



Heat of Formation of the CN Radical

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explained by temperature differences between the clusters and the surrounding medium. Density differences must also be important. In any case, since $\Delta c/c$ is a multiplicative term, the shape of the curve would not be altered appreciably by the use of a different value, and thus the conclusion that scattering is primarily responsible for the high sound absorption at these frequencies seems justified. Richardson²³ has reached the same conclusion.

Finite amplitude distortion at the critical point has been postulated by Fisher.²⁴ Although the waveform

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the signal amplitude plotted on a logarithmic scale showed a fairly linear decrease with distance, which indicated that the finite amplitude distortion was not excessively large in the critical region. No measurements could be made at the critical point.

could not be observed with the apparatus available,

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Heat of Formation of the CN Radical*

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The vapor in equilibrium with graphite and nitrogen in the temperature range 2200°-2500°K has been analyzed with a mass spectrometer. The partial pressure of CN radicals measured in this way has been used to calculate $\Delta H_f^{\circ}(CN) = 109$ kcal/mole, equivalent to $D_0(CN) = 7.5 \pm 0.1_5$ ev. The results of a variety of experiments are compared with this one, and in some cases, reinterpreted. The appearance potential of CN^+ from CN is found to be 14.2±0.3 ev. Other possible azocarbon species up to C_6N_6 have been investigated and found to be much less abundant than CN.

THE heat of formation of CN has been the subject **L** of a great deal of research effort and considerable controversy in recent years. At least part of this interest exists because of the relationship of this quantity to the sublimation energy of graphite and the dissociation energy of the nitrogen molecule. It may easily be shown by a thermochemical cycle that

$$D(\mathrm{CN}) = \frac{1}{2}D(\mathrm{N}_2) + L(\mathrm{C}) - \Delta H_f(\mathrm{CN}), \quad (1)$$

where D(CN) is the dissociation energy of CN, $D(N_2)$ is the dissociation energy of N_2 , L(C) is the heat of sublimation of graphite, and $\Delta H_f(CN)$ is the heat of formation of CN. With the values for $D(N_2)$ and L(C) now rather well established, emphasis has shifted to the determination of one or the other of the remaining unknowns in Eq. (1). In an excellent review, Gaydon¹ summarized the experimental situation as of 1950. At that time, Gaydon selected D(CN) = 7.6 ev as the most probable value, based largely on two experiments. The first was an extrapolation of vibrational energy levels observed² in the CN spectrum to a convergence limit, which depended upon an uncertain interpretation of an observed predissociation. The second was based on the energy for onset of the process

$$C_2 N_2 \rightarrow 2CN, \qquad (2)$$

which is related to D(CN) via the relatively well-known heat of formation of C₂N₂.

Subsequent to Gaydon's 1950 analysis, several different types of experiments were reported3-5 which disagreed with this value for D(CN) but were more or less in agreement among themselves. These results pointed to a value $D(CN) \approx 8.35$ ev. Taking due cognizance of the new data, Gaydon⁶ revised his analysis in 1953 to accommodate this value. In 1960, Herron and Dibeler⁷ confirmed this result with some

² R. Schmid, L. Gerö, and J. Zemplen, Proc. Phys. Soc. (London) 50, 283 (1938).
^a D. P. Stevenson, J. Chem. Phys. 18, 1347 (1950).
⁴ C. A. McDowell and J. N. Warren, Trans. Faraday Soc. 48,

- 1084 (1952). ⁵ L. Brewer, L. K. Templeton, and F. A. Jenkins, J. Am. Chem.
- Soc. 73, 1462 (1951). A. G. Gaydon, Dissociation Energies (Chapman and Hall,

Ltd., London, 1953). ⁷ J. T. Herron and V. H. Dibeler, J. Am. Chem. Soc. 82, 1555 (1960).

²³ E. G. Richardson, Revs. Modern Phys. 27, 15 (1955).

²⁴ I. Z. Fisher, Soviet Phys.—Acoustics 3, 225 (1957).

^{*} Work performed under the auspices of the U. S. Atomic Energy Commission.

¹A. G. Gaydon, Dissociation Energies (Dover Publications, New York, 1950).



further electron-impact experiments. During the course of the work to be presented here, the results of some x-ray densitometry measurements⁸ of shock waves in cyanogen mixed with krypton yielded information supporting Gaydon's original interpretation and casting doubt on the results of the other experiments subsequent to 1950.

EXPERIMENTAL METHODS

The approach attempted here was to react nitrogen gas directly with graphite at a temperature in the neighborhood of 2500°K and to obtain the partial pressure of CN radicals in equilibrium with the reacting species. The reaction was to be carried out in a Knudsen cell lined with graphite and also containing tiers of graphite (Fig. 1) to increase the surface area available for reaction and to enhance the rate of approach to equilibrium. The composition of the vapor phase in the Knudsen cell was sampled through a small effusion orifice (1 mm in diameter), the effusing vapor being ionized by electron impact and mass analyzed in the usual fashion.⁹ In order to check on the attainment of equilibrium, additional experiments were performed with C₂N₂ (Matheson Company) gas substituted for the nitrogen. In the latter experiments the sequence of operations was as follows: (1) The mass spectrometer was tuned to the mass-52 ion peak. (2) Cyanogen gas was introduced into the Knudsen cell through a needle valve. The mass-52 ion peak could be seen to increase considerably. (3) The Knudsen cell was then heated. With application of sufficient heat, the mass-52 ion peak could be seen to decrease, almost to its background level. (4) A search was then made for CN⁺ ions at mass 26. In these experiments the energy of the ionizing electrons was maintained at 20 ev, for reasons to be

discussed below. (5) If no conclusive evidence was found for CN^+ , steps (2), (3), and (4) were repeated, more C_2N_2 being introduced in each sequence.

Positive identification of CN^+ was predicated on satisfying two criteria: (1) A clearly discernible "shutter effect"⁹ produced by blocking the molecular beam from the oven, then permitting it to pass into the ionization chamber. (2) Measurement of an appearance potential for CN^+ which was in the range to be expected from established thermochemical data.

The temperature of the Knudsen cell was measured with a Leeds and Northrup optical pyrometer by sighting on a blackbody hole drilled into the wall of the Knudsen cell. A tilting McLeod gauge was used to measure the pressure of noncondensable gases at the inlet to the Knudsen cell. An ionization gauge of the Bayard-Alpert type was used to measure the pressure in the vacuum chamber where the Knudsen cell was located.

EXPERIMENTAL RESULTS

Positive identification of CN^+ (according to the criteria of the above section) was achieved in both the N₂ and C₂N₂ experiments. Figure 2 shows the ionization efficiency curves of CN^+ and $C_2N_2^+$ formed from cold cyanogen (~100°-200°C). The appearance potential of CN^+ is seen to be about 6 ev higher than that of $C_2N_2^+$. The ionization efficiency curves for the same mass peaks shown in Fig. 3 were obtained with the



FIG. 2. The appearance potentials of C⁺, CN⁺, and $C_2N_2^+$ from cold cyanogen. The energy scale has not been corrected.

⁸ H. T. Knight and J. P. Rink, J. Chem. Phys. **35**, 199 (1961). ⁹ W. A. Chupka and M. G. Inghram, J. Phys. Chem. **59**, 100 (1955). See also W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959); D. J. Meschi, W. A. Chupka, and J. Berkowitz, *ibid.* **33**, 530 (1961).

Knudsen oven at about 2100°C. In this instance, the appearance potential of CN+ was very close to that of $C_2N_2^+$. The appearance potential of $C_2N_2^+$ from C_2N_2 has previously been reported as 13.0,10 14.1,11 and 13.57 ev⁴ by electron-impact methods, and around 13.8 ev by a spectroscopic method¹² involving an estimate of the wavelength where some diffuse bands crowd together in the vacuum ultraviolet region. The curves shown in Figs. 2 and 3 are uncorrected for the various perturbations, such as contact potential, which affect the electron voltage scale. A correction was made in Fig. 3 by determining the appearance potential (AP) of Hg⁺ from the residual mercury vapor in the vacuum system, and of Ar⁺ due to a slight air leak. With this correction, the most probable value for $AP(C_2N_2^+)$ deduced from the current experiments is 14.2 ± 0.3 ev. Any possible significance of the discrepancy between this value and some of the lower values is of no consequence to the ensuing discussion.

The appearance potential of CN⁺ produced by electron impact has been variously reported as 18.0,10 21.3,11 20.3,3 20.4,3 and 20.75 ev.13 As seen from Fig. 2, the current investigation yields $AP(CN^+) = 20.4 \pm 0.3$ ev, which is 6.2 ev greater than $AP(C_2N_2^+)$. By use of a retarding potential method,¹³ this process has been found to form CN⁺ ions with an excess kinetic energy of 0.57 ev. H. E. Stanton of Argonne National Laboratory has confirmed (in a private communication) this result by use of an electrostatic analyzer. Although Stanton's experiments show that the energy distribution of CN⁺ has a high-energy tail extending for perhaps 0.5 ev, most of the ions appear to have the normal Maxwellian distribution of thermal energies.

No previous direct measurements of the ionization potential of CN radicals has been found in the literature. From thermochemical arguments regarding the



FIG. 3. The appearance potentials of CN^+ and $C_2N_2^+$ with the Knudsen cell at 2100°C. The energy scale has not been corrected.



FIG. 4. The appearance potentials of CN^+ and $C_2N_2^+$ with the Knudsen cell at about 2100°C. The tail on the CN^+ curve is most probably due to $C_2H_2^+$. The energy scale has not been corrected.

energy of dissociation of C₂N₂ into two CN radicals and the previously discussed appearance potential of CN⁺ from C₂N₂, Stevenson³ has proposed either 13.4 or 14.55 ev for this ionization potential, depending upon the electronic excitation of one of the products formed. Kandel¹³ has used similar arguments to arrive at a value of 15.13 ev. The current investigation yielded an ionization potential of 14.2 ± 0.3 ev, almost identical to the value previously obtained for C_2N_2 . In some experiments at higher intensity (Fig. 4) a small tail on the ionization efficiency curve for mass 26 extended down to about 11.5 ev, with a clearly discernible break in the curve near 14.2 ev. The low-energy tail was most probably C₂H₂+, formed by direct primary ionization of C2H2. Acetylene is the most abundant hydrocarbon to be expected at elevated temperatures.^{14,15} Any hydrocarbon impurity finding its way to the Knudsen oven would presumably be a source of C₂H₂. The relative importance of the tail was minimized by using prepurified nitrogen passed through a liquid nitrogen trap.

The primary purpose of the appearance-potential experiments was to establish the presence of CN radicals and to determine "safe" operating conditions, i.e., pressure and temperature regions in which equilibrium is reasonably assured, and electron-impact energies such that primary ionization is the only significant process.

The reaction that was studied is represented by the equation

$$C(g) + \frac{1}{2}N_2(g) \rightarrow CN(g).$$
 (3)

It should be noted that this is a homogeneous, gasphase reaction. The free energy change in this reaction

¹⁰ K. E. Dorsch and H. Kallman, Z. Physik 60, 376 (1930). ¹¹ J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. 48,

^{525 (1935)} ¹² W. C. Price and A. D. Walsh, Trans. Faraday Soc. 41, 381

^{(1945).} ¹³ R. J. Kandel, J. Chem. Phys. 22, 1496 (1954).

¹⁴ W. A. Chupka, D. J. Meschi, and J. Berkowitz, paper pre-sented at the Congress of the International Union of Pure and Applied Chemistry, Symposium on Chemical and Thermodynamic Properties at High Temperatures, Montreal, August 6–12, 1961. ¹⁵ R. Duff and S. H. Bauer, "Equilibrium Composition of the C/H System at Elevated Temperatures," Los Alamos Scientific

Laboratory Rept. LA-2556.

Ion	Measured with 20-ev electrons	Corrected for ionization energy above threshold	Corrected for relative ionization cross section	Corrected for relative efficiency of electron multiplier
C ⁺ (mass 12)	3.63×10 ⁴	3.63×10 ⁴	3.63×104	3.63×104
N_2^+ (mass 29)	3.08×10 ⁶	6.23×10 ⁶	3.37×106	2.58×10 ⁶
CN+ (mass 29)	2.36×105	3.50×10 ⁵	1.82×105	1.55×10 ⁵

 TABLE I. Significant changes in ion intensities as a result of the "shutter effect" (arbitrary units) in the nitrogen-graphite experiment. The measured temperature in this experiment, when corrected for the transmission of the Pyrex window, was 2340°K.

depends upon $\frac{1}{2} \ln P_{N_2}$, where P_{N_2} is the partial pressure of N₂ in the Knudsen oven.

The ion intensities of C⁺ and CN⁺ due to primary ionization of C atoms and CN molecules, respectively, could be measured without much difficulty when using ionizing electrons of 20 ev energy. The N_2^+ intensity was not quite as satisfactory. The pumping speed in this part of the vacuum apparatus is such that nitrogen molecules effusing from the Knudsen oven and passing through the ionization region remain in this vacuum chamber for some time before being pumped away. They have ample opportunity to find their way to the ionizing region several times before being removed. The fractional diminution in N₂⁺ ion intensity upon interposing the shutter plate is relatively small. In the experiments reported herein, the best effect observed amounted to about 4% of the total peak height, and the average was approximately 2-2.5%.

On the other hand, carbon atoms effusing from the Knudsen oven make only a single pass through the ionization region before colliding with some relatively cold surface and condensing. The CN radicals suffer a similar fate, most likely combining with metal surfaces in the vacuum chamber or recombining to form C_2N_2 after a very few collisions. Hence, their fractional shutter effects were almost 100% in the case of C⁺ and 10–50% for CN⁺, the particular value depending upon background conditions.

The equilibrium constant corresponding to Eq. (3) may be written in the form

$$K_{eq} = \frac{I^+(\mathrm{CN})/\sigma(\mathrm{CN})}{I^+(\mathrm{C})/\sigma(\mathrm{C})} \frac{1}{(P_{\mathrm{N}_2})^2},\tag{4}$$

where $I^+(CN)$ and $I^+(C)$ refer to the respective ion intensities of CN⁺ and C⁺, and $\sigma(CN)$ and $\sigma(C)$ refer to the ionization cross sections of CN and C, respectively. The σ 's have a rather special meaning in this instance. The shutter effects were generally measured at 20 ev. This is 8.9 ev above the ionization potential of C⁺, and only about 6 ev above the ionization potential of CN⁺. The cross sections were therefore "normalized" by assuming a linear behavior of the ionization efficiency curve for CN⁺ for an additional 3 ev above threshold. The measured ionization efficiency curve for CN⁺ departs only slightly from linearity between 20 and 23 ev. The relative ionization cross sections calculated by Otvos and Stevenson¹⁶ were used in determining these σ 's. These calculations are most likely to be dependable in the region in which the Born approximation is applicable (>250 ev) but the error incurred here is not very significant for the present type of measurement. It is thus a relatively simple matter to dispose of the first factor in Eq. (4). The remaining factor is $1/(P_{N_2})^{\frac{1}{2}}$.

To rule out any spurious effects that might give rise to such a small shutter effect, and to more firmly establish the origin of this diminution in peak height, several methods were used.

(1) The shutter effect itself was measured on both mass 28 and 29. Because of the huge intensity of mass 28, which overloaded the electron multiplier used as detector, the measurement on mass 29 was more reliable. The vapor pressure of graphite was used as a standard. Then the partial pressure of N_2 could be measured by comparing the intensity of N_2^+ with that of C⁺, and making the aforementioned corrections for the cross section and energy above threshold.

(2) At low oven temperatures, at which there was little outgassing of the vacuum chamber, the pressure measured by the ionization gauge was almost entirely due to the N₂ or C_2N_2 effusing from the Knudsen cell into the vacuum. With a knowledge of the pressure in this vacuum chamber and the effective pumping speed of the vacuum system for these gases (about 10 l/sec) one may compute the pressure in the Knudsen cell, knowing the orifice area and assuming Knudsen flow conditions. It is thus possible to relate the pressure measured by the ionization gauge to the pressure in the Knudsen cell when outgassing does not represent a significant effect.

(3) The tilting McLeod gauge measures the approximate pressure at the inlet to the Knudsen cell. There is a sizable pressure drop across the cell, so that the pressure of gas near the orifice is substantially smaller than that at the inlet. Nevertheless, by monitoring the latter pressure either with the ionization gauge or with the intensity of an appropriate mass peak in the mass spectrometer (e.g., mass 52 when C_2N_2 was being used as a pressure-calibrating gas), it was possible to show that the two pressures were proportional.

¹⁶ J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).

Ion	Measured with 20-ev electrons	Corrected for ionization energy above threshold	Corrected for relative ionization cross section	Corrected for relative efficiency of electron multiplier
C ⁺ (mass 12)	2.20×104	2.20×104	2.20×104	2.20×104
N ₂ ⁺ (mass 29)	1.01×106	2.04×106	1.10×10 ⁶	0.84×10 ⁶
N_{2}^{+} (mass 28)	1.82×10^{8}	3.68×10 ⁸	1.99×10 ⁸	1.52×10 ⁸
CN ⁺ (mass 26)	1.65×10^{5}	2.45×10 ⁵	1.27×10 ⁵	1.08×10^{5}

TABLE II. Significant changes in ion intensities as a result of the "shutter effect" (arbitrary units) in the cyanogen-graphite experiment. The measured temperature in this experiment, when corrected for the transmission of the Pyrex window, was 2312°K.

(4) A rough check on the C^+ ion intensity as a standard for pressure calibration was afforded by the following method. The mass-analyzed ions were measured by two independent detectors in this mass spectrometer. The first is simply a wire grid, the second an electron multiplier. Whereas the multiplier has been known to vary in gain over a period of time, the wire grid is more reliable and records similar ion intensities for similar pressures and geometrical arrangements in the ion-source region. From previous experiments on other thermodynamic systems, a calibration was thus available for use with this detector.

These experiments will be considered later in assessing possible errors in pressure measurements.

The pertinent ion intensities observed during the N₂ experiment are shown in Table I, and those obtained with C_2N_2 as the inflowing gas are given in Table II. In both tables, the various corrections are explicitly indicated.

By combining the generally accepted value¹⁷ for the partial pressure of carbon atoms at the temperatures indicated in Tables I and II with the measured ion intensities at mass 12, the calibrations and resulting thermodynamic quantities of Tables III and IV are obtained. The free energy functions $-\Delta [(F^{\circ} - E_{0}^{\circ})/T]$ in these tables were computed from the molecular parameters given by Herzberg.¹⁸ The values for the

TABLE III. Pressure calibration and derived thermodynamic quantities, based on data in Table I, for the reaction $C(g) + \frac{1}{2}N_2(g) \rightarrow CN(g)$.

=

Pressure calibration	$1.0 \text{ atm} = 2.11 \times 10^{12} \text{ units}$
Equilibrium constant	330 atm ⁻¹
ΔF° (2340°K)	-26.97 kcal/mole
$-\Delta[(F^\circ - E_0^\circ)/T]$	-13.365
ΔE_0°	-58.2 kcal/mole

¹⁷ D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., Advances in Chemistry Series, No. 18. ¹⁸ G. Herzberg, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., New York, New York,

Princeton, New Jersey, 1950).

free energy functions of the individual species agreed very closely with previous tabulations.^{19,20}

The error in pressure calibration was assessed by employing the methods described above. The wire-grid detector yielded a nitrogen pressure equal to 0.75 of that obtained by the electron-multiplier detector, as computed in the above tables. The pressure measured by the McLeod gauge at the inlet to the Knudsen cell was calibrated against the Knudsen cell pressure at the exit, which in turn, was computed from the ionization gauge pressure in this vacuum chamber. This calibration, which could be made only at low temperatures at which outgassing was not significant, was nevertheless applied to the high-temperature observations. The nitrogen pressure obtained by this method, which admittedly made no correction for the temperature dependence of the pressure drop across the Knudsen cell, was only 0.03 of that obtained by the electron multiplier. However, even if one used the nitrogen pressure deduced by the McLeod gauge method, the equilibrium constant would only change by a factor of 5.6 because K_{eq} depends on the square root of the nitrogen pressure. The extreme range of equilibrium constants determined in this way in all experiments was from 175.6 to 1459. From these observations and

TABLE IV. Pressure calibration and derived thermodynamic quanties, based on data in Table II, for the reaction C(g) + $\frac{1}{2}N_2(g) \rightarrow CN(g).$

Pressure calibration	$1.10 \text{ atm} = 2.00 \times 10^{12} \text{ units}$
Equilibrium constant	646,* or 564 ^b
ΔF° (2312°K)	-29.73° or -29.11° kcal/mole
$-\Delta[(F^{\circ}-E_0^{\circ})/T]$	-13.355
ΔE_0°	-60.6° or -60.0° kcal/mole

* Obtained by using mass 29 as a measure of N₂⁺.

^b Obtained by using mass 28 as a measure of N₂⁺.

¹⁹ J. S. Gordon, "Thermodynamics of High-Temperature Gas Mixtures, and Application to Combustion Problems,' Development Center, Tech. Rept. 57-33. ' Wright Air

²⁰ 'JANAF Interim Thermochemical Tables," prepared under the auspices of the Joint Army-Navy-Air Force Thermochemical Panel by the Thermal Laboratory, Dow Chemical Company, Midland, Michigan (December 31, 1960).

the rather satisfactory agreement of the two isotopic methods used to measure nitrogen pressure (by use of masses 28 and 29), it was concluded that the shutter effects observed on these mass peaks were significant and were adequate for estimating the equilibrium concentration of nitrogen.

Although most of the experiments were performed at pressures within Knudsen conditions (mean free path>orifice diameter of cell), some of the runs intentionally violated Knudsen conditions in order to increase intensity for other requirements. No significant change in equilibrium constant was observed. Indeed, the data of Table I can be seen to be at the boundary of Knudsen conditions.

The value of ΔE_{0}^{0} in Table III, when combined with the now widely accepted dissociation energy of 9.76 ev for N₂ yields D(CN) = 7.40 ev while that from Table IV yields 7.50 ev. If the correct value were Gaydon's⁶ 1953 value of 8.35 ev, the equilibrium constant would be about 40 000. The corresponding error in P_{N_2} would be a factor of 750 if the pressure calibration were responsible for the entire discrepancy between this 40 000 and 1459, the highest K_{eq} measured in the current experiments.

An attempt was made to determine the enthalpy change in the reaction

$$C(s) + \frac{1}{2}N_2(g) \rightarrow CN(g)$$
(5)

by measuring the equilibrium constant for this reaction and plotting $\log K_{eq}$ vs 1/T (second-law method) but the points were too scattered to permit drawing any reliable slope. The third-law method is far more reliable for this experiment. The molecular parameters of all of the participating species are well known. An error of 20°C in temperature measurement represents only 1% in $\Delta E_0^{\circ}(\sim 0.6 \text{ kcal/mole})$. The averaged value of the enthalpy change in reaction (3), as determined by the third-law method, can be combined with the heat of sublimation of carbon¹⁷ to yield the enthalpy change for reaction (5). This quantity, which is the heat of formation of CN, has the value 109 ± 3 kcal/mole.

During the nitrogen experiments, a search was made for other possible molecular species, involving all possible combinations of C and N up to 6 carbons and 6 nitrogens. At a temperature of 2270°K and a nitrogen pressure of approximately 2×10^{-4} atm, the largest significant peaks (in addition to the aforementioned ones, and C_2^+ and C_3^+) were mass 38 $(C_2N^+ ?)$, mass 50 $(C_3N^+ ?)$, mass 66 $(C_2N_3^+ ?)$, mass 80 ($C_2N_4^+$?), mass 128 ($C_6N_4^+$?), mass 132 $(C_4N_6^+?)$, and mass 142 $(C_6N_5^+?)$. In each of these instances, the maximum partial pressure was less than 10⁻⁸ atm, whereas the partial pressure of CN was near 10-7 atm.

DISCUSSION

The results of the thermodynamic experiments described above clearly point to the value D(CN) = $7.5 \pm 0.1_5$ ev. This is in good agreement with the recent shock-wave determination,⁸ $D(CN) = 7.60 \pm 0.13$ ev, and Gaydon's initial interpretation¹ of the older vibrational level extrapolation,² which yields 7.5 ev as a limit, as well as the $D(C_2N_2)$ measurement of White,²¹ which implies $D(CN) = 7.5 \pm 0.12$. Knight and Rink⁸ have discussed some of the possible errors in the various determinations in the literature which differ significantly from this value. The present discussion will be restricted to some points that may not have been covered.

Stevenson's³ electron-impact experiments on CN⁺ from C_2N_2 yield an appearance potential of 20.3 ± 0.2 ev. The corresponding results reported here are $20.4\pm$ 0.3 ev. The appearance potential of CN⁺ from CN presented herein is 14.2 ± 0.3 ev. Combining these results yields an electron-impact value of $D(C_2N_2) = 6.2$ ev for the process in Eq. (2). Combining Eq. (1) and the corresponding expression for the process (2) yields D(CN) = 7.55 ev, in excellent agreement with the above results. Indeed, Stevenson obtained 6.9 ev as a possible value for reaction (2) which implies D(CN) =7.2 ev. However, he rejected this possibility, and chose to accept an alternative possibility that the electronic ground state of CN was not formed in the dissociative ionization of C_2N_2 . He reasoned that the C-C bond in C_2N_2 could not be stronger than the C-C bond in C_2H_4 , and he obtained $D(H_2C--CH_2) = 5.6$ ev by combining his value of 15.7 ev for the appearance potential of CH_2^+ from electron impact on C_2H_4 with the previous value of 11.9 ev for the appearance potential CH_2^+ formed directly from methylene radicals.22 There is now some evidence14,23 that the ionization potential of CH₂ is somewhat lower than 11.9 ev. Since this quantity enters twice into the computation of $D(H_2C--CH_2)$, the latter is quite sensitive to it. Lowering the ionization potential of CH_2 would have the effect of raising $D(H_2C-CH_2)$. If the ionization potential of CH_2 were reduced to 11.2 ev, $D(H_2C-CH_2)$ would become 6.9 ev and the argument for invoking the excited state of CN would vanish. Indeed, the ionization potential obtained by Herzberg²³ from analysis of a Rydberg series in CH₂ is 10.396 ev, which implies a still stronger carbon-carbon bond in ethylene.

The afore-mentioned argument receives further support from some recent equilibrium experiments involving hydrogen and graphite.14 The heat of formation of CH₂ measured in these experiments was 86.0 kcal/mole. When combined with the heat of formation

 ²¹ J. U. White, J. Chem. Phys. 8, 459 (1940).
 ²² A. Langer and J. A. Hipple, Phys. Rev. 69, 691 (1946).
 ²³ G. Herzberg, Can. J. Phys. 39, 1511 (1961).

of ethylene, this yields 6.92 ev for the energy required to break the carbon-carbon bond in ethylene.

Both Kandel¹³ and McDowell and Warren⁴ place considerable stress on the excess kinetic energy expected or observed in the formation of CN⁺ from C_2N_2 . According to Stanton's measurements, a large fraction (probably most) of the CN+ ions formed have thermal energy. Stanton's measurements were made on ions produced by 100-ev electrons. There remains a possibility that the ions formed at threshold have excess kinetic energy but are in low abundance relative to those formed with electronic excitation but only thermal kinetic energy. Most probably, however, these appearance-potential measurements should not need correction because of excess kinetic energy.

Herron and Dibeler,⁷ in their electron-impact study of the cyanogen halides, interpreted their data on the basis of Stevenson's excited state hypothesis. On the alternative assumption that CN molecules in the electronic ground state were formed in their process

$$CNX + e^{-} \rightarrow CN + X^{+} + 2e^{-}, \qquad (6)$$

their results imply that D(CN) = 7.29 ev if X = Cl or I and 7.22 ev if X=Br, in reasonable agreement with the present results. In addition, they studied the process

$$CNX + e^{-} \rightarrow CN^{+} + X + 2e^{-}, \tag{7}$$

where X is Cl, Br, or I. Their appearance-potential measurements, when combined with the heats of formation quoted by these authors, yield $\Delta H_f(CN^+) \leq 425$ kcal/mole for the chloride, 439 kcal/mole for the bromide, and 444 kcal/mole for the iodide. Using the appearance potential for CN⁺ from CN, as measured in the current experiments, together with Eq. (1)enables one to deduce from the above data that D(CN) = 7.96, 7.35, and 7.13 ev, respectively. In view of the apparent error inherent in the method, these values appear to be in good agreement with the present results.

The lone previous attempt⁵ to directly study the reaction described by Eq. (5) relied upon the emission of characteristic CN bands as a measure of the partial pressure of CN. However, there was evidently a systematic error due to self-absorption²⁴ which would tend to bring the result of this study into better agreement with the present one, although the magnitude of the error has never been reported by the authors.

The most recent spectroscopic studies of the CN molecule^{25,26} tend to support a value of D(CN) = 8.2 ev, although in both instances the authors regard these results as being inconclusive. Although the interpretation of a predissociation in the early work of Schmid, Gerö, and Zemplen² is vital to the conclusions the latter workers drew about the dissociation limit, Douglas and Routley²⁵ doubt that this interpretation was warranted by the evidence presented.

The results of Knight and Rink⁸ are in good agreement with the present work, but earlier shock-tube experiments involving CN have been equivocal. Measurements of detonation velocities in C₂N₂-O₂ mixtures by Kistiakowsky, Knight, and Malin,27 while yielding very valuable information on $D(N_2)$ and D(CO), were able only to bracket D(CN) between 7.6 and 8.5 ev. In addition to the high accuracy required in the experiments involving velocity measurements, there remains the uncertainty regarding the establishment of thermodynamic equilibrium in the shock front. Information on this point has been obtained by a Russian group,28 which used a C2N2 shock to produce CN and did not observe a good vibrational temperature. They attributed their difficulty to the finite vibrational relaxation times required to dissociate C_2N_2 into 2CN and to come to equilibrium with the hot gas. More recently, Parkinson and Nicholls²⁹ were successful in using the rotational intensity distribution of CN bands as a thermometer in a shock tube.

In summary, then, the dissociation energy of CN has been determined to be $7.5\pm0.1_5$ ev by an equilibrium study involving the reaction of nitrogen and graphite in a Knudsen cell and mass spectrometric detection. This result is in good agreement with recent shock-wave experiments⁸ and in disagreement with a number of electron-impact experiments.^{3,4,7} Many of the latter have been reinterpreted, with the result that they are now in reasonable agreement with the value of D(CN)reported here. The current result also vindicates the earlier work of White²¹ on $D(C_2N_2)$, which has not been favored for many years. The spectroscopic studies of CN still remain inconclusive.

²⁴ In a footnote on p. 207 of their paper, Knight and Rink refer to a private communication from Professor Brewer in which he evidently feels that the work of Brewer, Templeton, and Jenkins would agree with that of Knight and Rink if Brewer *et al.* made appropriate self-absorption corrections.

²⁵ A. E. Douglas and P. M. Routly, Astrophys. J. Suppl. Ser. 1, 295 (1954)

P. K. Carroll, Can. J. Phys. 34, 83 (1956).
 G. B. Kistiakowsky, H. T. Knight, and M. E. Malin, J. Chem. Phys. 20, 876 (1952).

 ²⁸ N. N. Sobolev, A. V. Potapov, V. F. Kitaeva, F. S. Faizullov,
 V. N. Aliamovskii, E. T. Antropov, and I. L. Isaef, Optics and ²⁹ W. H. Parkinson and R. W. Nicholls, Can. J. Phys. **38**, 715

^{(1960).}