

## Problem Set 5

Dissociation energy of a diatomic molecule is the energy required to dissociate the molecule from the lowest level ( $v=0$ ) of the electronic ground state into the normal (ground state) atoms.

Predissociation limit — the place in the energy level diagram of a molecule at which a predissociation begins — is an upper limit to the dissociation energy.

Facts: (from spectroscopy)

- energies at which predissociation begins are 9.8 eV in the  $a^1\Pi_g$  excited state of  $N_2$   
9.839 eV in the  $B^3\Pi_g$  state
- highest observed vibrational state of the ground electronic state lies at 6.6 eV

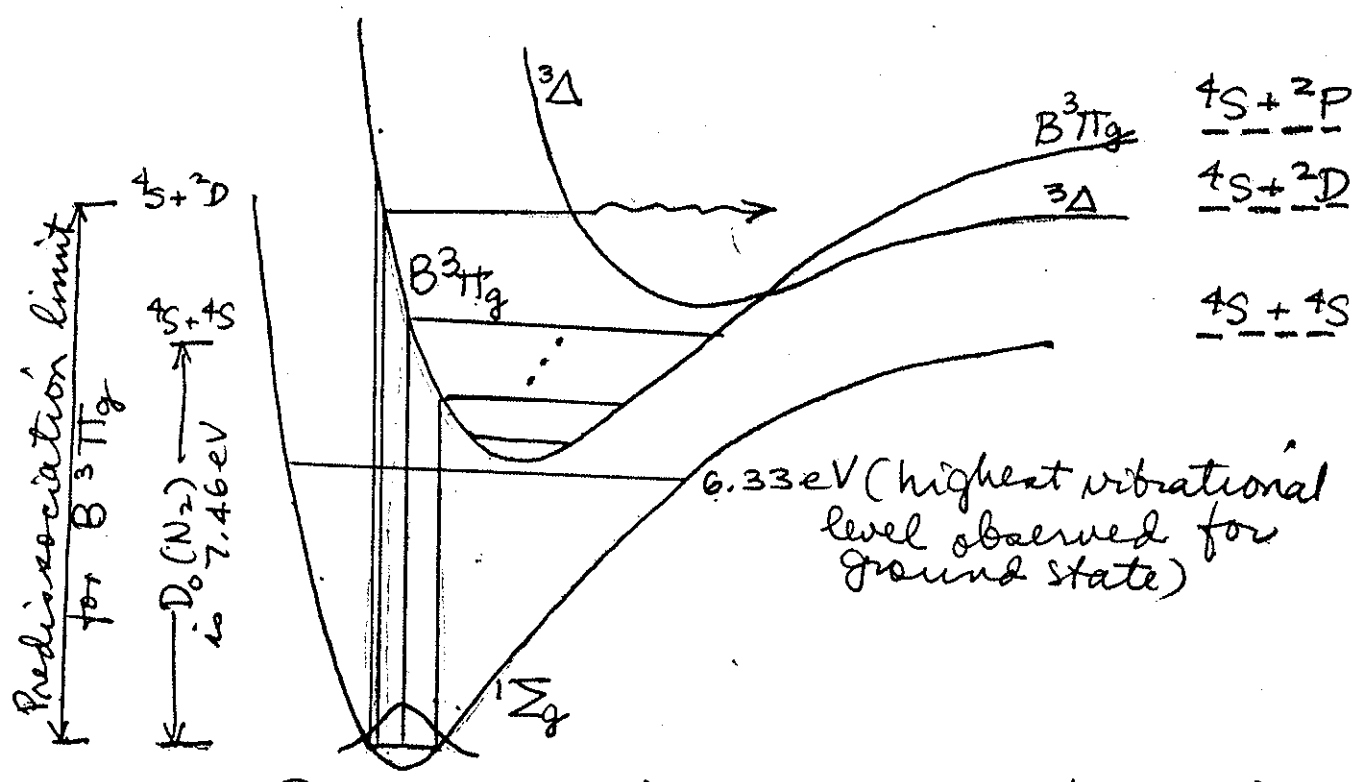
① Herzberg: From these and the nature of the breaking-off observed in the spectra, Herzberg reasons out:

The  $B^3\Pi_g$  predissociation is caused by a  $\Pi$  or  $\Delta$  state. A  $\Pi$  or  $\Delta$  state cannot result from the  $4S+4S$  atoms. Thus the dissociation products at the 9.839 predissociation must be  $4S+^2D$ . All other possibilities,  $4S+^2P$  etc, lead to dissociation energies smaller than 6.6 eV, the highest vibrational level observed for the ground state  $N_2$ . This leads to  $D_0(N_2)$  of  $(4S+^2D)$  atoms —  $(4S+4S)$  atoms]

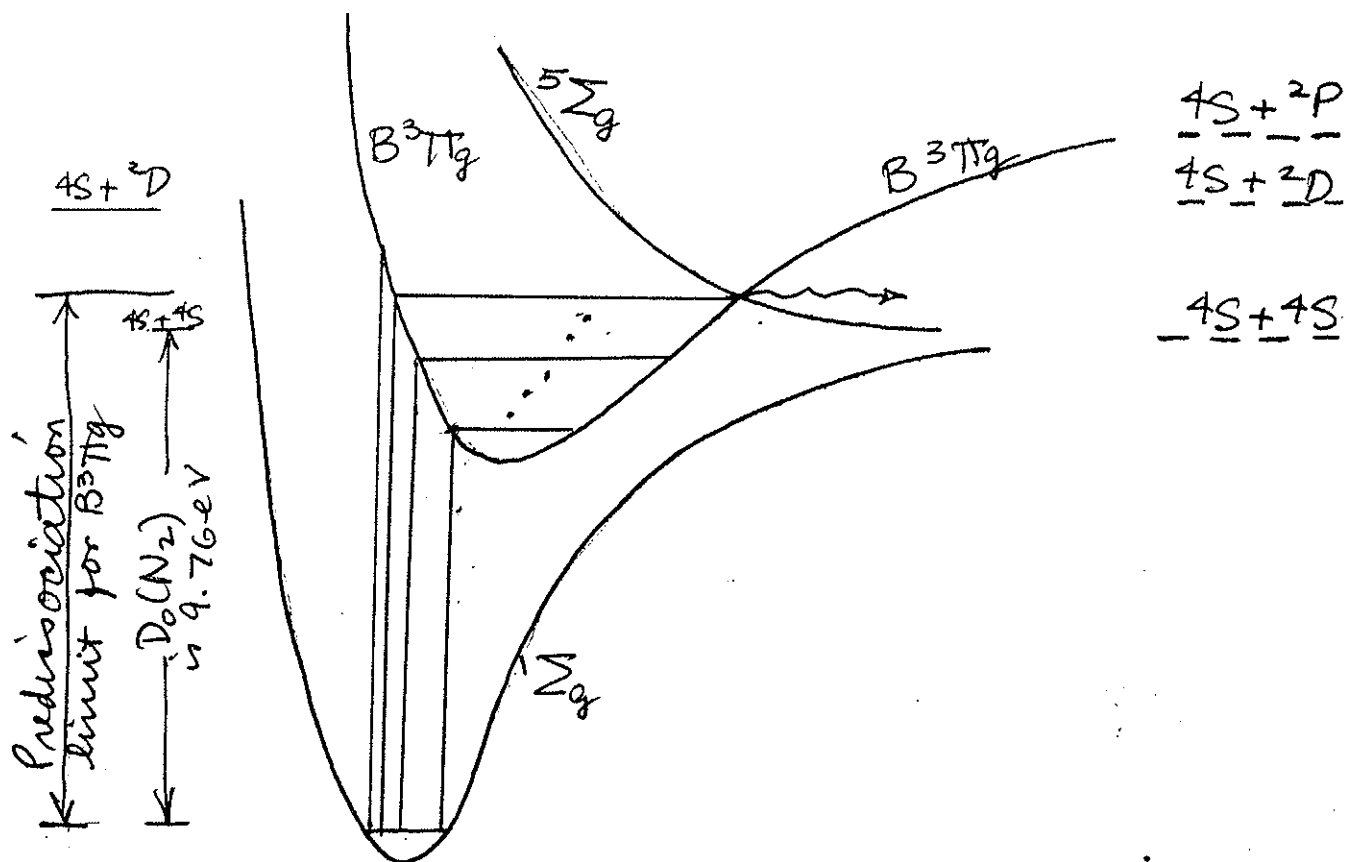
$$9.839 \text{ eV} - [(4S+^2D) \text{ atoms} - (4S+4S) \text{ atoms}]$$

$E(^2D-^4S)$  is  $19202 \text{ cm}^{-1} = 2.383 \text{ eV}$   
 Thus,  $D_0(N_2) = 9.839 \text{ eV} - 2.383 \text{ eV} = 7.456 \text{ eV}$

② Gaydon: Herzberg's arguments are ok provided that predissociation observed occurs by the way he describes. But with the alternative explanation (by Gaydon) that the  $B^3\Pi_g$  predissociation is caused by a  $5\Sigma$  level (which results from the same  $4S+4S$  separated N atoms as the ground state does) then  $D_0(N_2) = 9.76$  cannot be ruled out.



Dramatization of Herzberg's version



Dramatization of Gaydon's version

SAMPLE SOLUTION TO THE EXAM:

③  $\Delta G^\circ = -RT \ln K_p$

$G = -RT \ln Q$

(Moore pp. 635-637 shows the same solution to #3, but for  $\text{Na}_2$ )

Standard state  $\frac{Q^\circ}{N_{\text{Avo}}}$  (1 mole at a partial pressure of 1 atm) are same as given in last page of exam for  $Q_{\text{vib}}$ ,  $Q_{\text{rot}}$ ,  $Q_{\text{elec}}$  but  $Q_{\text{trans}}^\circ$  (standard state) =  $\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{RT}{1 \text{ atm}}$

where we substituted  $v = RT/1 \text{ atm}$

Thus  $\Delta G^\circ = -RT \ln K_p = -RT \left\{ \sum \ln \left( \frac{Q^\circ}{N_{\text{Avo}}^{\text{prod}}} \right) - \sum \ln \left( \frac{Q^\circ}{N_{\text{Avo}}^{\text{react}}} \right) \right\}$

or  $K_p = \frac{\prod_{\text{products}} \left( \frac{Q^\circ}{N_{\text{Avo}}} \right)^p}{\prod_{\text{reactants}} \left( \frac{Q^\circ}{N_{\text{Avo}}} \right)^r}$

with energies in  $Q^\circ$  expressions all measured from the same base. If  $Q_{vib}$  for  $N_2$  is to be measured from  $v=0$  level as in  $Q_{vib} = \frac{1}{1 - e^{-h\nu/kT}}$  then the difference between the zero of energies for 2 N atoms and the zero of energy for  $N_2$  molecule is just  $D_0(N_2)$ . We can factor this out.

$$K_p = \frac{(Q^\circ/N_{Av})^2 N}{(Q^\circ/N_{Av})_{N_2}} e^{-D_0(N_2)}$$

where now the  $Q_{elec}$  in both atoms and molecule are measured from their respective ground states

$$Q^\circ_{N_{atom}} = Q_{elec} \cdot \left( \frac{2\pi m_N kT}{h^2} \right)^{3/2} \frac{RT}{10^5 \text{ atm}}$$

$$Q^\circ_{N_2 \text{ molecule}} = Q_{elec} \cdot Q_{vib} \cdot Q_{rot} \left( \frac{2\pi 2m_N kT}{h^2} \right)^{3/2} \frac{RT}{10^5 \text{ atm}}$$

N atom electronic levels:

$$19,202 \text{ cm}^{-1} = 2.383 \text{ eV}$$

$$28,808 \text{ cm}^{-1} = 3.574 \text{ eV}$$

$$kT \text{ at } 3410^\circ \text{K} = .293845 \text{ eV}$$

$$kT \text{ at } 3530^\circ \text{K} = .304186 \text{ eV}$$

$$e^{-E/kT} \text{ for excited N} \begin{cases} \text{for } E = 2.383 \text{ eV} \\ i_1 \sim e^{-8} \ll 1 \\ \text{for } E = 3.574 \text{ eV} \\ i_2 \sim e^{-12} \ll 1 \end{cases}$$

$N_2$  molecule

$$\text{for excited } N_2 \begin{cases} \text{for } E \sim 6 \text{ eV} \\ i_3 \sim e^{-20} \ll 1 \end{cases}$$

Thus we need not consider  $g_i e^{-E_i/kT}$  other than ground states of N and  $N_2$ .

$Q_{elec} = 1$  for  $N_2$  and  $Q_{elec} = 4$  for N atom

$$K_p = \frac{RT}{1 \text{ atm } N_{A00}} \frac{\left[ \frac{(2\pi m_N kT)^{3/2}}{h^2} \right]^2 4^2 e^{-D_0(N_2)/kT}}{\left( \frac{2\pi 2m_N kT}{h^2} \right)^{3/2} \frac{1}{1-e^{-h\nu/kT}} \frac{8\pi^2 I kT}{2h^2}} \quad (5)$$

where symmetry number  $\sigma = 2$  since  $N_2$  is made up of identical atoms, and

$$I = \mu r^2 = \frac{m_N}{2} r^2$$

$$K_p = e^{-D_0(N_2)/kT} \frac{(1 - e^{-h\nu/kT})^2 (kT)^{3/2} (m_N)^{3/2}}{h \pi^{1/2} r^2 (1 \text{ atm})}$$

Extent of dissociation  $\alpha$

$$N_2 = 2N$$

$$1 - \alpha$$

$$2\alpha$$

$$\text{Total mole} = 1 + \alpha$$

$$K_p = \frac{\left( \frac{2\alpha}{1+\alpha} P_{1 \text{ atm}} \right)^2}{\frac{1-\alpha}{1+\alpha} P_{1 \text{ atm}}} = \frac{4\alpha^2}{1-\alpha^2} P_{1 \text{ atm}}$$

Using  $D_{N_2}^{\circ\circ} = 7.385 \text{ eV}$  we get

$$\text{at } P = 0.61 \text{ mmHg } T = 3410^\circ \text{K}, \alpha = 0.143$$

$$\text{at } P = 1.11 \text{ mmHg } T = 3530^\circ \text{K}, \alpha = 0.163$$

Using  $D_{N_2}^{\circ} = 9.765 \text{ eV}$  we get

under both conditions  $\alpha \sim 0.0025$

Since level of detection was said to be about  $10^{-2}$ , this experiment clearly shows that  $D_{N_2}^{\circ}$  is greater than  $7.385 \text{ eV}$

Substitution of  $\alpha = 0.01$  (exptl limit)

$$\text{at } T = 3410^\circ \text{K}, P = 0.61 \text{ mmHg}$$

and solving for  $D_0(N_2)$  gives

$D_0(N_2) = 8.80 \text{ eV}$ . Therefore this experiment shows that  $D_0(N_2)$  has to be greater than  $8.80 \text{ eV}$ .

④  $N_2 + e = N^+(\text{some state}) + N(\text{some state}) + 2e$   
 Appearance potential for above reaction  
 $= D_0(N_2) + IP(N) + \text{energy of excitation of } N^+$   
 $+ \text{energy of excitation of } N$

Since  $IP(N)$  is given as  $14.53 \text{ eV}$ , the following are the possible values of appearance potentials:

state of N	state of $N^+$	Appearance potential
4S	3P	$D_{N_2}^0 + 14.53 \text{ eV} + 0 + 0$
2D	3P	$D_{N_2}^0 + 14.53 \text{ eV} + E(2D-4S) + 0$
2P	3P	$D_{N_2}^0 + 14.53 \text{ eV} + E(2P-4S) + 0$
4S	1D	$D_{N_2}^0 + 14.53 + 0 + E(1D-3P)$
4S	1S	$D_{N_2}^0 + 14.53 + 0 + E(1S-3P)$
etc		

or some other combinations of excitations for both  $N$  and  $N^+$

Assume  $D_{N_2}^0 = 9.765$  we get  
 $4S, 3P \text{ A.P.} = 9.765 + 14.53 + 0 + 0 = 24.295 \text{ eV}$   
 $2D, 3P \text{ A.P.} = 9.765 + 14.53 + 2.383 + 0 = 26.678 \text{ eV}$   
 $2P, 3P \text{ A.P.} = 9.765 + 14.53 + 3.574 + 0 = 27.864 \text{ eV}$   
 etc.

On the other hand, if we assume  $D_{N_2}^0 = 7.385$  we get  
 $4S, 3P \text{ A.P.} = 7.385 + 14.53 + 0 + 0 = 21.915 \text{ eV}$   
 $2D, 3P \text{ A.P.} = 7.385 + 14.53 + 2.383 + 0 = 24.298$   
 $2P, 3P \text{ A.P.} = 7.385 + 14.53 + 3.574 + 0 = 25.489$   
 etc.

Observed A.P. 's are

- 24.32 ± 0.02 eV
- 26.66 ± 0.05 eV
- 27.93 ± 0.05 eV

Although 24.298 (from previous page) is ~ 24.32 ± 0.02 eV, not any of 21.915 or 25.489 eV or numbers within experimental error from these appeared in the experiment. On the other hand

24.32 ± 0.02	compares with	24.295
26.66 ± 0.05	" "	26.678
27.93 ± 0.05	" "	27.864

Thus this experiment agrees with  $D_0(N_2)$  value of 9.765 but not with 7.385. (If I had remembered to supply you with  $N_2^+$  excited states also, it would really clinch it.)

### SUMMARY + CONCLUSIONS

- ① Herzberg:  $D_0(N_2)$  has to be 7.46 eV (more accurately 7.385)
- ② Gaydon:  $D_0(N_2) = 9.76$  eV (more accurately 9.765) if spectral results are interpreted in an alternative way.
- ③ Hendrie:  $D_0(N_2) \geq 8.8$  eV since thermal dissociation would have been observed if  $D_0(N_2)$  were less than 8.8 eV
- ④ Frost + McDowell:  $D_0(N_2) = 9.76$  eV is the value which fits all three breaks in the ionization curve.

CONCLUSION -  $D_0(N_2) = 9.765$  rather than  $7.385$  eV.

Thus the electron impact measurements of Frost and McDowell, and the thermal dissociation measurements of Hendrie show that Gaydon's interpretation of the  $N_2$  electronic spectra was right and Herzberg's interpretation was wrong. Note that from the spectra alone, the choice between  $9.765$  and  $7.385$  could not be clearly resolved.

P.S. This write-up is of course much more detailed than one which could have obtained a passing grade!

Jameson