

TOPIC

Dr. R. K. Hazra

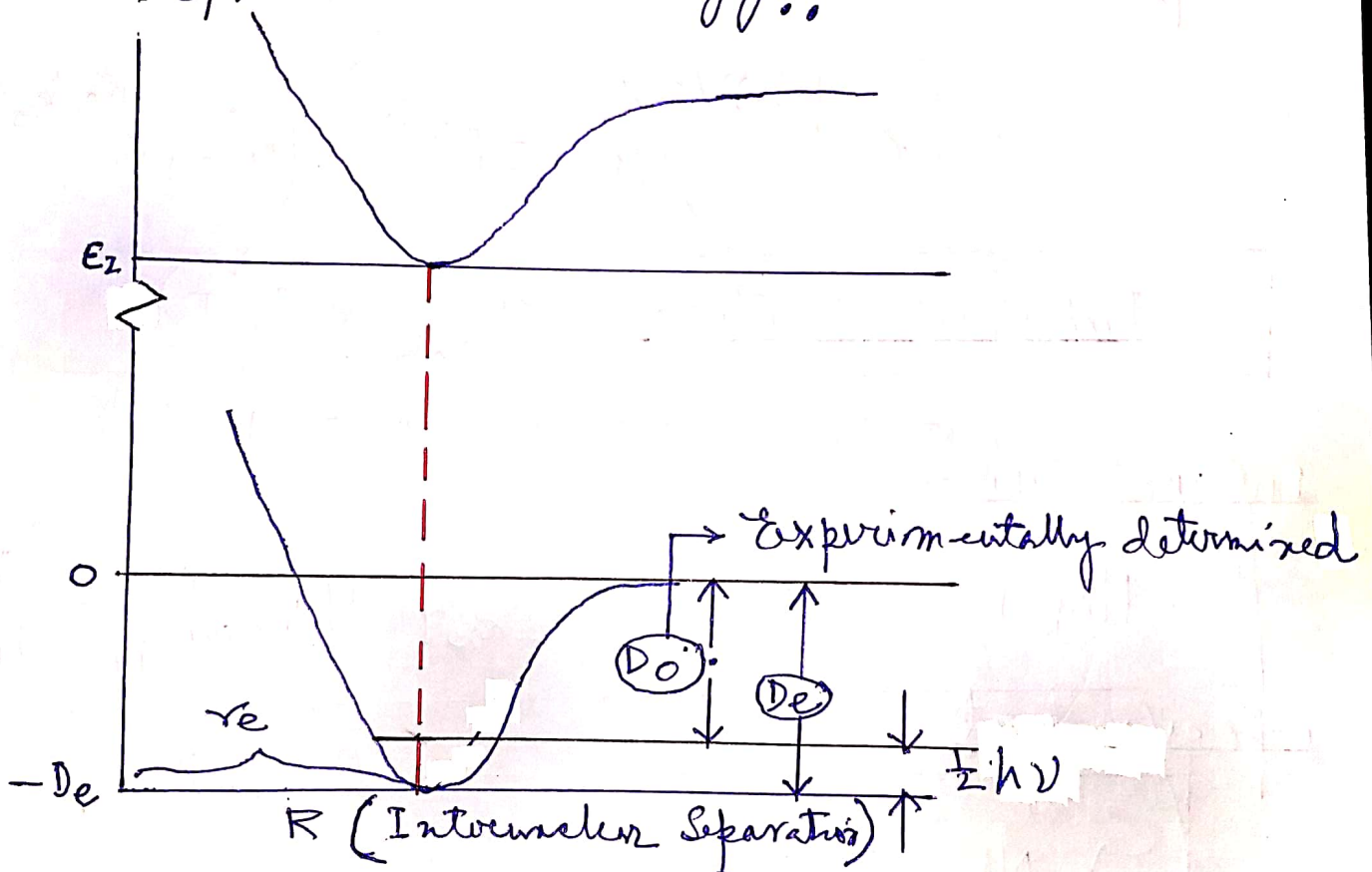
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Electronic Partition Functions of Diatomic Molecules

$$q_{elec} = \sum_{i=1}^{\infty} w_i e^{-\beta \epsilon_i}$$

How & where to set origin for Ground state energy!!



When $R \rightarrow \infty$, D_0 dissociates molecule (diatomic)

when $R \rightarrow r_e$, diatomic molecule has bottom of the internuclear potential with background vibrational energy added to yield D_0

Thus $D_0 = D_e - \frac{1}{2} h \nu$

We can reset $\sum_{i=1}^{\infty} = \text{Ground state energy} = -D_e$

$$\rightarrow q_{v,elec} = \omega_{e1} e^{-E_{e1}/k_B T} + \omega_{e2} e^{-E_{e2}/k_B T} + \dots$$

TOTAL PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS OF DIATOMIC MOLECULES

$$q_{tot} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) \times \left\{ \frac{e^{-\beta h\nu/2}}{(1 - e^{-\beta h\nu})} \right\} \left(\omega_{e1} e^{-E_{e1}/k_B T} + \dots \right)$$

Important feature $q_{tot} = f(T) V$

alike monoatomic gases

Internal Energy

$$\left(\frac{E}{N k_B T} \right) = \frac{5}{2} + \frac{h\nu}{2 k_B T} + \left(\frac{h\nu/k_B T}{e^{h\nu/k_B T} - 1} \right) - \frac{E_{e1}}{k_B T}$$

Specific heat

$$\left(C_v / N k_B \right) = \frac{5}{2} + \left(\frac{h\nu}{k_B T} \right) \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2}$$

Pressure

$$\bar{p} = \frac{N k_B T}{V}$$

$$\Rightarrow \bar{p} V = N k_B T$$

Entropy

$$S = \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \left(\frac{V e^{5/2}}{N} \right) \right] + \ln \left(\frac{8\pi^2 I k_B T e}{\sigma h^2} \right) + \left(\frac{h\nu/k_B T}{e^{h\nu/k_B T} - 1} \right) - \ln(1 - e^{-h\nu/k_B T}) + \ln(\omega_{e1}) + \dots$$