THE HEAT OF DISSOCIATION OF NITROGEN

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The heat of dissociation of nitrogen has been studied many times and the latest values are shown in *Table 1*. The three experimental methods give somewhat discordant results. By methods I, II and IV, $D(N_2)$ = 9·765 eV.* Method I does not eliminate $D(N_2)$ = 7·373 eV. $D(N_2)$ = 11·8 eV by methods III and IV. $D(CN)$ = 8·2 and 8·5 eV respectively by methods II and III, while method IV gives a lower result. It is evident that $D(N_2)$ = 9·765 eV is the most likely value[1–6].

However, a higher value $D(N_2)$ = 11·8 eV, was suggested on the basis of the following comparisons. The internuclear distance (R_0) and the force constants (k_e) of the structures MH_x(M = C, N, O, F; x = 1 to 4) were plotted against the number of H atoms, giving plots of great regularity (*Figure 1, Table 3*). The basic sequence is C, N, O, F. It should be noted

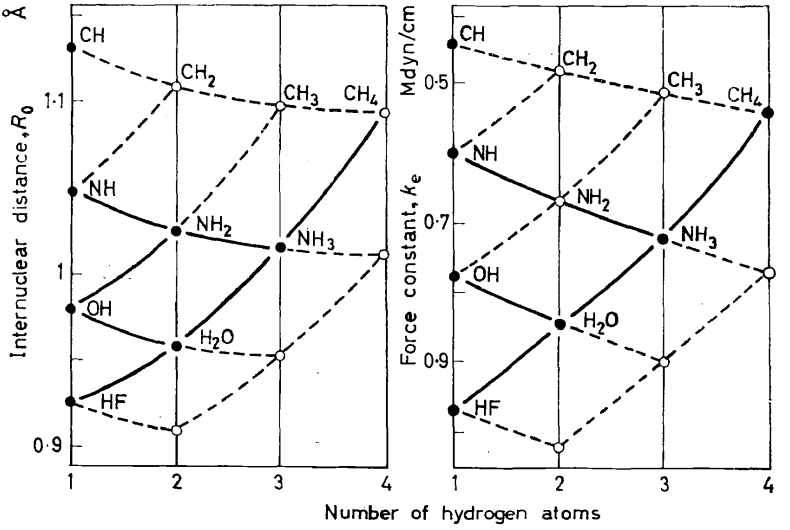

Figure 1

that every point must lie on two crossing curves and on the vertical lines of a given number of hydrogen atoms, in order to produce these networks. It was expected that bond energies would behave similarly (*Figure 2*). However, with[7] $L(C)$ = 170·4 kcal and the likely $D(N_2)$ = 9·765 kcal, the sequence is N, C, O, F. This change seemed rather unexpected since bond energies are known to behave in a regular manner with internuclear

* Symbols are defined at the end of the paper.

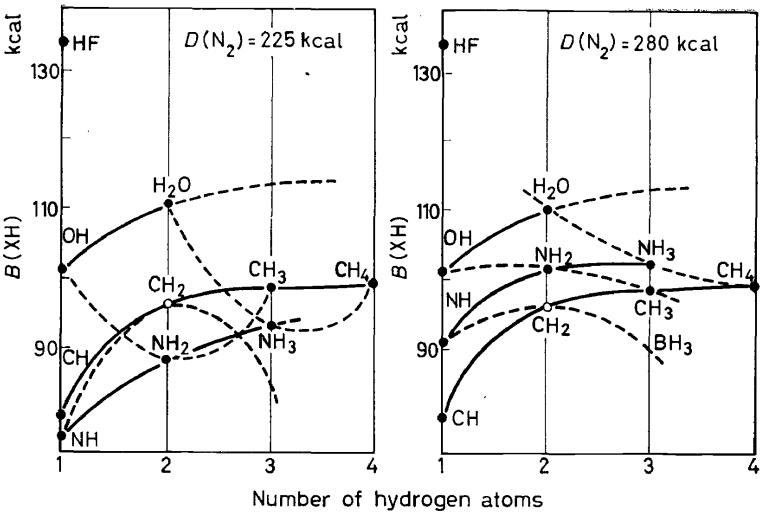

Figure 2

Table 1. Heat of dissociation of nitrogen

Method	$D(N_2)$ (eV)		$D(CN)$ (eV)	*Ref.*
I. Spectroscopy	9·765	7·373	—	1
II. $Qf(CN)$; $T(CN)$	9·765	—	8·2	2, 3
III. N_2/CO terms	—	11·8	8·5	4
IV. Shock-wave	9·765	11·8	7·6	5
,,	9·765	—	—	6

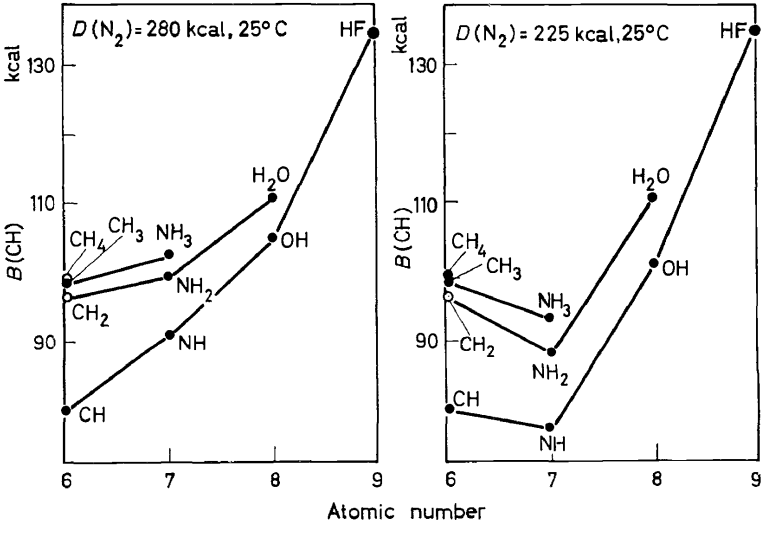

Figure 3

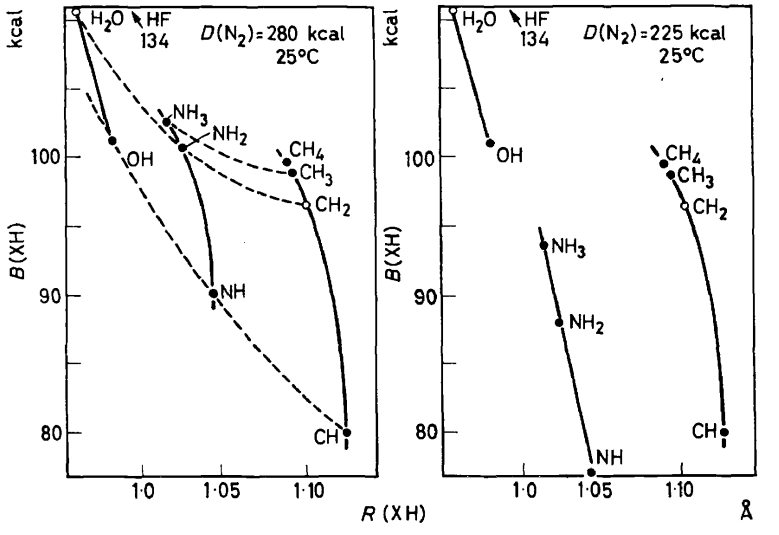

Figure 4

distances. An increase in $D(N_2)$ would raise all B(NH) values. $D(N_2)$ = 11·8 eV was suggested because the term values of N_2 and CO stand in the ratio[4] 1 : 1·066. Another possible value is $D(N_2)$ = 12·14 eV since a pre-dissociation exists in the nitrogen energy level system at 97944 cm^{-1}. If this level is connected with the dissocation process, then lower levels must be perturbations. A lower value ($D(N_2)$ = 265 kcal) was also studied, since then the NH curve would still lie above the CH curve. The comparison of these $D(N_2)$ values is shown in *Table 2.*

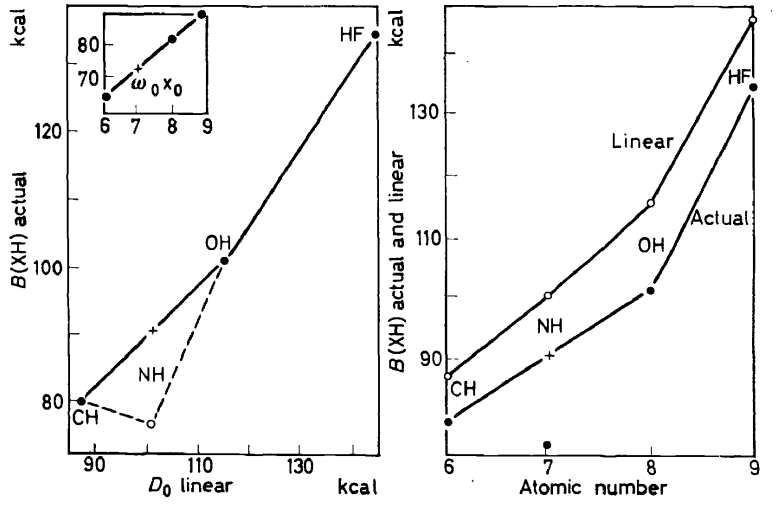

Figure 5

Table 2. Comparison of $D(N_2)$ values

Reference	(2, 3)	(5)	(6)	(4)
$D(N_2)$ (kcal)	225·0	225·0	265·0	280·0
D(NC—CN) (kcal)	114·0	141·5	141·5	141·5
$2C_{(gr)} + N_{2(g)} \rightarrow C_2N_{2(g)}$	− 73·6	− 73·6	− 73·6	− 73·6
$2C \rightarrow 2C_{(gr)}$	340·7	340·7	340·7	340·7
$2N \rightarrow N_{2(g)}$	225·0	225·0	265·0	280·0
$2C + 2N \rightarrow C_2N_{2(g)}$	492·1	492·1	532·1	547·1
$C_2N_{2(g)} \rightarrow 2CN$	−114·4	−141·5	−141·5	−141·5
$2C + 2N \rightarrow 2CN$	377·7	350·6	390·6	405·6
$C + N \rightarrow CN$	188·8	175·3	195·3	202·8
$N_{2(g)} \rightarrow 2N$	−225·0	−225·0	−265·0	−280·0
$2C_{(gr)} \rightarrow 2C$	−340·7	−340·7	−340·7	−340·7
$2C + 2N \rightarrow 2CN$	+377·7	+350·6	+390·6	+405·6
$2C_{(gr)} + N_2 \rightarrow 2CN$	−188·0	−215·1	−215·1	−215·1
$C_{(gr)} + \frac{1}{2}N_{2(gr)} \rightarrow CN$	−94·0	−107·6	−107·6	−107·6

Table 3. Bond energies, distances and force constants of (MH)x; M = C, N, O, F; x = 1, 2, 3, 4. $L(C) = 171{\cdot}7$; $D(H_2) = 104{\cdot}2$; $D(O_2) = 118{\cdot}3$; $D(F_2) = 37{\cdot}6$; $D(N_2) = 225$ or 280 kcal

	R(CH) (A°)	B(CH) (kcal)	Q_a (kcal)	D (kcal)	$10^6 k_e$ (Mdyn/cm)
CH_4	1·093	99·5	398·0		0·539
				101·6	
CH_3	(1·096)	98·8	296·4		(0·470)
				(103·4)	
CH_2	(1·108)	(96·5)	(193·0)		(0·450)
				(113·0)	
CH	1·13	80·0	80·0		0·448
				80·0	
				398·0	
NH_3	1·016	99·9	299·7		0·717
				104·0	
NH_2	1·023	97·9	195·7		0·615
				105·7	
NH	1·048	90·0	90·0		0·600
				90·0	
($D(N_2)$=265 kcal)				299·7	
NH_3	1·106	93·5	280·5		0·717
				104·1	
NH_2	1·025	88·2	176·4		0·615
				99·4	
NH	1·048	77·0	77·0		0·600
				77·0	
($D(N_2)$=225 kcal)				280·5	
H_2O	0·957	110·6	221·2		0·843
				120·0	
OH	0·980	101·2	101·2		0·779
				101·2	
				221·2	
HF	0·926	135·0	135·0	135·0	0·966

From appearance potentials D(NC—CN) = 6·9 eV uncorrected for the kinetic energy of the products[8]. The correction[9] is 0·57 eV and gives D(NC—CN) = 6·3 eV or 145 kcal, in good agreement with the results of shock-tube experiments (141·5 kcal).

Electron-impact experiments[10, 11] show that N^+ ions appear at 24·3 eV, leading to $D(N_2)$ = 225 kcal. In the past such experiments on CO yielded D(CO) = 9·6 eV. However, the latest value is 11·1 eV. A similar change in $D(N_2)$ would bring the higher value suggested here within the range of possibilities.

The relationships shown in *Figure 2* are shown in a different manner in *Figures 3–5*. It seems that any method that might elucidate this problem of hydride energies should be tried since theoretical calcuations are of extreme difficulty[12]. The only suggestion made here is that the value accepted at present will only stand if the supposed anomaly in the sequence of B(MH) values is accounted for.

Notation

B(AB, ABC) = bond energy of the bond AB in the molecule or radical ABC
D(AB) = bond energy or bond dissociation energy in the diatomic molecule or radical AB
D(AB—CD) = bond dissociation energy of ABCD into AB and CD
k_e = force constant (Mdyn/cm)
L(C) = heat of sublimation of graphite at 0°K = 170·4 kcal
R_0 = effective internuclear distance

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