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The Thermal Dissociation of Cyanogen into Cyanide Radicals

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The thermal dissociation of cyanogen into cyanide radicals around 1200°C has been studied. Determining the variation of CN concentration with temperature by the intensity of absorption bands, the heat of dissociation 77 ± 4 kg cal. has been obtained. With this quantity the heat of dissociation of hydrogen cyanide into hydrogen

atoms and cyanide radicals is calculated as 94.5 ± 4 kg cal. By the use of existing thermochemical data these quantities are shown to be the most probable values for the energies of the C-C and C-H bonds, respectively. The heat of sublimation of carbon is calculated as 154 ± 3 kg cal.

THERE exists at present considerable difference of opinion as to the correct values for the energies of the carbon-carbon and carbon-hydrogen bonds,¹ the heat of sublimation of carbon^{2, 3} and the heat of dissociation of nitrogen.⁴ An experimental determination of the heat of dissociation of cyanogen into two cyanide radicals would make possible, if not an exact determination, at least a closer estimate of these magnitudes. There have, however, been no direct measurements of this dissociation energy. On the ground of a relation between electron affinity and heats of dissociation Lederle⁵ has calculated a value of 61 kg cal. Mooney and Reid⁶ have studied the photochemical dissociation of cyanogen and have indirectly obtained an upper limit for the heat of dissociation into two normal CN radicals.

Therefore, when it was found that cyanogen gas heated to 1000°C showed CN bands in absorption, it was decided to attempt a determination of the heat of thermal dissociation by a method originally used by Franck and Grotian

and others⁷ for the reaction $\text{Hg}_2 \rightarrow 2 \text{Hg}$, and by Bonhoeffer and Reichardt⁸ for the reaction $2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 4 \text{OH}$. This method consists essentially of taking the absorption spectra of cyanogen at various pressures and temperatures, matching absorption bands of equal intensities, assuming that this denotes equal pressures of CN, and calculating the heat of the reaction by means of the van't Hoff isochore.

EXPERIMENTAL

The cyanogen was prepared in an all glass apparatus by dropping a concentrated solution of potassium cyanide into 200 g of copper sulfate in 400 cc of water. The gas evolved passed through a calcium chloride tube and was collected in a trap cooled by a mixture of carbon dioxide snow and ether. It was found that the yield of cyanogen could be considerably improved by keeping the pressure in the apparatus down to about 20 mm of mercury by means of a water pump. Because the vapor pressure of cyanogen at -80°C is 8 mm it was not advisable to keep the pump running continuously. Therefore the system was evacuated at the beginning and then at ten minute intervals, in order to draw off the more volatile impurities (nitrogen and carbon dioxide) which slowly accumulated and built up the pressure. The potassium cyanide was added at a rate of about 2 cc per minute, and when the

¹ Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

² Vaughan and Kistiakowsky, Phys. Rev. **40**, 457 (1932).

³ Marshall and Norton, J. Am. Chem. Soc. **55**, 431 (1933).

⁴ Kaplan, Phys. Rev. **42**, 97 (1933). By what appears to be a typographical error Kaplan ascribes to Tate and Lozier (Phys. Rev. **39**, 254 (1932)) a corrected value of 9.0 volt-electrons. It is, however, the corrected value of Datta (Proc. Roy. Soc. (London) **A138**, 84 (1932) and Nature **129**, 870 (1932)). The value of Tate and Lozier (8.4 ± 0.5 v.e.) has been adversely criticized by Arnot (Nature **129**, 617 (1932)).

⁵ E. Lederle, Zeits. f. physik. Chemie **B17**, 362 (1932).

⁶ Mooney and Reid, Nature **128**, 271 (1931) and Proc. Roy. Soc. (Edinburgh) **52**, 152 (1932).

⁷ Franck and Grotian, Zeits. f. tech. Physik **3**, 194 (1922). Koernicke, Zeits. f. Physik **33**, 219 (1925). Kuhn and Freudenberg, Zeits. f. Physik **76**, 38 (1932).

⁸ Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

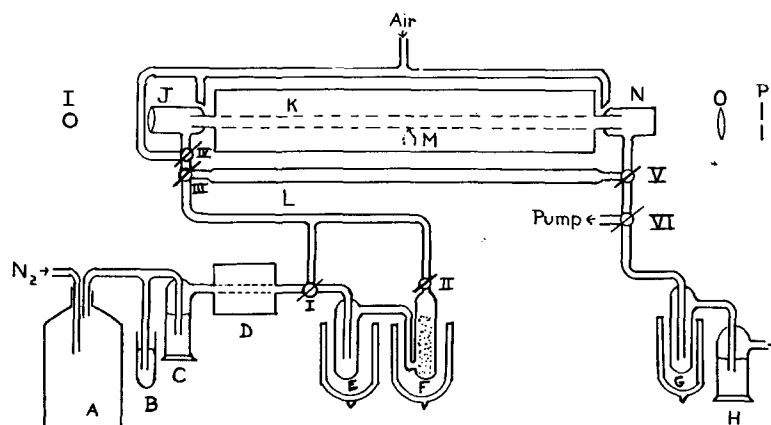


FIG. 1.

calculated amount (about 100 g) had been added the reaction vessel was heated in a water bath for fifteen minutes. When the preparation was made at atmospheric pressure the solution quickly turned black, indicating some reaction with the cyanogen, and the gas evolved contained mostly nitrogen and carbon dioxide. At reduced pressure the solution remained greenish and almost pure cyanogen was obtained. To remove the less volatile impurities such as water and hydrogen cyanide the cyanogen was twice distilled at -35°C and collected at -80°C .

Fig. 1 shows the experimental set-up. Since cyanogen slowly decomposes at the temperatures employed in the present work, it was necessary to use a flowing gas system. This was accomplished by adding to nitrogen known partial pressures of cyanogen and passing the mixture through the furnace at atmospheric pressure. Nitrogen from a tank entered a twenty liter bottle *A*, which acted as a barostat, passed through a wash bottle *C*, containing concentrated sulfuric acid, and then through a furnace *D*, which was packed with activated copper filings heated to 250°C , thus removing the little oxygen present in tank nitrogen. The purified gas then passed through the wash bottle *E*, which contained cyanogen at a temperature at which its vapor pressure was about 30 percent greater than that desired.⁹ The gases entered next the vessel *F*, filled with glass wool and maintained at a temperature that

gave the desired vapor pressure of cyanogen. Frequent observations showed that considerable amounts of cyanogen condensed in *F*, thus proving that saturation was obtained.

E and *F* were maintained at the desired temperatures by ether cooled by carbon dioxide snow contained in large Pyrex Dewar tubes. By hand regulation these baths could be kept constant ($\pm 0.05^{\circ}\text{C}$) for more than a half hour with gas flowing through the system. The temperature in *E* was read by a toluene thermometer, that in *F* by a triple copper constantan thermocouple and a Leeds and Northrup thermocouple potentiometer. This thermocouple was calibrated against the standard tables of Southard and Andrews¹⁰ at the freezing point of mercury and the sublimation point of carbon dioxide. The correction curve was a straight line that passed through the origin. The maximum correction necessary was 50 parts in 2500; at the freezing point of mercury the correction was 23 parts in 1450. According to the discussion of Southard and Andrews the assumption of linear correction would introduce no error, especially since the desired accuracy was only $\pm 0.05^{\circ}\text{C}$.

The gases then entered the furnace. The latter was made of a Sillimanite tube 2.54 cm by 152.6 cm, 132.6 cm of which was closely and evenly wound with chromel A ribbon, 0.05 ohm per foot resistance. The total resistance of the winding was two ohms. Alundum cement served to keep the windings separated and to hold the wire tightly against the wall of the tube. At the center

⁹ The vapor pressure of cyanogen as a function of temperature has been determined by Perry and Bardwell, *J. Am. Chem. Soc.* **47**, 2629 (1923).

¹⁰ Southard and Andrews, *J. Frank. Inst.* **207**, 323 (1929)

TABLE I.

Distance from center in cm	60	40	30	20	10	0	10	20	30	40	60
Temperature °C	1039	1098	1098	1093	1098	1098	1094	1095	1095	1076	1070
Temperature °C	1200	1235	1240	1236	1248	1246	1248	1242	1248	1240	1235

of the furnace a platinum-platinum-rhodium thermocouple was cemented onto the wall of the tube between two turns of the ribbon. The wired part of the tube was packed in Sil-o-cel bricks. To the 10 cm of the tube sticking out at each end were affixed short lengths of 32 mm Pyrex tubing, *J* and *N*, by means of porcelain cement made gas tight by coating it with de Khotinsky cement. The cement was kept cold by air blasts. To the ends of the glass tubes were affixed, also with de Khotinsky cement, windows, to *J* a quartz lens and to *N* a piece of optically plane quartz. For reasons that will be given below a satin walled quartz tubing of 3/4 inch outside diameter and the length of the furnace was used as a lining, so that the hot gases did not come in contact with the Sillimanite.

The thermocouple was calibrated to give directly the temperature inside the furnace by plotting its e.m.f. readings against the temperature of a movable carbon block, with a conical hole in it, as read by a Leeds and Northrup optical pyrometer with no windows in the way. This calibration was carried out over a range of 300° with an uncertainty of not more than $\pm 3^\circ$ at the extreme limits. The temperature gradient in the furnace could be obtained by moving the block back and forth. It was found that for a range of 60 cm in the center of the tube the temperature was constant ($\pm 3^\circ\text{C}$). Then it dropped off slowly until at the ends there was a sharp drop. Table I shows the temperature distribution in the furnace. To reach a temperature of 1250°C a current of about 22 amperes was necessary. It took about six hours to heat the furnace to a steady temperature but when equilibrium was reached the temperature would stay constant ($\pm 3^\circ\text{C}$) for long intervals of time.

By turning the three way stopcock III the mixture of nitrogen and cyanogen could be passed through the bypass *L* until it and the furnace were in the state desired. By turning I the furnace could be flushed with nitrogen and by turning IV it could be thoroughly cleansed of all

oxidizable matter by passing air. After flowing through the furnace (or *L*) the gases passed through the cold trap *G* and three wash bottles *H* containing potassium hydroxide solution.

Two electronic transitions from the normal state of cyanide radicals are known, one giving rise to bands in the red ($^2\Pi \rightarrow ^2\Sigma$), the other to bands in the near ultraviolet ($^2\Sigma^* \rightarrow ^2\Sigma$). Both represent dipole radiation and thus the ultraviolet bands, having higher frequency, may be expected to be more intense. This transition was therefore used in the present work. On the plates obtained only the O→O band at 3883Å was sufficiently intense. A tungsten lamp can be conveniently used to furnish the continuous background at this wave-length.

The light source *I*, a 500 watt G. E. tubular projection bulb, was placed at the focus of the lens *J* so that parallel light passed through the furnace, reducing reflection from the walls. The lens *O* focussed this beam on the slit *P* of a Hilger E-1 quartz spectrograph. An exposure of thirty seconds was necessary.

For the accurate matching of bands equal intensities of background were quite essential. The light source was very constant since it operated on a regulated 110 volt line. Therefore it was only necessary to make equal the times of exposure. For this purpose the snap of a camera shutter, adjusted for a time exposure, was attached to a piece of laminated iron which hung above the core of an electromagnet. The leads of the electromagnet were connected to the 110 volt line through a rotating commutator driven by a Telechron motor. The commutator was adjusted to give two current impulses thirty seconds apart. The first of these opened, the second closed the shutter.

To make more certain equality of background the bands to be compared were taken on the same plate, which insured equal developing and fixing. Therefore from fifteen to twenty exposures were taken on each plate, at two different temperatures and at pressures determined by preliminary

experiments to give approximately equivalent absorption, and the resulting bands were matched.

PROCEDURE AND RESULTS

It was originally intended to run the cyanogen through the Sillimanite tube. When this was done the CN bands were observed only in the first two runs. Thereafter four strong atomic lines and one diffuse band were obtained but the CN band was no longer on the plate. Using higher temperatures and higher pressures of cyanogen resulted in the formation of carbon in the furnace and its consequent blocking. The absorption lines appeared only when cyanogen was run through the furnace, not when blank runs were made with pure nitrogen. The furnace was cleaned (after oxidation with air) and a reddish brown powder was scraped off the walls. Upon analysis this proved to be an oxide of iron. The wave-lengths of the absorption lines were determined and they were identified as being due to copper (3274Å and 3248Å) and silver (3383Å and 3281Å). The weak band (3778Å) could not be identified. It was obvious that the hot cyanogen was reducing the metallic compounds present in the tube as impurities and that the resulting metals were catalyzing the reaction $C_2N_2 \rightarrow 2C + N_2$. Therefore the quartz tubing described above was introduced as a lining for the furnace. During the rest of the research no further trouble from this source was encountered.

It was found that pressures of cyanogen higher than 350 mm caused a deposit to form on the cold window. This deposit sublimed upon heating and was probably para-cyanogen. A copper diaphragm inside the glass tube in front of the window helped reduce this polymerization, but in order to avoid frequent removal of the window for cleaning it was found most convenient to work at lower pressures and higher temperatures. Since there were no stresses on the quartz tube, which was evenly supported along its entire length, prolonged heating at 1250°C did not result in any damage. The amount of carbon deposited in the furnace after the quartz tubing was introduced was negligible, and since it is known¹¹ that

cyanogen does not polymerize above 800° there was no interference from side reactions.

To determine the effect of the rate of flow through the furnace upon the intensity of the CN bands, nitrogen with a constant partial pressure of cyanogen was sent through the furnace at various speeds. When the linear rate of flow was less than 0.2 or greater than 4 cm per second the intensity of the band was diminished. Rates from 0.5 to 3 cm per second resulted in unchanging intensities. A velocity of 1 cm per second was taken as most convenient. By taking spectra at intervals of three, five, ten and fifteen minutes with the gas flowing at the rate of 1 cm per second it was demonstrated that the gas in the furnace reached a constant composition five minutes after the flow was started. However, to give a margin of safety, the shortest interval used was ten minutes.

For technical reasons the work was limited to temperatures and pressures at which the absorption by CN radicals is quite weak. The bands on the plates consisted actually of only the head of the *P* branch (see Fig. 2), the remainder being



FIG. 2a. Shows a typical absorption band, $T = 1250^\circ\text{C}$, $P(C_2N_2) = 100$ mm.



FIG. 2b. The microphotometric record of this band showing the fine structure.

¹¹ Troost and Hautefeuille, *Comptes Rendus* **66**, 795 (1868).

too faint to be used for comparison. This circumstance can introduce a serious error if the rotational energy of the quantum states that give rise to lines forming the head of the band is considerably higher than the mean energy. By means of the data given by Weizel¹² this energy was calculated and found to be slightly lower than the mean thermal rotational energy at 1400°–1500°K. Therefore the variation of the intensity of the band head can be taken as a measure of CN concentration.

Since the pressure of the cyanogen could be varied much more easily than the temperature of the furnace, on each plate the spectra were taken at only two temperatures, with from six to ten pressures corresponding to each. Then the bands taken at one temperature were compared with the others and those of equal intensity matched. At first the plates were run through a recording microphotometer, but it was soon found that the eye could distinguish variations to which the microphotometer was insensitive. This agreed with the experience of Bonhoeffer and Reichardt.⁸ Therefore the bands were matched entirely independently by three observers. There was unanimous agreement upon eight pairs. Values of ΔH calculated from several pairs concerning which there was disagreement were distributed equally on both sides of the values obtained from the other eight, showing that the pressure intervals had been too great.

By combining the equation for the equilibrium constant $K = P^2(\text{CN})/P(\text{C}_2\text{N}_2)$ with the van't Hoff isochore $d \ln k/dT = \Delta H/RT^2$ and assuming that $P(\text{CN}) \ll P(\text{C}_2\text{N}_2)$ and that ΔH is constant over the temperature range covered, values of ΔH are easily calculated from the matched bands. Table II gives the results.

To obtain the true heat of dissociation from the above, it is necessary to bring in a correction taking care of the gradually falling temperature at the ends of the furnace.⁸ In the present case the temperature was sufficiently constant throughout the major part of the furnace to make this correction negligible in comparison with other sources of error.

To reduce the observed ΔH to ΔH at 0°K it is necessary to calculate the specific heats of

TABLE II.

$T^{\circ}\text{C}$	P (mm)	ΔH	$T^{\circ}\text{C}$	P	ΔH
1124	337	76.5 kg cal.	1202	60.6	72.5 kg cal.
1171	137.4		1238	33.6	
1124	147.4	84	1202	64.8	81
1171	55.2		1238	33.6	
1138	425	73	1202	83.7	70
1228	89.3		1238	47.3	
1202	102.3	85.5	1202	74.0	74
1229	60.6		1238	40.5	
Arithmetic mean = 77 ± 4					

cyanogen and cyanide radicals. Rotation and translation were taken as classical and the oscillations considered harmonic. Cyanogen has seven vibrational degrees of freedom but due to its symmetry it has only five distinct frequencies. These frequencies were obtained from data on the infrared absorption¹³ and Raman spectra¹⁴ of liquid cyanogen, and were distributed as follows. The three longitudinal vibrations were taken as 2336, 2150 and 860 cm^{-1} ; 756 and 512 cm^{-1} were considered the deformation oscillations, each being double. The specific heat of cyanogen, assuming a linear structure with only two rotational degrees of freedom, becomes,

$$c_p = (7/2)R + \varphi(2336/T) + \varphi(860/T) + \varphi(2150/T) + 2\varphi(756/T) + 2\varphi(512/T).$$

The vibrational frequency¹² of CN is 2056 cm^{-1} and its specific heat,

$$c_p = (7/2)R + \varphi(2056/T)$$

$\varphi(v/T)$ is the Einstein formula for the specific heat of a harmonic oscillator.

By using these values it is found that the total contribution of the integral is only 0.2 kg cal. This was considered negligible, in consideration of the assumptions involved in the calculation of the specific heats. Therefore for the reaction $\text{C}_2\text{N}_2 \rightarrow 2\text{CN}$, $\Delta H_0 = 77 \pm 4$ kg cal.

It was also considered desirable to calculate

¹³ Burmeister, Verh. deut. phys. Ges. **15**, 589 (1913).

¹⁴ Petrikaln and Hochberg, Zeits. f. physik. Chemie **B8**, 440 (1930).

¹² Weizel, *Bandenspektren*, p. 370. Leipzig, 1931.

the equilibrium pressure of the CN radicals. For this purpose the entropies of cyanogen and of CN are necessary. The first was calculated from the equation given by Mayer, Brunauer and Mayer.¹⁵ To calculate the moment of inertia of cyanogen the C—C distance was taken to be 1.55Å as in aliphatic hydrocarbons and the C≡N distance 1.17Å, from the spectroscopic value for CN radicals.¹² P_e was taken as 1 and σ set equal to 2. The frequencies were assigned as in the calculation of specific heat.

For CN a similar equation was used with only one term involving frequency and no σ term. Since the normal state of CN is a $^2\Sigma$, $P_e = 2$. The practical molar entropies (neglecting nuclear spin) of cyanogen and cyanide radicals, gases at 1500°K and 1 atm. pressure, are then 38.8R and 28.3R, respectively. On substituting in the proper thermodynamic equations the following data were obtained. $\Delta F^\circ 1500^\circ\text{K} = 22$ kg cal.; $K = 7 \times 10^{-4}$; and for $P(\text{C}_2\text{N}_2) = 100$ mm, $P(\text{CN}) = 0.3$ mm. This pressure appears to be of a reasonable magnitude considering the length of the furnace used and the absorption intensity obtained.

DISCUSSION AND CONCLUSIONS

From a study of the ultraviolet absorption spectrum, Mooney and Reid⁶ obtain a value of 154 kg cal. for the heat of photochemical dissociation of cyanogen. The excitation energy of a CN radical ($^2\Sigma^* \rightarrow ^2\Sigma$) is 74 kg cal. (3.2 v.e.).¹² If, therefore, we assume that the photochemical dissociation produces one excited and one normal CN radical, we get 80 kg cal. for the heat of dissociation into normal products. This is in good agreement with our value of 77 ± 4 kg cal. which makes unnecessary the assumption of vibrating CN radicals which Mooney and Reid invoked to explain the disagreement with existing thermochemical data. Lederle's⁵ theoretical calculation of the heat of dissociation from electron affinity gives 61 ± 3 kg cal. His method has been very severely criticized by Kuhn,¹⁶ who claims that the correct order of magnitude is all that can be expected from it.

For the calculation of the heat of dissociation of hydrogen cyanide into hydrogen atoms and cyanide radicals we have now the following data:

	ΔH
$(1/2)\text{C}_2\text{N}_2 \rightarrow \text{CN}$	$+ 38.5 \pm 2$ kg cal.
$\text{HCN} + (9/4)\text{O}_2 \rightarrow \frac{1}{2}\text{H}_2\text{O} + \text{CO}_2 + \frac{1}{2}\text{N}_2$	$- 159 \pm 1^{17}$
$\frac{1}{2}\text{N}_2 + \text{CO}_2 \rightarrow \frac{1}{2}\text{C}_2\text{N}_2 + \text{O}_2$	$+ 130 \pm 1$
$\frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{4}\text{O}_2$	$+ 34$
$\frac{1}{2}\text{H}_2 \rightarrow \text{H}$	$+ 51^{18}$
<hr/> $\text{HCN} \rightarrow \text{H} + \text{CN}$	<hr/> 94.5 ± 4 kg cal.

There now remains the question as to whether the energies of the carbon-carbon and carbon-hydrogen bonds are approximately independent of the compound in which they occur. While this principle is exceedingly doubtful in the case of highly phenylated compounds where there is considerable steric hindrance, it seems quite plausible for aliphatic hydrocarbons and their usual

derivatives. To determine whether the above values apply to aliphatic hydrocarbons the following equations can be set up:

	ΔH
$\text{C g} + 2\text{H}_2 \rightarrow \text{CH}_4$	$- 18.5$ kg cal. ¹⁹
$\text{CH}_4 \rightarrow \text{C vapor} + 4\text{H}$	$+ 378$ kg cal. ²⁰
$4\text{H} \rightarrow 2\text{H}_2$	$- 205$ kg cal. ¹⁸
<hr/> $\text{C g} \rightarrow \text{C vapor}$	<hr/> $+ 154$ kg cal.

¹⁵ Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 38 (1933), Eq. (4).

¹⁶ Kuhn, Zeits. f. physik. Chemie **B19**, 217 (1932).

¹⁷ All thermochemical data are from Landolt-Bornstein unless otherwise noted.

¹⁸ Weizel, reference 12, p. 249.

¹⁹ Egloff, Schaad and Lowry, J. Phys. Chem. **34**, 1617 (1930).

²⁰ Calculated on the assumption that the energy of the C—H bond is 94.5 kg cal.

If these data are now set into the equations for ethane we should be able to get a value for the energy of the carbon-carbon bond.

Thus

	ΔH
$2C\text{ g} + 3H_2 \rightarrow C_2H_6$	- 23 kg cal. ²¹
$6H \rightarrow 3H_2$	- 308 ¹⁸
$2C\text{ vapor} \rightarrow 2C\text{ g.}$	- 309
$C_2H_6 \rightarrow C-C + 6H$	+ 563 ²⁰
<hr/> $2C\text{ vapor} \rightarrow C-C$	<hr/> - 76 kg cal.

This value checks better than should be expected with the 77 ± 4 obtained for the heat of dissociation of cyanogen. Hence, it seems very probable that the principle of constancy of bonding energies is sufficiently valid to justify assigning, to ordinary compounds, as the energy of the carbon-carbon bond 77 kg cal. and that of the carbon-hydrogen bond 94.5 kg cal.

As an intermediary quantity in the above calculation we found 154. kg cal. for the heat of sublimation of carbon. The quantity can now be calculated in several other ways. According to the valence theory of Heitler and London²² the carbon atom with a valence of four, as for instance in diamond, must be in the 5S state. Accordingly the heat of sublimation of carbon should be equal to twice the energy of a carbon bond minus the energy of the transition $^5S \rightarrow ^3P$. Assuming 1.6 v.e. (37 kg cal.)¹² for the energy of excitation, this would give 116 kg cal. for the heat of sublimation, an improbably low value. However, according to the Hund-Mulliken theory²³ carbon compounds in the normal state can dissociate directly into 3P -atoms. Therefore we would get 154 kg cal. for the heat of sublimation.

For the heat of dissociation of CO Weizel¹² gives 10.3 v.e. (234 kg cal.). Therefore we have:

	ΔH
$CO \rightarrow C\text{ vapor} + O$	+ 234 kg cal.
$C\text{ g} + \frac{1}{2}O_2 \rightarrow CO$	- 22
$O \rightarrow \frac{1}{2}O_2$	- 59 ¹²
<hr/> $C\text{ g} \rightarrow C\text{ vapor}$	<hr/> + 153 kg cal.

²¹ Parks and Huffman, *Free Energies of Some Organic Compounds* (Chem. Cat. Co. 1932), p. 60.

²² Heitler and London, *Zeits. f. Physik* **44**, 455 (1927); Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

Mulliken,²⁴ on the other hand, gives 10.0 volts for the dissociation energy of CO which would give 147 kg cal. for the heat of sublimation. This is equal to the corrected value of Fajans²⁵ calculated from pressure-temperature data. Marshall and Norton,³ however, point out that the temperatures used may be as much as 200° too high, which would make the calculated values of the heat of sublimation too low.

There is still another way of calculating the heat of sublimation making use of the heat of dissociation of CN radicals. Herzberg and Heitler²⁶ have determined 9.7 v.e. as the energy of dissociation of the $^2\Sigma$ CN bond by the Birge-Sponer method. On the basis of the Heitler-London theory they assume that the dissociation products are a 5S carbon and a 4S nitrogen. Therefore assuming 1.6 v.e. as the excitation energy of the transition $^5S \rightarrow ^3P$ we get 8.1 v.e. for the dissociation of $^2\Sigma$ CN into normal atoms. This is the value given by Weizel.¹² Due to the fact that a considerable extrapolation was necessary, under which conditions the Birge-Sponer method gives results that are too high, this value is rather uncertain. By the Hund-Mulliken theory, however, the normal $^2\Sigma$ CN should dissociate into normal atoms. Rejecting Herzberg's analysis of the CN $^2\Sigma$ Mulliken²² takes a more accurate determination by Birge of the heat of dissociation of the CN $^2\Sigma^*$ (6.3 e.v.) and assuming that the excited radical breaks up into 2D nitrogen and 3P carbon gets 7.1 v.e. (161 kg cal.) for the dissociation of the $^2\Sigma$ into normal atoms. There is, however, another possibility which Mulliken rejects although stating that it is just as probable, namely the CN $^2\Sigma^*$ may yield 4S nitrogen and 5S carbon atoms. This gives 8.0 v.e. (185 kg cal.) for the heat of dissociation of $^2\Sigma$ into normal atoms. For the heat of dissociation of nitrogen Kaplan⁴ shows that the most recent and most accurate determinations give a mean value of 9.0 ± 0.1 v.e. (208 kg cal.). The use of this value in the following computations will introduce into the heat of sublimation of carbon an uncertainty

²³ Mulliken, *Rev. Mod. Phys.* **4**, 38 (1932). *Hund, Zeits. f. Physik* **63**, 719 (1930) and earlier papers.

²⁴ Mulliken, *Rev. Mod. Phys.* **4**, 78 (1932).

²⁵ Fajans, *Zeits. f. Elektrochemie* **31**, 63 (1925).

²⁶ Herzberg and Heitler, *Zeits. f. Physik* **53**, 52 (1929); Herzberg, *ibid.* **52**, 815 (1929).

of half the magnitude and of opposite sign to that of the energy of dissociation of nitrogen.

	ΔH
$\text{CO}_2 + \frac{1}{2}\text{N}_2 \rightarrow \frac{1}{2}\text{C}_2\text{N}_2 + \text{O}_2$	+130 kg cal.
$\text{C g} + \text{O}_2 \rightarrow \text{CO}_2$	- 94
$\text{N}^4\text{S} \rightarrow \frac{1}{2}\text{N}_2$	-104
$\text{CN}^2\Sigma \rightarrow \text{C}^3\text{P} + \text{N}^4\text{S}$	+185
$\frac{1}{2}\text{C}_2\text{N}_2 \rightarrow \text{CN}^2\Sigma$	+ 38
<hr/>	<hr/>
$\text{C g} \rightarrow \text{C}^3\text{P}$	+155 kg cal.

If we substitute Mulliken's value of 161 kg cal. for the energy of dissociation of CN we get only 131 kg cal. for the heat of sublimation, which appears to be much too low, indicating that the most probable dissociation products of the $\text{CN}^2\Sigma$ are an excited carbon atom and a normal nitrogen.

Thus by four different methods, we get 154 ± 1 kg cal. for the heat of sublimation of carbon. Considering the probable deviations of the thermochemical data used, the most probable value is 154 ± 3 kg cal. By measurements of the loss of weight of carbon rings in vacuo Marshall and Norton^{3, 27} calculate the heat of sublimation to be 177 kg cal. In their computations they make use of two doubtful assumptions, first that the accommodation coefficient is unity, secondly that the surface of the carbon ring is equal to the geometric surface. The questionable validity of these assumptions make difficult an interpretation of their data.

Concerning the theoretical values of Vaughan and Kistiakowsky, the Hund-Mulliken theory would point to 5.5 v.e. as the heat of dissociation of C_2 molecules and hence make the lower limits of the calculations the most probable values. The

value of 154 ± 3 kg cal. falls within these limits. The consistency of the results obtained by the use of these values for the energies of the C—C and C—H bonds and the heat of sublimation of carbon is a favorable indication of their validity.

Note added in proof: Since the completion of this paper McMorris and Badger²⁸ have obtained for the heat of combustion of cyanogen a new value of 251.4 ± 1.2 kg cal. In our calculations we have made use of the difference between one-half the heat of combustion of cyanogen and the heat of combustion of hydrogen cyanide. Although Thomsen and Berthelot give different values for each of these quantities, the difference calculated from the two sets of values is the same. Thus it would seem that whatever errors were made in the calorimetric determinations were systematic, and therefore it would not be correct to use the new value for the heat of combustion of cyanogen and the old one for hydrogen cyanide. In an earlier paper Badger²⁹ announced that he expected to redetermine the heat of combustion of hydrogen cyanide. Until this new value is forthcoming it would seem safest to use the old values of Thomsen and Berthelot which give perfectly consistent results.

In their calculation of the entropy of cyanogen McMorris and Badger make use of a frequency of 240 cm^{-1} . The introduction of this frequency into our calculations would raise ΔH_0 for the reaction $\text{C}_2\text{N}_2 \rightarrow 2\text{CN}$ by about 1.4 kg cal. However, there is practically no experimental evidence for the existence of this low frequency and, indeed, its adoption would compel one to regard the Raman line at 756 cm^{-1} as a combination frequency.

²⁸ McMorris and Badger, J. Am. Chem. Soc. **55**, 1952 (1933).

²⁹ Badger, J. Am. Chem. Soc. **54**, 3528 (1932).

²⁷ We wish to thank Drs. Marshall and Norton for allowing us to see their paper in manuscript.