ENERGY OF DISSOCIATION OF CYANOGEN*

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ABSTRACT. The energy of dissociation of CN into $C(^3P)$ and $N(^4S)$ atoms has been estimated to be 6.02 volts with the aid of known thermochemical and spectroscopic data.

I

Spectrum of CN

The spectrum of cyanogen has not been of much help in the determination of the energy of dissociation of this molecule in view of the scanty experimental data available. Only a few electronic states have been discovered and predissociation phenomena, which are known to give fairly reliable estimates of the limits, have not been established without ambuguity so far. The vibrational levels of the ground state, $X\ ^2\Sigma^+$ as well as those of the upper state, $A\ ^2\Pi$, of the red system $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ have been followed up to an energy level of about 3.4 volts above the ground level. The convergence limit, reached by a rather long Birge-Sponer extrapolation is not reliable. The appearance of perturbations in the violet system $B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$, however, has been made use of by Schmid, Gerö and Zemplen (1938) to reach up to $v=30$ of the $A\ ^2\Pi$ state corresponding to 51000 cm^{-1} (6.32 volts) and then locate the convergence limit of this state at 60500 ± 1000 cm^{-1} ($7.50 \pm .12$ volts) by only a short extrapolation. Schmid *et al* found evidence to conclude that the ground state, $X\ ^2\Sigma^+$, converges to the same limit as $A\ ^2\Pi$ state. The extrapolated convergence limit of the next upper state, $B\ ^2\Sigma^+$, is found to be 65500 ± 1000 cm^{-1} ($8.12 \pm .12$ volts). In Table I the limits located by Schmid, Gerö and Zemplen (1938) are given.

TABLE I

Limits above $X\ ^2\Sigma^+$ in volts	Nature of effect according to Schmid, Gerö and Zemplen
7.38—7.62	Convergence of $A\ ^2\Pi$ and $X\ ^2\Sigma^+$ states
8.00—8.24	Convergence of $B\ ^2\Sigma^+$ state
6.62	Perturbation in $v=15$ of $B\ ^2\Sigma^+$ state, probably in the vicinity of a predissociation limit
6.32	Perturbation in $v=14$ of $B\ ^2\Sigma^+$ state
3 93	Drop in intensity in $v=3$ of $B\ ^2\Sigma^+$ state, probably due to predissociation.

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In this table, the effects at 6.62, 6.32 and 3.93 volts require further confirmation, particularly the exact locations of the limits. The exact positions of even the two convergence limits at $7.50 \pm .12$ and $8.12 \pm .12$ volts are not known with certainty. Therefore it is not surprising that the attempts to propose a dissociation scheme which will satisfactorily interpret the limits have not been successful.

II

Value of D(CN)

A better estimate of the energy of dissociation can be formed in the case of CN by combining reliable spectroscopic and thermochemical data as given in the following calculations. The terms have their usual meanings and the atoms and molecules occur in the lowest spectroscopic states.

We have, by definition : ... $CN + D(CN) = C + N$

From spectroscopic evidence : ... $N = \frac{1}{2}N_2 + \frac{1}{2}D(N_2)$

$\frac{1}{2}O_2 = O - \frac{1}{2}D(O_2)$

$C + O = CO + D(CO)$

$\frac{1}{2}C_2N_2 = CN - \frac{1}{2}D(C_2N_2)$

From heats of combustion $CO + \frac{1}{2}N_2 + 130$ Kcal $= \frac{1}{2}C_2N_2 + O_2$

$CO + \frac{1}{2}O_2 = CO_2 + 67$ Kcal.

By addition we get,

$$D(CN) = \tfrac{1}{2}D(N_2) + D(CO) - \tfrac{1}{2}D(O_2) - \tfrac{1}{2}D(C_2N_2) - 63 \text{ Kcal} \quad \ldots \quad (1)$$

In this expression the following figures are being adopted :

(*i*) $D(O_2) = 5.08$ volts. This is the generally accepted value for the heat of dissociation of oxygen.

(*ii*) $D(CO) = 8.87$ volts. This value of the energy of dissociation of carbon monoxide has been recently proposed by the author, (Sen Gupta, 1951) and found to give a satisfactory explanation of known predissociation phenomena in CO and the results of the experiments on the sublimation of graphite.

(*iii*) $D(N_2) = 9.76$ volts. Although this is the generally accepted figure for the heat of dissociation of nitrogen (Gaydon, 1947), other investigators (Glockler, 1948 ; Long, 1949 : Springall, 1950) have made use of an earlier figure, 7.38 volts, for comparison in their discussions. Datta's (1932) experiments on the photodissociation of N_2O and the author's (Sen Gupta, 1934) experiments on the fluorescent radiation from N_2O, both confirm that the value is nearer 9.76 than 7.38 volts.

(*iv*) $D(C_2N_2) = 4.93$ volts, being the energy of dissociation of C_2N_2 into two CN radicals. Long (1949) arrived at this figure from a study of the absorption spectra of CH_3CN, ICN and HCN, and found it to be comparable with Glockler's (1948) values, *viz.*, 117.6 and 119.6 Kcal for NaCN and KCN respectively, calculated with

the aid Born-Haber cycles. The value given by Hogness and Lui-Sheng (1932) as well as Robertson and Pease (1942), that is, 5.52 volts is also worth consideration. Some of the investigators have made use of 6.34 volts evaluated by White (1940).

In view of the above it is proposed to consider the three values, 4.93, 5.52 and 6.34 volts for $D(C_2N_2)$ in the expression (1). The deduced value of $D(CN)$ corresponding to each of the figures for $D(C_2N_2)$ are given in Table II.

TABLE II

$D(C_2N_2)$ in volts	4.93	5.52	6.34
$D(CN)$ in volts	6.02	5.72	5.31

Herzberg (1942) has pointed out that as the C≡N bond in CN is much stronger than the C−C bond in C_2N_2, the value of $D(CN)$ should be much higher than $D(C_2N_2)$. Rejecting the figures given in the last two columns of the above table by this test, we get $D(CN)=6.02$ volts, which indirectly confirms Long's estimate of the value of $D(C_2N_2)$.

On the basis of $D(CN)=6.02$ volts, a probable dissociation scheme for the spectrum of CN may now be drawn up as follows (Table III).

TABLE III

Products of dissociation	Calculated limits above $X\ ^2\Sigma^+$ in volts
$C(^3P)+N(^4S)$	6.02
$C(^1D)+N(^4S)$	7.28
$C(^3P)+N(^2D)$	8.39

It will be seen from Table I that there are some observed limits in the vicinity of the above calculated positions, but for reasons already mentioned, no attempt at a correlation is being made in this paper, pending further work on the spectrum of CN.

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