CHM 421/621
Statistical Mechanics

Lecture 32 Chemical Equilibrium

Applications of Statistical Mechanics

Lecture Plan

Total partition function of ideal diatomic gas

Application to Chemical Equilibrium

Applications

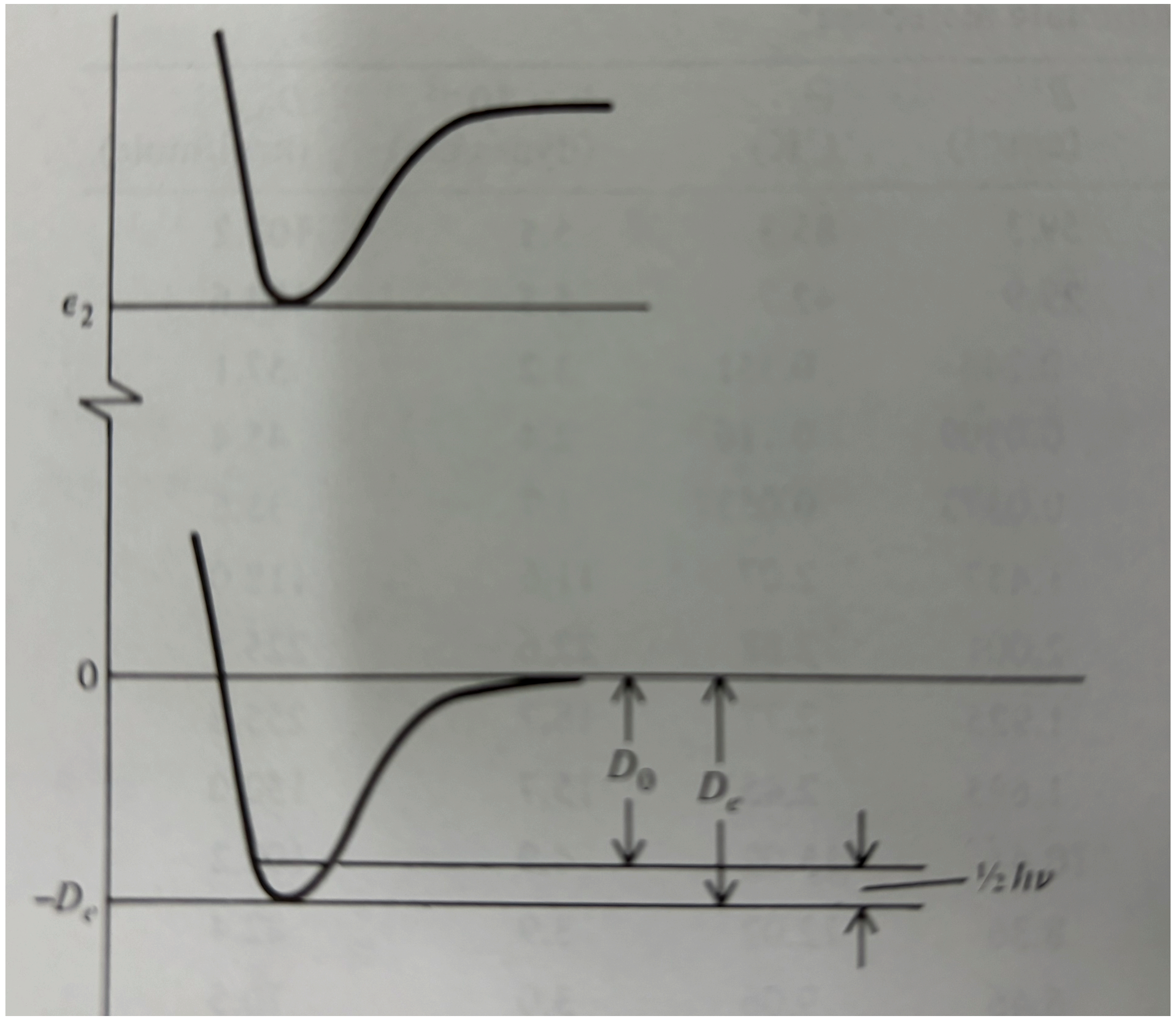
Electronic partition function

Conventionally, we take the zero of energy of the diatomic to be the isolated atoms.

Then, the dissociation energy of the molecule is D_0 (spectroscopically measurable).

We take the energy of the ground electronic state as $-D_e$.

The zeros of the vibrational and rotational sub-systems were with respect to this ground state.



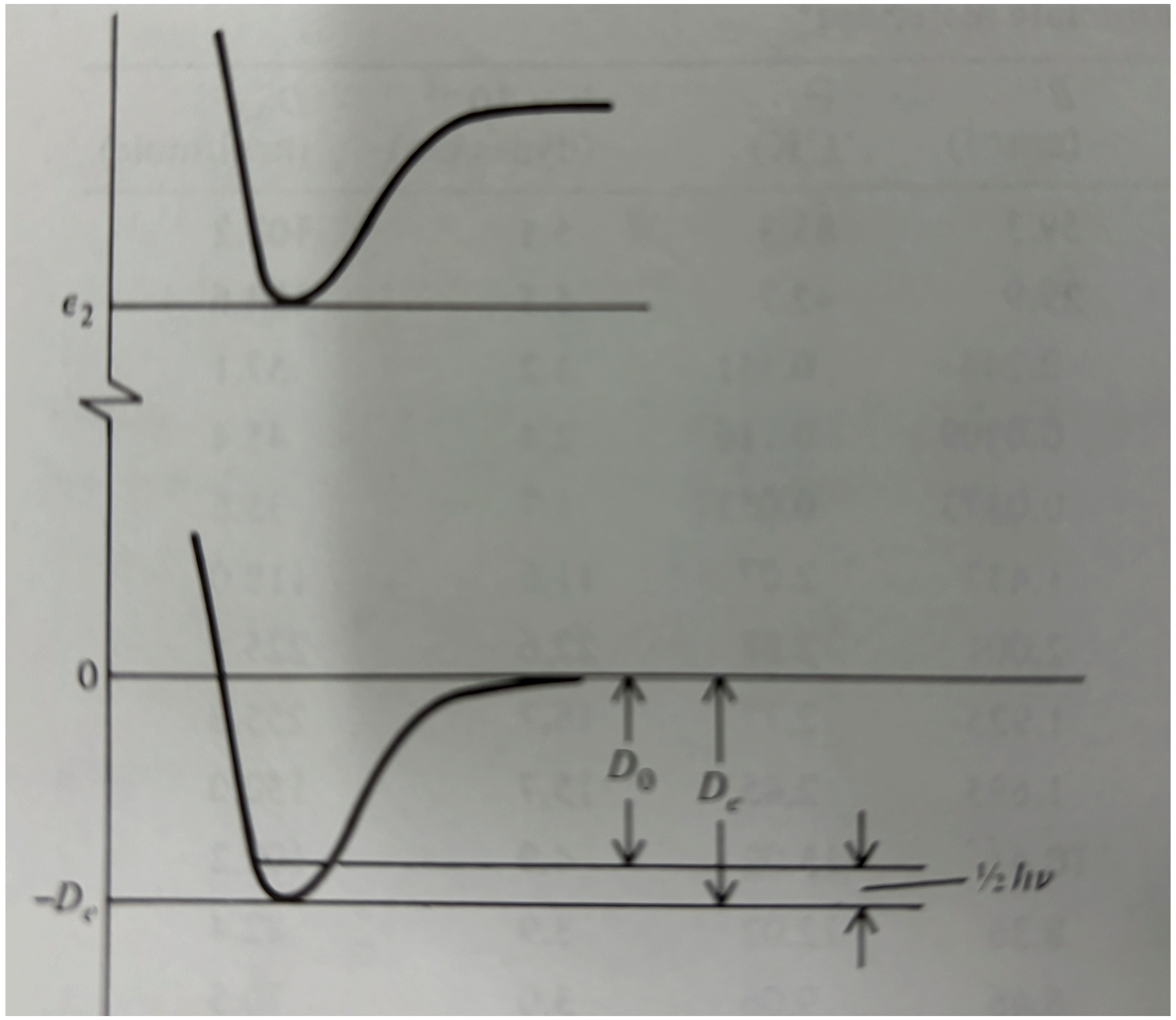
Applications

Electronic partition function

Assuming that the molecules are independent of each other, we can write down the molecular electronic partition function as

$$z_{elec} = \omega_{e1} \mathrm{e}^{\frac{D_e}{k_B T}} + \omega_{e2} \mathrm{e}^{\frac{-\epsilon_2}{k_B T}} + \cdots$$

Level degeneracies



For most diatomics D_e ~ electron-volts
(~100 kcal/mol or ~1000 K)

Therefore, we do not expect much contribution from higher electronic levels than the ground-state.

Applications

Total molecular partition function of the ideal diatomic gas

Assembling together all the contributions, we get

$$z(V,T) = z_{trans}\; z_{rot}\; z_{vib}\; z_{elec}\; z_{nucl}$$

$$z_{trans} = \frac{V}{\Lambda^3} \qquad \Lambda = \frac{h}{\sqrt{2\pi M k_b T}}$$

$$z_{rot} = \frac{T}{\sigma\Theta_r}\left(1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + O\left(\left(\frac{\Theta_r}{T}\right)^3\right)\right)$$

$$z_{vib} = \frac{\exp(-\beta\frac{\hbar\omega}{2})}{1-\exp(-\beta\hbar\omega)}$$

Non-degenerate

$$z_{elec} = \omega_{e1}\mathrm{e}^{\frac{D_e}{k_B T}} \quad z_{nucl} = (2I+1)^2$$

Total partition function $Z = \dfrac{z^N}{N!}$

Applications

Chemical Equilibrium

Calculating the equilibrium constant from statistical mechanics

Consider the following gaseous reaction at equilibrium at constant temperature and volume

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

For any infinitesimal change in molecule numbers along the reaction we must have

$$dN_j = \nu_j d\lambda$$

Now, in this process of infinitesimal change the change in the Helmholtz free energy is

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

$$= \sum_j \nu_j \mu_j d\lambda$$ At constant T and V

Convention

Here v_j are (+) for products and (-) for reactants

Therefore, condition for equilibrium is

$$\boxed{\frac{dA}{d\lambda} = \sum_j \nu_j \mu_j = 0}$$

Applications

Chemical Equilibrium

The statistical mechanical connection

Assuming all components are all ideal gases we can write

$$\begin{aligned} Z(N_A, N_B, N_C, N_D, V, T) &= Z(N_A, V, T) Z(N_B, V, T) Z(N_C, V, T) Z(N_D, V, T) \\ &= \frac{z(V,T)^{N_A}}{N_A!} \frac{z(V,T)^{N_B}}{N_B!} \frac{z(V,T)^{N_C}}{N_C!} \frac{z(V,T)^{N_D}}{N_D!} \end{aligned}$$

And,

$$A(\{N_j\}, V, T) = -k_B T \ln\, Z(\{N_j\}, V, T)$$

So for each component we can write,

$$\mu_A = -k_B T \left(\frac{\partial \ln Z}{\partial N_A} \right)_{N_j, V, T} = -k_B T \ln \frac{z_A(V,T)}{N_A}$$

Applications

Chemical Equilibrium

Calculating the equilibrium constant from statistical mechanics

Substituting in the previous expression we get

$$\frac{N_C^{\nu_C}\,N_D^{\nu_D}}{N_A^{\nu_A}\,N_B^{\nu_B}} = \frac{z_C^{\nu_C}\,z_D^{\nu_D}}{z_A^{\nu_A}\,z_B^{\nu_B}}$$

$$K_c(T) = \frac{\rho_C^{\nu_C}\,\rho_D^{\nu_D}}{\rho_A^{\nu_A}\,\rho_B^{\nu_B}} = \frac{(z_C/V)^{\nu_C}\,(z_D/V)^{\nu_D}}{(z_A/V)^{\nu_A}\,(z_B/V)^{\nu_B}}$$

Since for ideal gas *z* = f(T) V

Applications

Chemical Equilibrium

Example

$$2Na \rightleftharpoons Na_2$$

K_p(1000 K) = ?

Given,

$$\Theta_v = 229K$$

$$D_0 = 17.3kcal/mol$$

$$\Theta_r = 0.221K$$

Ground electronic state of Na_2 is $^2S_{1/2}$

Second excited state is 16000 cm^{-1} above ground state.