Reaction Dynamics and Kinetics
– Practical Statistical Theory of Chemical Reactions

1. Introduction – Statistical Mechanics

1.1 Microcanonical ensemble

= isolated molecule exchanging energy between internal motions; $E_{\text{molecule}} = \sum\limits_{\text{internal modes}} \varepsilon_i = \text{const.}$

[application] photo-excited molecules, unimolecular reactions

· probability of finding a molecule in state i

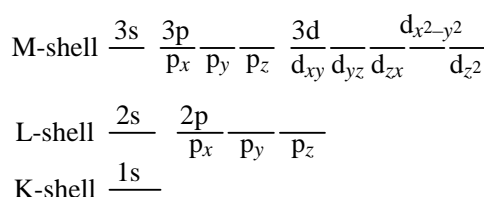$$P_i \propto g_i \qquad\qquad\qquad (1.1)$$

g_i : degeneracy of state i

⟨Degeneracy⟩

= multiplicity of a quantum mechanical eigenstate (number of solutions found at the same eigenvalue)

[example] Hydrogen atom

$$P(2^2S\,[2s^1]) : P(2^2P\,[2p^1]) = 1 : 3$$

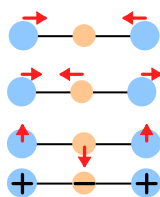· 2s orbital is not degenerated but 2p orbital is triply degenerated, namely, $2p_x$, $2p_y$, $2p_z$

[example] CO_2 vibrational states (v_1, v_2, v_3)

· ν_1 : symmetric C=O stretching
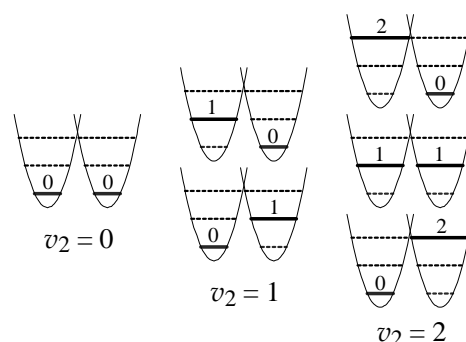
· ν_3: asymmetric C=O stretching

· ν_2: degenerated bending vibration

$$P(1, 0, 0) : P(0, 2, 0) = 1 : 3$$

since $g(v_1, 0, 0) = 1$ and

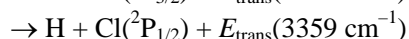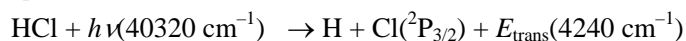$g(0, v_2, 0) = v_2 + 1$ (see the figure right ward for explanation)

⟨Density of states⟩

= number of states per unit energy

[example] Photo dissociation of HCl at 248 nm ($40320\ \text{cm}^{-1}$)

$$\text{HCl} + h\nu(40320\ \text{cm}^{-1}) \rightarrow \text{H} + \text{Cl}(^2P_{3/2}) + E_{\text{trans}}(4240\ \text{cm}^{-1})$$
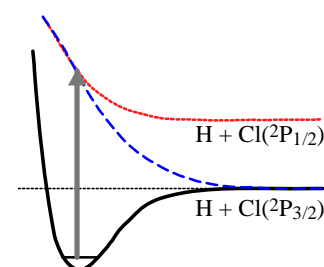$$\rightarrow \text{H} + \text{Cl}(^2P_{1/2}) + E_{\text{trans}}(3359\ \text{cm}^{-1})$$

· statistical branching ratio;

$$P_{3/2} : P_{1/2} = g[\text{Cl}(^2P_{3/2})]\rho_{\text{trans}}(4240\ \text{cm}^{-1}) : g[\text{Cl}(^2P_{1/2})]\rho_{\text{trans}}(3359\ \text{cm}^{-1})$$

with $g[\text{Cl}(^2P_J)] = 2J + 1$ and $\rho_{\text{trans}}(E) \propto E^{1/2}$,

$$P_{3/2} : P_{1/2} = 4\times(4240)^{1/2} : 2\times(3359)^{1/2} \sim 2.25 : 1$$

H + Cl($^2P_{1/2}$)

H + Cl($^2P_{3/2}$)

Problem-1

Calculate the statistical branching ratio between H + I($^2P_{3/2}$) and H + I($^2P_{1/2}$) upon the photolysis of HI at 266 nm. Bond dissociation energy of HI [$\rightarrow$ H + I($^2P_{3/2}$)] is 298 kJ mol^{-1} and excitation energy of I($^2P_{1/2}$) form I($^2P_{3/2}$) is 0.943 eV.

1.2 Canonical ensemble

= ensemble of molecules exchanging energy between molecules; $E_{\text{ensemble}} = \sum\limits_{\text{molecules}} E_i = \text{const.}$

[application] usual chemical equilibrium, transition state theory

⟨Boltzmann distribution⟩

· Probability of finding a molecule in state i;
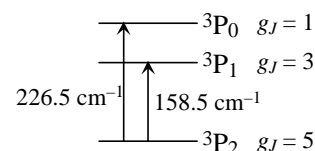
$$P_i \propto g_i \exp(-\varepsilon_i / k_{\text{B}}T) \tag{1.2}$$

[example] Distribution of fine structure of ground state oxygen atom @ 298 K
· 1 cm^{-1} = 1.4388 K

$N(^3P_2) \propto 5 \exp(-0 / 298) = 5.00$
$N(^3P_1) \propto 3 \exp(-158.5 \times 1.4388 / 298) = 1.40$
$N(^3P_0) \propto 1 \exp(-226.5 \times 1.4388 / 298) = 0.34$

$^3P_0 \quad g_J = 1$
$^3P_1 \quad g_J = 3$
226.5 cm^{-1} | 158.5 cm^{-1}
$^3P_2 \quad g_J = 5$

⟨Partition function⟩

= sum of Boltzmann distribution probability over states (in relevant internal mode, in whole molecule, *etc.*)

$$P \propto Q = \sum\limits_i g_i \exp(-\varepsilon_i / k_{\text{B}}T) \tag{1.3}$$

⟨Chemical equilibrium⟩

· Equilibrium constant;

$$K = \frac{N(\text{B})}{N(\text{A})} = \frac{Q'_{\text{B}}}{Q'_{\text{A}}}$$

or

$$K = \frac{N(\text{B})}{N(\text{A})} = \frac{Q_{\text{B}}}{Q_{\text{A}}} \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right) \tag{1.4}$$

Q' : calculated from common energy origin
Q : calculated from the ground state of each molecule