] for his reactions one obtains 94.2 kcal. Either value is certainly in excellent agreement with our experimental determination.

Application.—As mentioned in the introduction one can use the heat of formation of CN to get the dissociation energy of $\mathrm{N_2}$. A multitude of values ranging from 5 ev. to 12 ev. have been proposed by different investigators for the dissociation energy of $\mathrm{N_2}$.

Kaplan[9] found that predissociation occurs in the $\mathrm{c^3\Pi_u}$ level of $\mathrm{N_2}$. He suggested $D_{\mathrm{N_2}} = 9.1$ e.v. from his observations. Büttenbender and Herzberg[10] showed that this predissociation occurs at 12.145 e.v. Considering the 3 lowest lying levels of atomic nitrogen as possible products the predissociation limit in $\mathrm{c^3\Pi_u}$ leads to $D_{\mathrm{N_2}} = 12.145$, 9.76, 8.57 and 7.38 e.v. Other still lower values can be eliminated because they lie below the highest vibrational level of the ground state ($v = 26$ at 6.33 e.v.). The high value of $D_{\mathrm{N_2}} = 12.145$ e.v. can be eliminated, because another predissociation which produces just a weakening and modification of the band structure was observed by Kaplan. Van der Ziel[11] studied this predissociation in $\mathrm{B^3\Pi_g}$ in detail and found that it starts in around 9.84 e.v. This leaves then the following values for $D_{\mathrm{N_2}}$: 9.76, 8.57, and 7.38 e.v. Van der Ziel using one explanation of why predissociation occurs in $\mathrm{B^3\Pi_g}$ concludes that 7.38 e.v. is the most probable value. Gaydon[12] using an alternate explanation gets 9.76 e.v. Van der Ziel has accepted this new interpretation. Thus a great deal depends on the interpretation of the spectroscopic data and one is really still left with the three most probable values.

We may now see if it is possible to distinguish between these three values using our data on the heat of formation of CN. Now we can put actual values into equation (1). We had

$$(1)\quad \mathrm{N_2(g)} = 2\mathrm{N(g)} \qquad \Delta H = a - 2\Delta H_{\mathrm{S}} + 2D_{\mathrm{CN}} + D_{\mathrm{N}}$$

a is twice the heat of formation of CN or 2 × (94 ± 6) kcal. $\Delta H_{\mathrm{S}} = 170 \pm 0.2$ kcal.[1a] $D_{\mathrm{CN}} =$

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(8) L. H. Long, *Proc. Roy. Soc.* (*London*), *A* **198**, 62 (1949).

(9) J. Kaplan, *Phys. Rev.*, **37**, 1406 (1931).

(10) G. Büttenbender and G. Herzberg, *Ann. Phys. Lpz.*, **21**, 577 (1935).

(11) A. Van der Ziel, *Physica*, **1**, 353 (1934); A. Van der Ziel, *ibid.*, **4**, 373 (1937).

(12) A. Gaydon, *Nature*, **153**, 407 (1944); "Dissociation Energies," Chapman and Hall, London, 1947.

173 ± 2.8 kcal.[12a] So $D_{N_2} = 188 \pm 12 - 2 \times (170 \pm 0.2) + 2 \times (173 \pm 2.8) = 194 \pm 15$ kcal. We had the following three possible values for D_{N_2}: 9.76, 8.57 and 7.38 e.v. or 225, 197.6 and 170.1 kcal. Our value for the heat of formation of CN together with Schmidt, Gerö and Zemplén's[3] D_0 value for CN thus fixes $D_{N_2} = 8.57$ e.v. or 197.6 kcal.

Even if one does not accept the value used here for the heat of sublimation of graphite, one can obtain only $D_{N_2} = 8.57$ e.v. from the data. For example, if one assumes that the observed dissociation limit of CN of 173 kcal. corresponds not to unexcited dissociation products but to excited carbon atoms and likewise if one assumes that the heat of sublimation of graphite of 170 kcal. corresponds to sublimation to excited carbon atoms with a lower heat of sublimation to carbon atoms in the ground ^{3}P state, then both D_{CN} and ΔH_S will be changed by the same amount assuming the same state of carbon. Thus the calculation of D_{N_2} is unaffected. If one assumes different excited states of carbon for the two quantities or if one assumes that the $^2\Pi$ state of CN leads to excited nitrogen atoms, one cannot obtain any check between the heat of formation of CN determined here and any of the possible heats of dissociation of N_2. For example there is a possibility[3] that there is predissociation in the $B^2\Sigma^+$ state of CN which gives rise to product atoms $C(^1D) + N(^4S)$ where the C atom is in the first excited state. This would give $D_{CN} = 6.24$ e.v. or 144 kcal. Then: $D_{N_2} = 188 - 340 + 2 \times 144 = 136 \pm 15$ kcal. We see that this is too low a value, since the lowest D_{N_2} possible is 7.38 e.v. or 170 kcal. If one accepts $D_{CN} = 173$ kcal., but takes ΔH_S as 141 kcal., the next value below 170 kcal. allowed by the CO predissociation data,[1a] then one calculates $D_{N_2} =$ 252 kcal. which is impossibly high. But if we take $\Delta H_S = 141$ kcal. and $D_{CN} = 144$ kcal., $D_{N_2} =$ 194 kcal. as obtained in the very first calculation. This is really not so surprising, since in both the ΔH_S and the D_{CN} values, the observed values have both been assumed to correspond to the first excited state of carbon and therefore the difference between the two quantities is the same as when one assumes no excitation for either quantity. Thus it is seen that to determine the heat of dissociation of N_2 from these data, it is immaterial whether the ΔH_S is taken as 170 or 141 kcal. and whether D_{CN} is taken as 173 or 144 kcal.

Another application for the heat of formation of CN is to use it to obtain the dissociation energy of C_2N_2.

$$\begin{array}{ll}
2C(gr) + N_2(g) = 2CN(g) & \Delta H_0^0 = 188 \pm 12 \text{ kcal.} \\
C_2N_2(g) = 2C(gr) + N_2(g) & \Delta H_0^0 = -73.6 \text{ kcal.}^6 \\
\hline
C_2N_2(g) = 2CN(g) & \Delta H_0^0 = 114 \pm 12 \text{ kcal.}
\end{array}$$

White[13] measured directly the heat of dissociation of C_2N_2 into 2CN and got 146 kcal. He estimated the concentration of CN radical present by using the absorption bands of CN. His heat of dissociation of 146 kcal. gives a lower CN pressure than our heat of 114 kcal. White assumed that C_2N_2 was in equilibrium with CN. However, he noticed that the CN was very short lived. One can think of two ways in which the CN can disappear rapidly: the CN can either dissociate, for example into C(gr) and N_2(g), or it can polymerize together with C_2N_2. If the reaction $C_2N_2 = 2CN$ were followed by a rapid step in which the CN was used up as fast as it was formed, then the P_{CN} that White measured would be much smaller than the equilibrium pressure of CN.

Other data from the literature which bear on the values determined here have been reviewed in detail by Gaydon.[12] They are on the whole consistent with the values obtained here.

We have tried to evaluate all important sources of error in our determination and we believe the uncertainty of ±15 kcal. in the value of D_{N_2} obtained from our results is the greatest absolute error that is likely. If we can accept the uncertainty of ±2.8 kcal. given by Schmid, Gerö and Zemplén[3] for their determination of the convergence limit of CN, then the D_0 of N_2 must be 197.6 kcal. Schmid, Gerö and Zemplén determined the spacing of all the vibrational levels of the $A^2\Pi$ state of CN up to the $v = 20$ level at 42,000 cm.$^{-1}$ above the ground state. They also assigned $v = 26$ and $v = 29$ to two higher levels at 48,000 cm.$^{-1}$ and 52,000 cm.$^{-1}$ by making the reasonable assumption that the regular behavior of the first twenty vibrational levels would continue. Also on this basis they extrapolated to a convergence for $v = 47$ at 60,500 ± 1,000 cm.$^{-1}$. Although their procedure appears reasonable, it is conceivable as pointed out by Herzberg,[14] that the regular decrease in vibrational energy spacing with vibrational quantum number may change suddenly above $v = 20$ resulting in a different assignment of vibrational quantum number for the $v = 26$ and $v = 29$ levels and a different convergence limit which could be either higher or lower than the one given. Thus until additional data are obtained to fix vibrational levels above $v = 20$ for CN, the possibility suggested by Herzberg introduces enough uncertainty concerning the convergence limit given by Schmid, Gerö and Zemplén that it still does not appear possible to definitely fix beyond controversy the D_0 value of N_2.

Acknowledgment.—We are very grateful to Dr. Harold Weaver of the Lick Observatory who greatly expedited this work by furnishing us with the metal film filters.

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(12a) Schmid, Gerö and Zemplén[3] determined the dissociation limit of $A^2\Pi$ of CN and got 173 kcal. Due to their theory of the ^{5}S level of carbon they give a D_{CN} of only 90 kcal. But the usually accepted interpretation is that $A^2\Pi$ leads to normal dissociation products $C(^3P)$ and $N(^4S)$. See Herzberg's diagram in his book "Molecular Spectra and Molecular Structure: Diatomic Molecules." Therefore $D_{CN} = 173$ kcal. if their extrapolation to convergence is correct.

(13) J. White, *J. Chem. Phys.*, **8**, 459 (1940).

(14) G. Herzberg, private communication, 1950.