

Heat of Dissociation of Cyanogen

N. C. Robertson and R. N. Pease

Citation: *The Journal of Chemical Physics* **10**, 490 (1942); doi: 10.1063/1.1723755

View online: <http://dx.doi.org/10.1063/1.1723755>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/10/7?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Ionization and Dissociation by Electron Impact: Cyanogen, Hydrogen Cyanide, and Cyanogen Chloride and the Dissociation Energy of Cyanogen](#)

J. Chem. Phys. **18**, 1347 (1950); 10.1063/1.1747475

[Heats of Dissociation of Cyanogen](#)

J. Chem. Phys. **16**, 600 (1948); 10.1063/1.1746952

[The Heat Capacity of Cyanogen Gas](#)

J. Chem. Phys. **7**, 1115 (1939); 10.1063/1.1750385

[The Heat Capacity of Cyanogen Gas](#)

J. Chem. Phys. **7**, 1114 (1939); 10.1063/1.1750384

[The Thermal Dissociation of Cyanogen into Cyanide Radicals](#)

J. Chem. Phys. **1**, 432 (1933); 10.1063/1.1749315



calcium is in agreement with the value, 40.085, obtained by Hönigschmid and Kempter,⁸ and somewhat higher than the recent value given by Birge.⁹ It is in disagreement with the older value of Richards and Hönigschmid¹⁰ or the more recent value of Kendall, Smith, and Tait.¹¹ The value obtained for the atomic weight of fluorine is in agreement with the gas density data² but in disagreement with the mass spectrographic value of 18.999.²

If the mass spectrographic value of the atomic weight of carbon is used, the value obtained for calcium is improbably high but the value obtained for fluorine is much nearer the mass spectrographic value and in agreement with only the highest of the gas density values.²

¹ C. A. Hutchison and Johnston, *J. Am. Chem. Soc.* **62**, 3165 (1940).

² C. A. Hutchison and Johnston, *J. Am. Chem. Soc.* **63**, 1580 (1941).

³ J. A. Bearden, *Phys. Rev.* **54**, 698 (1938).

⁴ Y. Tu, *Phys. Rev.* **40**, 662 (1932).

⁵ *International Critical Tables*, Vol. 3, p. 21.

⁶ See reference a, Table I.

⁷ C. D. Cooksey and D. Cooksey, *Phys. Rev.* **36**, 85 (1930).

⁸ Hönigschmid and Kempter, *Zeits. f. anorg. allgem. Chemie* **163**, 315 (1927); **195**, 1 (1931).

⁹ See reference d, Table II.

¹⁰ Richards and Hönigschmid, *J. Am. Chem. Soc.* **32**, 1577 (1910).

¹¹ Kendall, Smith, and Tait, *Nature* **131**, 688 (1933).

Heat of Dissociation of Cyanogen

N. C. ROBERTSON AND R. N. PEASE

Department of Chemistry, Princeton University, Princeton, New Jersey
May 28, 1942

In a recent communication Herzberg¹ has criticized the value given by White² for the heat of dissociation of cyanogen into two cyanide radicals. White found a probable value of 146(± 4) kcal./mole and assigned a minimum value of 138(± 1.5) kcal./mole for this quantity.

We have recently investigated the kinetics of the thermal reaction of hydrogen with cyanogen over the temperature range 575–675°, and the conclusions with regard to the nature of this process may throw some light on this question. The results of our study, the details of which are soon to be published, are consistent only with a chain mechanism. This appears to involve the initial dissociation

of cyanogen into free cyanide radicals with chain ending by the recombination of these radicals. The most plausible series of reactions is:

1. $(\text{CN})_2 \rightarrow 2 \text{CN}.$
2. $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}.$
3. $\text{H} + (\text{CN})_2 \rightarrow \text{HCN} + \text{CN}.$
4. $\text{H} + \text{HCN} \rightarrow \text{H}_2 + \text{CN}.$
5. $\text{CN} + \text{CN} \rightarrow (\text{CN})_2.$

If this mechanism is accepted, the absolute rate of formation of hydrogen cyanide, neglecting the inhibiting reaction 4, may be calculated as twice the rate of reaction of an equilibrium concentration of cyanide radicals with hydrogen. Hartel and Polanyi³ obtained the reasonable value of 7 kcal. for the activation energy of step 2. It develops that if the equilibrium concentration of cyanide radicals is calculated using the *minimum* value assigned by White for $\text{D}(\text{C}_2\text{N}_2)$, the calculated rate is too low by at least a power of ten. If the value of 77 kcal./mole found by Kistiakowsky and Gershinowitz⁴ is taken, the calculated rate is too high by about 10^6 . A value between these extremes in the range 120–130 kcal./mole seems to be indicated.

The over-all activation energy for the reaction with hydrogen is approximately 72 kcal., which is entirely consistent with the observed absolute rate and with the proposed mechanism. Combining this value with the activation energy for step 2, one obtains 125–130 kcal./mole for the heat of dissociation of cyanogen. It might be mentioned that Hogness and T'sai⁵ found that 2240Å, corresponding to 127 kcal./mole, is the maximum wave-length effective for the photo-polymerization of cyanogen; and this reaction from all evidence also involves the initial dissociation of cyanogen into radicals.

Herzberg's comment regarding the relative values of $\text{D}(\text{C}_2\text{N}_2)$ and $\text{D}(\text{CN})$ seems well taken from the chemical standpoint since the $\text{C}\equiv\text{N}$ bond is stable at very high temperatures.

¹ G. Herzberg, *J. Chem. Phys.* **10**, 306 (1942).

² J. U. White, *J. Chem. Phys.* **8**, 459 (1940).

³ H. v. Hartel and M. Polanyi, *Zeits. f. physik. Chemie* **B11**, 97 (1930).

⁴ G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.* **1**, 432 (1933).

⁵ T. R. Hogness and Liu-Sheng T'sai, *J. Am. Chem. Soc.* **54**, 123 (1932).