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THE HEAT OF FORMATION OF CN, N_2, AND NO

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November 30, 1949

Berkeley, California

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Introduction

The heats of dissociation of N_2, CN, CO and many other important molecules have not been unambiguously determined. The two main methods used to measure the heat of dissociation were spectroscopic and electron impact.

In the spectroscopic method, the energy levels of the molecule are determined and from this knowledge the dissociation limit is obtained. The dissociation limit is the energy required to take a molecule from the lowest possible energy state (ground electronic, vibrational and rotational) of the molecule to the condition in which the atoms can just be removed to an infinite distance apart. The resulting atoms are either in the ground state or in an excited state. The dissociation limit is equal to the dissociation energy, if the resulting atoms are normal. If the resulting atoms are excited, the energy of excitation of the atoms has to be subtracted from the dissociation limit to yield the dissociation energy. Usually the state of the products of the dissociation are not known. There are usually quite a few possible excited states of the atoms which must be considered.

In the electron impact method one usually measures the appearance of the ion. Taking nitrogen as an example:

$$N_2(g) = N^+(g) + N(g) + e^-$$ This is the appearance potential.

$$e^- + N^+(g) = N(g)$$ Then knowing the ionization of the atom,

Adding $$N_2(g) = 2N(g)$$ and adding the two equations one gets the dissociation energy,

if the atoms obtained from electron impact are not excited electronically or kinetically. So it is seen that here, as in the spectroscopic method some assumption as to the state of excitation of the dissociation

products has to be made. Thus we see how it is possible to get several values for the heat of dissociation.

The heats of dissociation of several of the above discussed molecules can be related. If sufficient data can be obtained, the relationship between the data for the various molecules will allow all to be resolved.

We are endeavoring to obtain data to help complete the cycle involving N_2 and CN.

I	$2C(gr) + N_2(g) = 2CN(g)$	$\Delta H = a$
II	$2C(g) = 2C(gr)$	$\Delta H = -2\Delta H_S$
III	$2CN(g) = 2C(g) + 2N(g)$	$\Delta H = 2D_{CN}$

Adding I + II + III $N_2(g) = 2N(g)$ $\Delta H = a - 2\Delta H_S + 2D_{CN} = D_{N_2}$

This gives us a relationship between D_{CN} and D_{N_2}. ΔH_S is the heat of sublimation of graphite which has been determined by Brewer, Gilles and Jenkins.(1) Reaction III is the dissociation of CN(g) into its gaseous atoms. The dissociation limit for this reaction has been determined by Schmid, Gerö and Zemplén.(2) The ΔH of reaction I was determined in the present research by measuring the variation of the equilibrium constant with temperature.

Discussion of the Method

From well known thermodynamics, it can be shown that:

$$\frac{R\, d\ln K_p}{d\left(\frac{1}{T}\right)} = -\Delta H_T \qquad \text{where } K_p = \frac{P_{CN}}{P^{\frac{1}{2}}_{N_2}}$$

So if $\ln K_p$ is plotted against $\frac{1}{T}$ the slope of the curve at each value of

(1) L. Brewer, P. Gilles and F. Jenkins, J. Chem. Phys. 16 797 (1948)

(2) R. Schmid, L. Gerö and J. Zemplén, Proc. Phys. Soc. 50 283 (1938)

T determines ΔH at that temperature. The N_2 pressure was measured with a mercury manometer. The CN emission spectrum was used to evaluate the CN pressure. 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; in short we are assuming that a certain fixed fraction is taking part in that transition. If the transition probability depends on concentration one would expect a broadening of the band at high temperatures. This was not the case even when the band head width was magnified 10 times in the microphotometer tracings. Another experiment was performed in which the nitrogen pressure was varied a factor of 5, still the width 10 times magnified was the same. The CN pressures are computed from the concentrations obtained by using the ideal gas law.

Experimental

The CN was produced in a King type furnace by resistance heating. The heating element was a graphite tube (National Carbon Co. C-18) 12 inches long and about 3/4 inch diameter. It was so machined, by trial and error, to give a uniform temperature zone in the middle of the tube for about 6 inches and slightly higher temperatures at the ends of the uniform temperature zone. We started out with about 10° higher but at the end of 2 runs we have about 50°. Diffusion was believed to be cut down by this temperature variation and also by the insertion of two small graphite baffles 1/2 inch in diameter, 1/2 inch in length at each end of the uniform temperature zone. The graphite is heat insulated by means of graphite cylinders which are electrically insulated from the copper end plates by mica washers and quartz rods. A vacuum line is attached to the furnace so that the tube can be evacuated and subsequently heated

in an atmosphere of nitrogen. The power is supplied by a 220 volt a.c. line. By means of step-down transformers and a powerstat the voltage could be so regulated as to yield steady furnace currents. Furnace currents used during a run varied ordinarily from 500 to 700 amps though the capacity is up to 1000 amps. The copper parts of the furnace were cooled with two water circuits of 3/8 inch tubing. The two optical quartz windows which were sealed in with dekhotinsky were kept cool with 1/4 inch copper tubing. For a more detailed description of the furnace and the electric circuit see Paul Gilles's thesis "The Vapor Pressure and Heat of Sublimation of Graphite", University of California, Summer 1947.

The original optical train was as follows: first the optical pyrometer, then the furnace, then a diaphragm with a 1/16 inch hole, then a holder for wire screens and finally the Hilger glass prism spectrograph. The purpose of the diaphragm was to cut down radiation from the walls of the graphite tube. The screens were used to cut down intensities. In the present research not only the furnace was clamped down on the table as Gilles had done, but also the telescopic part of the pyrometer and the spectrograph. The clamping of the telescopic part of the pyrometer was considered especially important by the author, because the cone of light from the gas inside the tube was extremely small (barely the area of the pyrometer lens) due to the baffles and only in this way could one be certain that the whole pyrometer lens was filled with light. The Leeds and Northrop pyrometer used had been previously calibrated by the Bureau of Standards. 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°C. 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 degree intervals between 2200°C and 2600°C. The N_2 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 wire screens. Then a set of calibration marks was put on the same plate by running the tungsten bulb at constant current from 2 storage batteries and cutting down the intensity of the beam with screens ranging from about 2% to 100% transmission. These calibration marks were only put on after cooling the furnace and removing the window facing the optical pyrometer. The window was removed and the bulb put in front of the open furnace, 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 5 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.

Before we are sure we can use this procedure for a heat measurement we must ascertain that we do have equilibrium. To check for equilibrium, two exposures were taken at the same temperature, but changing the nitrogen pressure a factor of 5 (.2 atm to 1 atm). The same K_p was obtained within experimental error.

The linear dispersion of the apparatus is about 30 $\frac{\text{Å}}{\text{mm}}$ around 4200Å. A line due to an impurity which would fall within several Angstroms 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. A check was made to make sure there is no line due to an impurity which would fall on the band head.

Taking an emission spectrum of CN every line in it was identified. The different lines belonging to an element were then assigned to the different multiplets to which they belonged. Thus it was found that the Ti line at λ 3882.9 was a missing line of a multiplet. Therefore the 0, 0 band head of CN at λ 3883 has also a line due to Ti on it and can not be used for the heat determination. The 0, 1 band head at λ 4216 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. However we wished to check this.

To be sure there was no electron impact though we checked it experimentally. We compared the vibrational temperature with that read with the pyrometer. The method used to determine the vibrational temperature was that described by Ornstein and Brinkman.[3]

If there is temperature equilibrium we have:

$$I = A \nu^4 p_{v'v''} e^{-\frac{E_{v'}}{kT}} \qquad (1)$$

I = intensity

A = constant

$E_{v'}$ = initial vibrational energy

ν = frequency

$P_{v'v''}$ = transition probability from initial vibrational state v' to v"

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

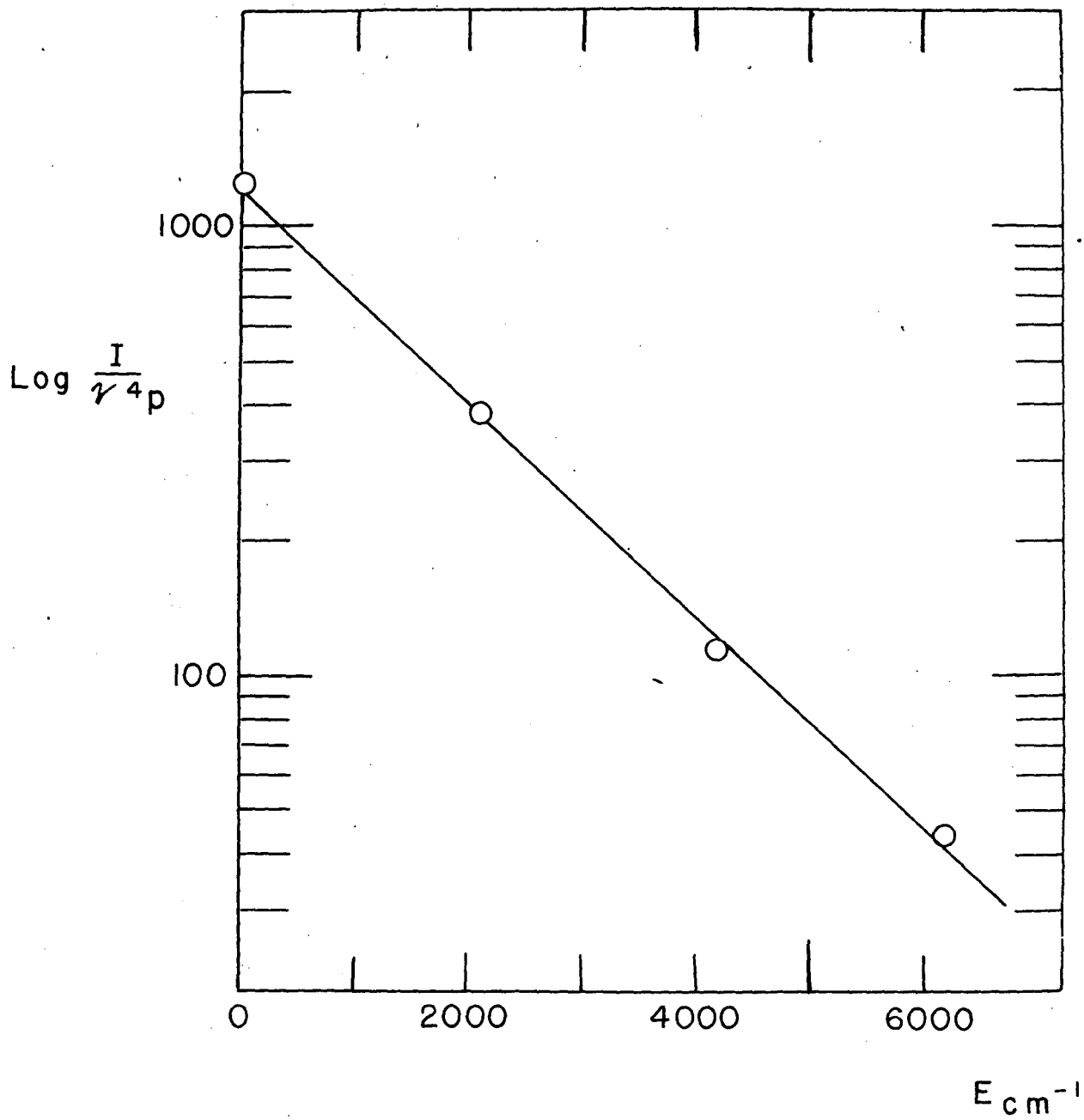

FIG I

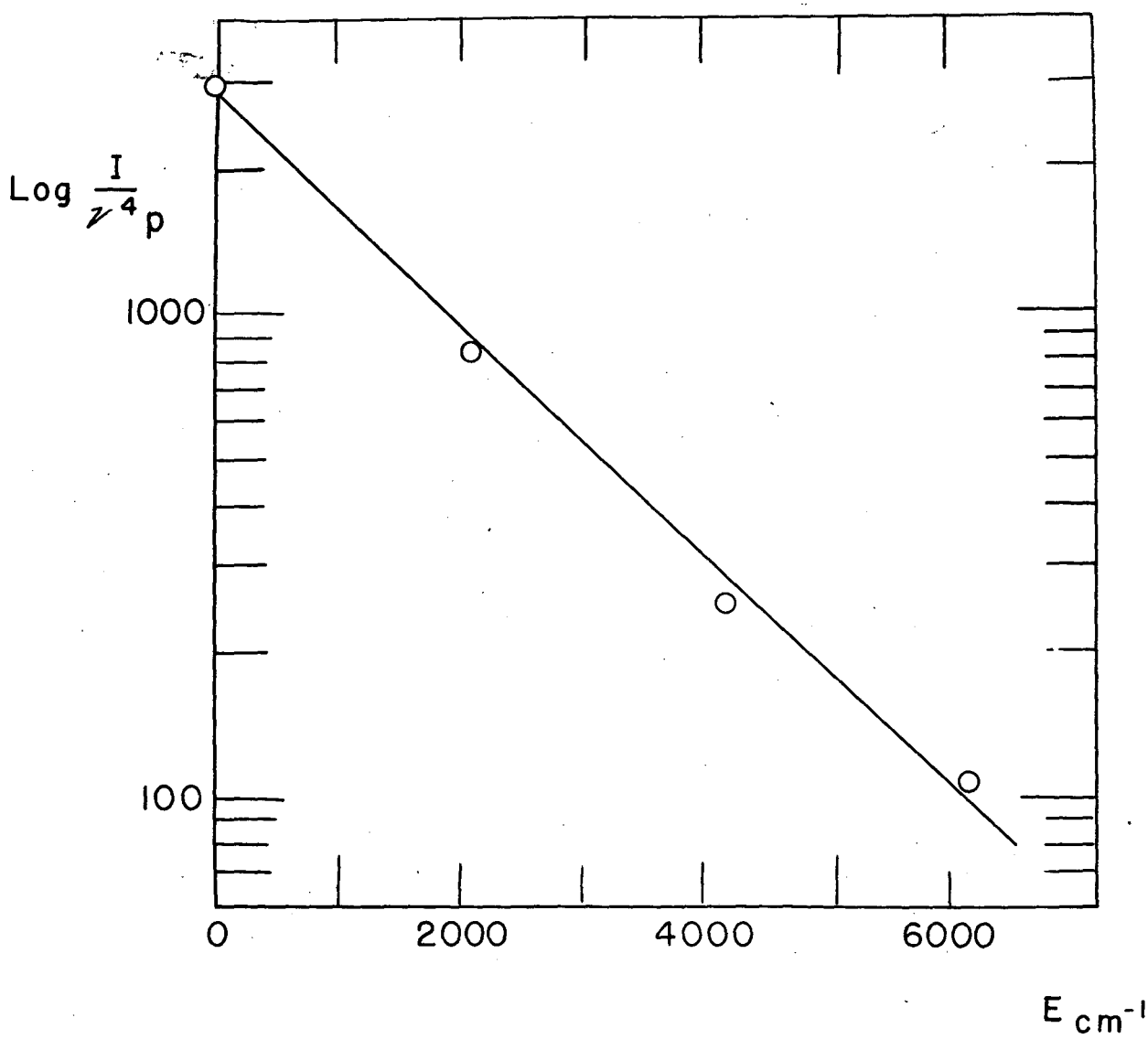

FIG. II

A straight line was obtained for the different sequences by plotting $\log \frac{I}{\nu^4}$ vs $E_{v'}$. This means that $\frac{I}{\nu^4}$ is proportional to $E_{v'}$, therefore the transition probabilities $p_{v'v''}$ in each sequence are proportional to $e^{-\alpha E_{v'}}$.

So now we can use equation (1) to obtain the temperature T. $\text{Log} \frac{I}{\nu^4 p_{v'v''}}$ was plotted against $E_{v'}$. See fig. I and II. This was done for 2 temperatures. The data for T = 2555°K are in table I, those for T = 2633°K in table II. These temperatures are those read with the optical pyrometer and corrected for the window absorption.

Table I

v'	v"	λ	$\nu^4 sec^{-1}$	I	p	$\frac{I}{\nu^4 p}$	Ev' cm^{-1}
0	1	4216A	25.6×10^{58}	17.5	.055	1243	0
1	2	4197.2	26.3	9.6	.095	384	2113.9 cm
2	3	4181.0	26.5	3.7	.12	116	4181.9
3	4	4167.8	26.9	1.8	.15	44.7	6189.8

T = 2555°K (pyrometer)

T_{vibr} = 2527°K from Fig. I

Note: the values of p were taken from Ornstein and Brinkman.[3]

Table II

v'	v"	I	$\frac{I}{\nu^4 p}$	$E_{v'}$
0	1	41.7	2962	0
1	2	20.7	828	2113.9
2	3	8	252	4181.9
3	4	4.3	107	6189.8

T = 2633°K (pyrometer)

T = 2660°K from slope of Fig. II

Note: λ, ν^4 and p are the same as in Table I.

We see that the vibrational temperatures agree with those read with the optical pyrometer to 1%, which is the experimental accuracy of these experiments.

Since we have equilibrium and do not have either a 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.

The intensities of the CN band head were computed by the following procedure. A calibration curve was obtained by plotting $\frac{i}{i_0}$ vs the transmission of the screens. The quantity $\frac{i}{i_0}$ is really the transmission of the calibration marks since i_0 is the distance from "clear plate" to "black" on the microphotometer tracing and i is the distance from the peak of the band head or the darkening produced by the calibration marks to "black" on the microphotometer tracings. Knowing $\frac{i}{i_0}$ for the CN band head the intensities can be read off the calibration curve. Graph 3 shows such a calibration curve for the wire screens. The screens were calibrated for transmission with a photomultiplier tube and using the same optical train as in the CN experiments.

To get a heat from the intensities certain substitutions were made in the van't Hoff isochore to straighten out the line by taking into account the variation of ΔH with temperature.

We start with the van't Hoff isochore:

$$\frac{R \, d\ln \frac{P_{CN}}{P_{N_2}}}{d\left(\frac{1}{T}\right)} = -\Delta H_T \qquad (2)$$

As mentioned above, the intensity was assumed to be proportional to the concentration of CN molecules which is in turn proportional to $\frac{P}{T}$.

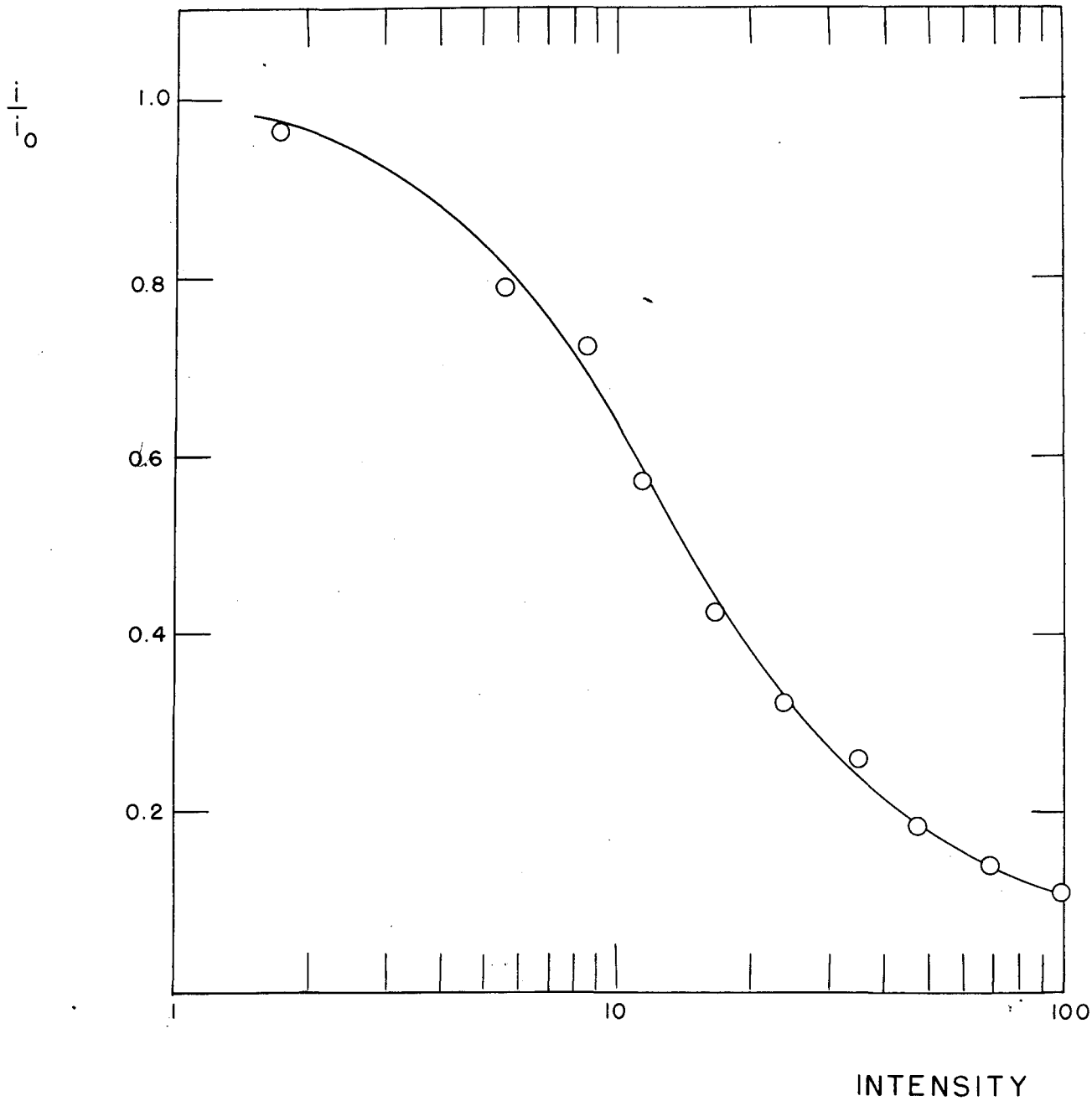

FIG. III

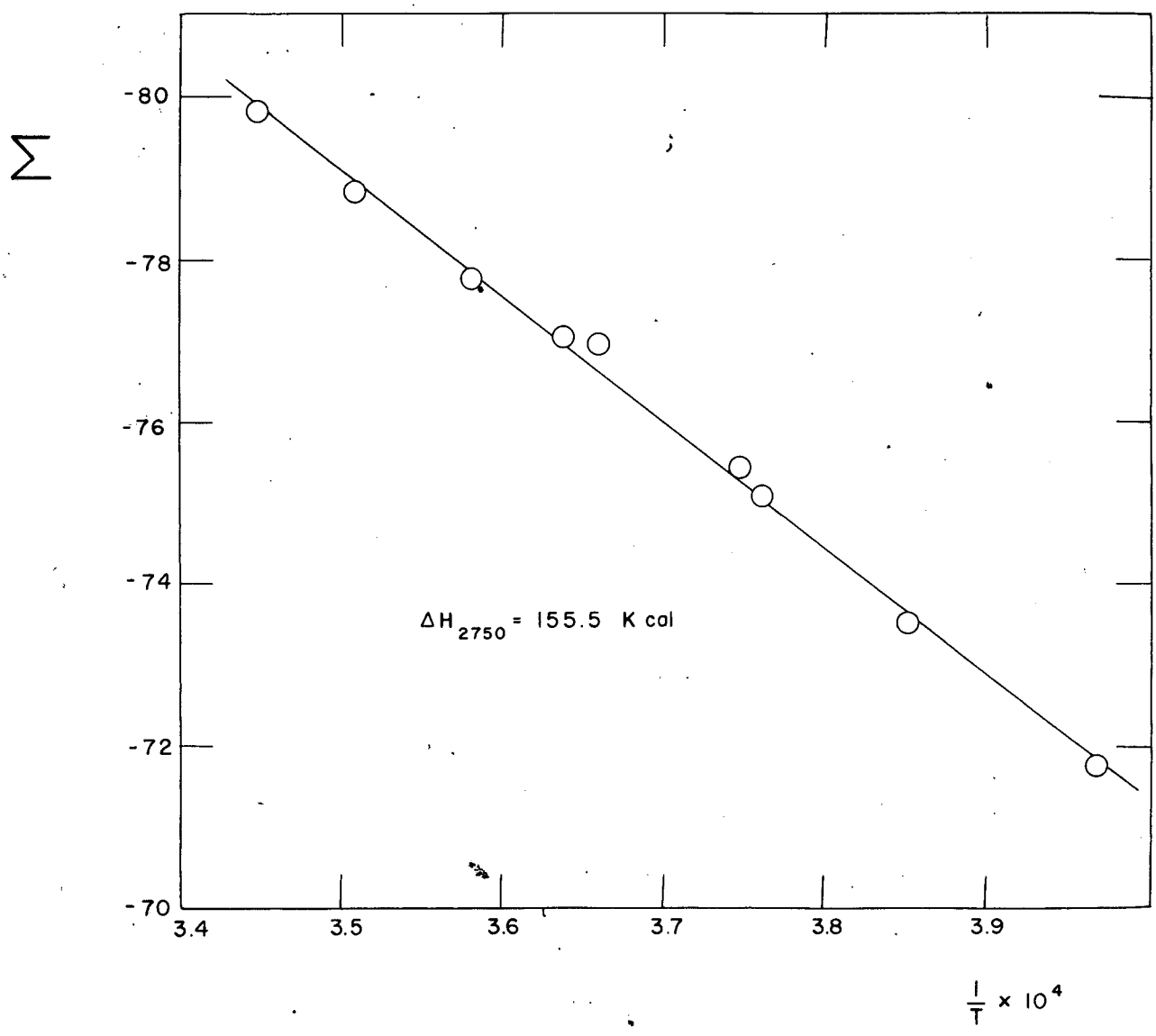

FIG. IV

Thus we get:

$$P_{CN} = kTI \tag{3}$$

where k is a proportionality constant and I = intensity of the band head. To account for the fact that ΔH is a function of temperature we made the following substitution:

$$\Delta H_T = \Delta H_{2750} + \Delta C_{p_{2750}} (T - 2750) \tag{4}$$

substituting equations (3) and (4) into equation (2) and integrating equation (2) we get

$$-R \ln TI + \frac{R}{2} \ln P_{N_2} = -2750 \frac{\Delta C_{p_{2750}}}{T} - \Delta C_{p_{2750}} \ln T$$

$$+ \frac{\Delta H_{2750}}{T} + R \ln k + M \tag{5}$$

M is a constant of Integration. For the purpose of plotting the data we used a quantity Σ which is obtained by rearranging equation (5).

$$\Sigma = -(R - \Delta C_{p_{2750}}) \ln T + \frac{R}{2} \ln P_{N_2} + 2750 \frac{\Delta C_{p_{2750}}}{T}$$

$$-R \ln I = \frac{\Delta H_{2750}}{T} + R \ln k + M$$

Plotting Σ against $\frac{1}{T}$ we should obtain a straight line the slope of which gives us ΔH_{2750}. ΔH_{2750} was chosen, because it is in the middle of the temperature range used. The $\Delta C_{p_{2750}}$ used was computed as follows:

$$\Delta C_p = C_{p_{CN}} - \frac{1}{2} C_{p_{N_2}} - C_{p_{graphite}} = 4.97 - 4.41 - 6.34 = -5.78$$

All these values are at 2750°K. The values for $C_{p_{N_2}}$ and $C_{p_{graphite}}$ were taken from "Selected Values of Chemical Thermodynamic Properties" National Bureau of Standards, Series 3, June 30, 1948. $C_{p_{CN}}$ was taken as $\frac{5}{2}$ 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. This energy difference is so small that our average state will have a heat capacity of 5/2 R.

The Σ plot for one run is shown in Fig. 4 and the data for it are in Table 3. The radius of the circles represents a 5° error in the temperature readings. The ΔH_{2750} for run No. 11 was 155.5 kcal. The ΔH_{2750} for run No. 12 gave 168.5 kcal. The straight line obtained for run No. 12 was just as straight as that for run No. 11. This discrepancy is due either to an error in temperature or in the intensity.

The uniform centre region actually had about a 5 degree gradient. It also is just about impossible to read temperatures above 2500°C to better than 5 degree accuracy. If we assume an error of 5 degrees at each end of the slope and in opposite direction, it would introduce an error of 2 kcal in the heat. So the temperature obviously does not introduce an appreciable error.

So we decided to investigate the intensity. It had been found as is also shown on Fig. 3 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 also 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

Table 3

Exposure	T°K	$-(R - \Delta C_p)\ln T$	P_{N_2} atm	$\frac{R}{2}\ln P_{N_2}$	$2750\Delta C_p$	I	$-R\ln I$	Σ	$\frac{1}{T}$
1	2520	-60.851	.2855	-1.246	-6.308	5.4	-3.351	-71.756	3.968×10^{-4}
2	2597	-61.085	.2901	-1.230	-6.121	13.0	-5.097	-73.533	3.851
3	2659	-61.268	.2934	-1.218	-5.978	28.0	-6.622	-75.086	3.761
4	2669	-61.298	.2954	-1.212	-5.955	33.7	-6.990	-75.455	3.747
5	2733	-61.481	.2980	-1.203	-5.816	70.7	-8.463	-76.963	3.659
6	2793	-61.651	.3007	-1.194	-5.691	104.5	-9.239	-77.775	3.580
7	2851	-61.810	.3033	-1.185	-5.575	174.0	-10.253	-78.823	3.508
8	2901	-61.946	.3063	-1.176	-5.479	282.0	-11.213	-79.814	3.447
9	2749	-61.527	.3059	-1.177	-5.782	74.3	-8.562	-77.048	3.638

intensity with the wire screens and made another set of calibration marks on the same plate. The intensities corresponding to the different currents were calculated using Wien's law

$$e_\lambda = \frac{E_{4216} c_1 e^{-\frac{c_2}{\lambda T}}}{\lambda^5}$$

E_{4216} = emissivity at 4216A

$c_1 = 2\pi hc^2$ = const.

$c_2 = \frac{hc}{k}$

λ = 4216A

T = true temperature

The emissivities used were taken from Forsythe and Adams.(5)

For the pyrometer bulb we know current vs. Brightness Temperature which is the temperature as read with a pyrometer. To convert Brightness Temperature to true temperatures the following formula was used:

$$\frac{1}{T} - \frac{1}{S_{665}} = \frac{\lambda \ln E_{665}}{c_2}$$

T and c_2 are the same as above.

E_{665} = emissivity at 6650A

S_{665} = the Brightness Temperature at 6650A

λ = 6650A which is the wave length at which the pyrometer reads temperatures.

In order to get sufficient darkening for the low intensities the current used for the highest intensity was 28.9 amps and Table 4 gives the intensities calculated for the different currents with Wien's Law. To supply this much current to the bulb, 3 sets of 3 batteries in series were put in parallel. Then in order to regulate the current sufficiently well 3 resistances were used in parallel one rated for 30 amps

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

Table 4

T_{true}	$T_{Brightness}$	Amps	Reading	Intensity
2560°K	2323°K	28.9	46.45	100%
2500	2274	27.85	44.75	72.4
2452	2233	26.9	43.25	55.20
2400	2192	26.03	41.8	41.50
2305	2109	24.3	39.00	22.9
2250	2068	23.5	37.6	16.2
2200	2026	22.60	36.00	11.00
2140	1976	21.75	34.75	7.49
2100	1943	20.95	33.4	5.53
2000	1860	19.4	31.0	2.47

one for 20 amps and the last one for 3 amps. The Ammeter used was a Weston D. C. Ammeter Model 45 which had previously been calibrated against a K 1 Leeds and Northrop potentiometer.

The calibration curve obtained by varying the current and calculating the intensities from Wien's Law was very nice and smooth as shown in Fig. 5. This is just one example of several runs made. 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 actually within experimental accuracy. It is obvious then that the scattering of points was due to the screens and not to the photometric procedure. Since the screens did not seem to be as reproducible as was desired it was decided to use filters to cut down intensities. These filters are pieces of glass on which are deposited metal films of chromel A of varying densities. These filters were made for us by Dr. Harold Weaver at Lick Observatory. 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 calibration curves obtained were nice and smooth. Now two sets of calibration marks were put on the same plate, one obtained by varying the current, the other obtained by keeping the current constant and cutting down the intensities with the filters. The two curves obtained coincide as shown in Fig. 6. 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.

Now some runs were made to determine the ΔH of CN, but using the filters instead of the screens. Quite a dark background was obtained. So another diaphragm with a 3/8 inch hole was centered on the filter

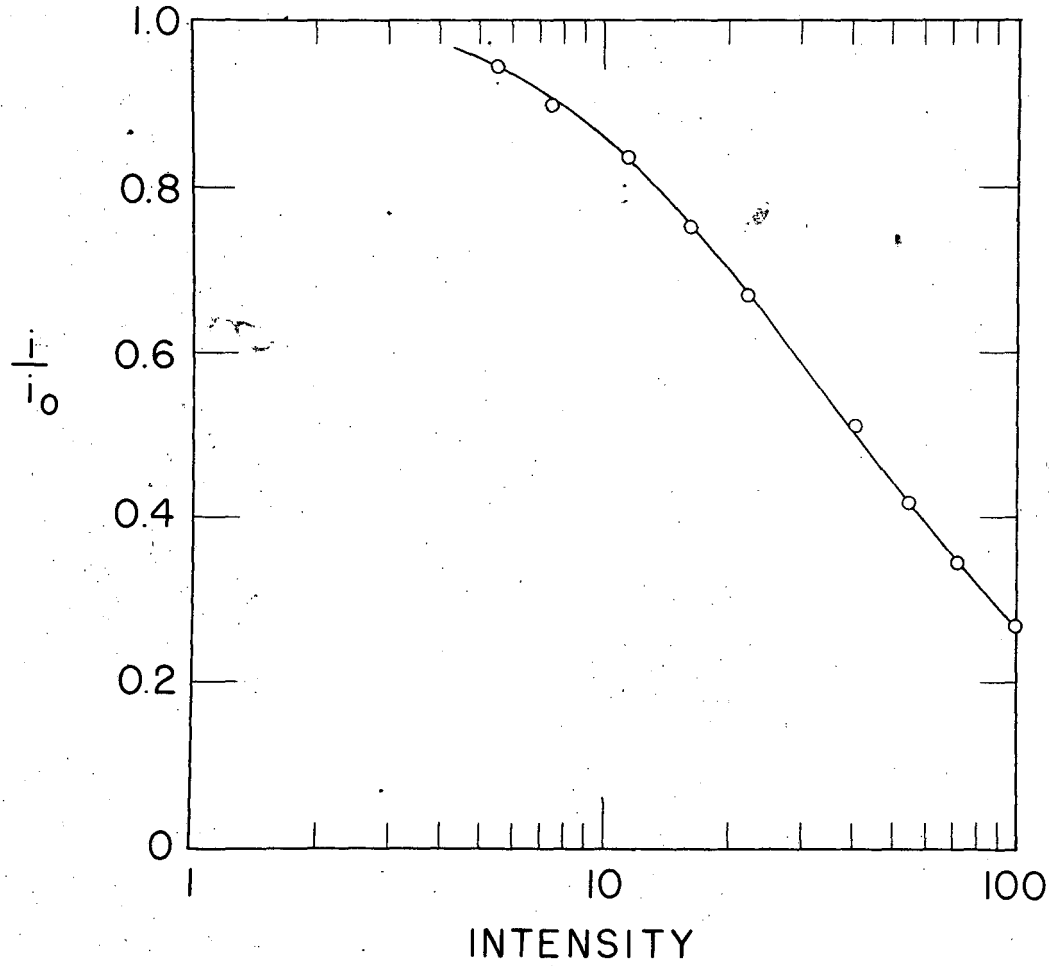

FIG. V

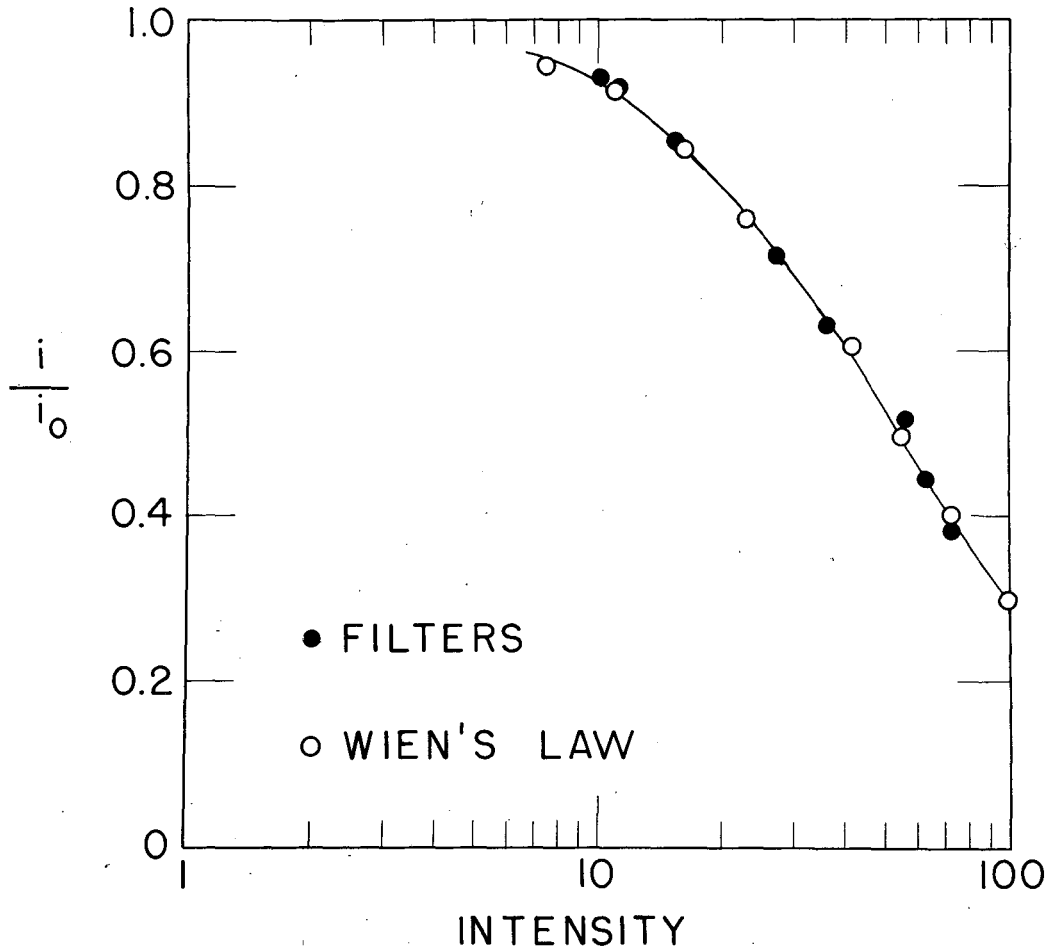

FIG. VI

holder. This way the background was practically eliminated, anyway it was about the same as with the screens. Several runs were made with the filters. The ΔH obtained by least squares were 160.5 kcal and 159.5 kcal. These results are certainly consistent. Let us examine, however, what the sources of error are.

As mentioned previously the error in temperature readings amounts to an error of 2 kcal in the heat.

The next question is, does the temperature gradient at the end of the uniform temperature zone introduce an error? In the following table are tabulated the different heats and temperature gradients.

ΔH_{2750} (with screens)	Temperature gradient
157 kcal	50 - 70°
155.5	10 - 30-
168.5	30 - 50
With filters	
159.5	35 - 50
160.5	10 - 30

It is clearly seen from the table that there is just a scattering of values for the different temperature gradients. Therefore the temperature gradient is not a source of error.

The error in the intensity is about 5% which introduces an error of about 2 kcal into the heat. To lessen the error due to intensity the CN spectra were taken so as to produce the same density on the plate.

The reproducibility of the microphotometer tracings is about 3 kcal.

Thus the total probable error is ± 5 kcal. The ΔH which we obtained

experimentally is for the following reaction:

$$C(gr) + \frac{1}{2} N_2(g) = CN \text{ (excited gas) at } 2750°K$$

$$\Delta H_{2750} = 160 \pm 5 \text{ kcal}$$

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.

So now we have for the reaction:

$$C(gr) + \frac{1}{2} N_2(g) = CN \text{ (g, ground)}$$

$$\Delta H_{2750}^{ground} = 160 - 73.7 - 2.8 = 83.5 \text{ kcal}$$

To get the heat of formation of CN at 0°K we have to subtract the heat content of the substances involved in the reaction. The $H_{2750}^{o} - H_{o}^{o}$ for C(gr) and $\frac{1}{2} N_2(g)$ were taken from "Selected Values of Chemical Thermodynamic Properties" National Bureau of Standards, June 30, 1948. The heat content of CN ground state is merely the translational energy and is therefore $\frac{5}{2}$ RT.

$$\Delta(H_{2750} - H_{o}^{o}) = -10.8 \text{ kcal}$$

$$\text{so } \Delta H_{o}^{o} = 83.5 + 10.8 = 94.3 \text{ kcal}$$

Thus for the reaction

$$C(gr) + \frac{1}{2} N_2(g) = CN(g) \qquad \Delta H_{o}^{o} = 94 \pm 5 \text{ kcal}$$

Application

As mentioned in the introduction we can use the heat of formation of CN to get the dissociation energy of N_2.

A multitude of values ranging from 5 e. v. to 12 e. v. have been proposed by different investigators for the dissociation energy of N_2.

Levels of the ground state of N_2 have been observed up to $v = 26$ at 6.33 e. v. We know therefore that we do not have any dissociation below this value. This gives us then a lower limit for the dissociation energy.

When the discrete term spectrum of one electronic state overlaps the continuous term spectrum of another electronic state there is the possibility of a radiationless transition from a discrete state into the continuous state lying at the same energy. If the continuous state corresponds to a dissociation, then the molecule dissociates after the radiationless transition. This process is called predissociation. Experimentally, one sensitive criterion for predissociation is to notice the breaking off of the band system in emission at a definite vibrational quantum number v'. The predissociation limit corresponds either exactly to the dissociation energy or it may lie higher. So one can get an upper limit for the dissociation energy.

Kaplan[6] found that no bands were observed above $v' = 4$ in the $c^3\Pi_u$ level of N_2.

Büttenbender and Herzberg[7] showed that this predissociation

(6) J. Kaplan, Phys. Rev. 37, 1406 (1931)

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

occurs at 12.145 e. v. Considering the 3 lowest lying levels of atomic nitrogen the predissociation limit in $c^3\Pi_u$ leads to D_{N_2} = 12.145 e. v., 9.76 e. v., 8.57 e. v., 7.38 e. v. Other still lower values can be eliminated because they lie below the highest vibrational level of the ground state. The high value of D_{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[8] studied this predissociation in $B^3\Pi_g$ in detail and found that it starts in around 9.84 e. v. This leaves then the following values for D_{N_2}: 9.76 e. v., 8.57 e. v. and 7.38 e. v. Van der Ziel using one explanation of why predissociation occurs in $B^3\Pi_g$ concludes that 7.38 e. v. is the most probable value. Gaydon[9] using an alternate explanation gets 9.76 e. v. Van der Ziel has accepted this new interpretation. So we see that a great deal depends on the interpretation of the spectroscopic data and we are really still left with the three most probable values.

Let's see if we can distinguish between these 3 values, using our data on the heat of formation of CN. Now we can put actual values into the equation shown on page 3. We had:

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

a is twice the heat of formation of CN and is 2 x 94 ± 10 kcal. ΔH_S = 170 ± .2 kcal.[1]

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(8) A. Van der Ziel, Physica, 1, 353 (1934)

A. Van der Ziel, Physica, 4, 373 (1937)

(9) A. Gaydon, Nature, London 153, 407 (1944)

$D_{CN} = 173 \pm 2.8$ kcal.*

So $D_{N_2} = 188 \pm 10 - 2 \times 170 \pm .2 + 2 \times 173 \pm 2.8 = 194 \pm 13$ kcal.

We had the following three possible values for D_{N_2}

9.76 e. v.	8.57 e. v.	7.38 e. v.
or 225 kcal	197.6 kcal	170.1 kcal

Our value for the heat of formation of CN then gives

$D_{N_2} = 8.57$ e. v. or 197.6 kcal.

There is a possibility[2] that there is predissociation in the $B^2\Sigma^+$ of CN which gives rise to product atoms $C(^1D) + N(^4S)$ where the C is in the first excited state. This would give

$D_{CN} = 6.24$ e. v. or 144 kcal. Then:

$D_{N_2} = 188 - 340 + 2 \times 144 = 136 \pm 13$ kcal.

We see that this is too low a value, since the highest D_{N_2} possible is 170 kcal. The heat of sublimation of graphite is quite a controversial subject. The experiments of Brewer, Gilles and Jenkins[1] on C_2 do definitely exclude $\Delta H_S = 125$ kcal. Even though they do show from their vapor pressure measurements on C that $\Delta H_S = 170$ kcal, if there were some mistake in the D_{CO} then one could possibly have $\Delta H_S = 141$ kcal. Taking $\Delta H_S = 141$ kcal and $D_{CN} = 173$ kcal, $D_{N_2} = 252$ kcal

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

which is too high. But if we take ΔH_S = 141 kcal and D_{CN} = 144 kcal, D_{N_2} = 194 ± 13 kcal. This is really not so surprising, since in both the graphite and the CN, the C just goes to the first excited state, therefore the difference between the two heats is the same. Therefore it is seen that to determine the heat of dissociation of N_2 it is immaterial whether the ΔH_S is 170 or 141 kcal and whether D_{CN} is 173 or 144 kcal.

We can use now the value we get for the heat of dissociation of N_2 to get the heat of dissociation of NO.

$NO(g) = \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$	$\Delta H = -21.6$ kcal[10]
$\frac{1}{2} O_2(g) = O(g)$	$\Delta H = 58.6$ [11],[12]
$\frac{1}{2} N_2(g) = N(g)$	$\Delta H = 98.8$ kcal
$NO(g) = N(g) + O(g)$	$\Delta H = 135.8$ kcal

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

$2C(gr) + N_2(g) = 2CN(g)$	$\Delta H_o^o = 188 \pm 10$ kcal
$C_2N_2(g) = 2C(gr) + N_2(g)$	$\Delta H_o^o = -73.6$ kcal[4]
$C_2N_2(g) = 2CN(g)$	$\Delta H_o^o = 114.4 \pm 10$ kcal

White[13] measured directly the heat of dissociation of C_2N_2 into 2CN and got 146 kcal. He estimated the concentration of CN

(10) Berthelot, Ann. Chim. Phys 6, 178 (1875)
" " " " 20, 255 (1880)

(11) R. Frerichs, Phys. Rev. 36, 398 (1930)

(12) G. Herzberg, Z. Phys. Chem. B, 10, 189 (1930)

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

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 assumes that C_2N_2 is in equilibrium with CN. He noticed that the CN is very short lived. One can think of two ways in which the CN disappears rapidly: the CN either dissociates, for example into C(gr) and $N_2(g)$, or it polymerizes with C_2N_2. If the $C_2N_2 \rightleftharpoons 2CN$ is followed by a rapid step in which the CN is used up as fast as it is being formed then the P_{CN} that White measured is not the equilibrium pressure of CN.

Conclusion

The heat of formation of CN has been determined by using the 0, 1 emission band head of CN.

$$C(gr) + \frac{1}{2} N_2(g) = CN(g) \qquad \Delta H_0^0 = 94 \pm 5 \text{ kcal}$$

Then using this value, the following dissociation energies were calculated.

$$N_2 = 2N(g) \qquad \Delta H_0^0 = 197 \text{ kcal}$$
$$D_{N_2} = 8.57 \text{ e. v.}$$

$$NO(g) = N(g) + O(g) \qquad \Delta H_0^0 = 135.8 \pm 5 \text{ kcal}$$
$$D_{NO} = 5.89 \text{ e. v.}$$

$$C_2N_2(g) = 2CN(g) \qquad \Delta H_0^0 = 114.4 \pm 10 \text{ kcal}$$
$$D_{C_2N_2} = 4.96 \text{ e. v.}$$

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