1. Introduction - Statistical Mechanics

1.1 Microcanonical ensemble
= isolated molecule exchanging energy between internal motions; \[ E_{\text{molecule}} = \sum E_i = \text{const.} \]

[application] photo-excited molecules, unimolecular reactions
\[ P_i \propto g_i \]  
\( g_i \): degeneracy of state \( i \)  

\langle \text{Degeneracy} \rangle = \text{multiplicity of a quantum mechanical eigenstate (number of solutions found at the same eigenvalue)}

\text{[example]} \text{ Hydrogen atom } 
\[ P(2^2S \ [2s^1]) : P(2^2P \ [2p^1]) = 1 : 3 \]
\cdot 2s orbital is not degenerated but 2p orbital is triply degenerated, namely, 2p_\text{x}, 2p_\text{y}, 2p_\text{z}

\text{[example]} \text{ CO}_2 \text{ vibrational states } (v_1, v_2, v_3)
\cdot v_1: \text{symmetric C=O stretching} 
\cdot v_2: \text{asymmetric C=O stretching} 
\cdot v_3: \text{degenerated bending vibration} 
\[ P(1, 0, 0) : P(0, 2, 0) = 1 : 3 \]
\text{since } g(v_1, 0, 0) = 1 \text{ and } g(0, v_2, 0) = v_2 + 1 \text{ (see the figure right ward for explanation)}

\langle \text{Density of states} \rangle = \text{number of states per unit energy}

\text{[example]} \text{ Photo dissociation of HCl at } 248 \text{ nm (40320 cm}^{-1}) 
\text{HCl} + h\nu(40320 \text{ cm}^{-1}) \rightarrow \text{H} + \text{Cl}(^2\text{P}_{3/2}) + E_{\text{trans}}(4240 \text{ cm}^{-1}) 
\rightarrow \text{H} + \text{Cl}(^2\text{P}_{1/2}) + E_{\text{trans}}(3359 \text{ cm}^{-1})

\cdot \text{statistical branching ratio; } 
\[ P_{3/2} : P_{1/2} = g[\text{Cl}(^2\text{P}_{3/2})]\rho_{\text{trans}}(4240 \text{ cm}^{-1}) : g[\text{Cl}(^2\text{P}_{1/2})]\rho_{\text{trans}}(3359 \text{ cm}^{-1}) \]
\text{with } g[\text{Cl}(^2\text{P}_J)] = 2J + 1 \text{ and } \rho_{\text{trans}}(E) \propto E^{1/2},
\[ P_{3/2} : P_{1/2} = 4 \times (4240)^{1/2} : 2 \times (3359)^{1/2} \approx 2.25 : 1 \]

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

© 2000-2006 by A. Miyoshi, all rights reserved.
1.2 Canonical ensemble
= ensemble of molecules exchanging energy between molecules; \( E_{\text{ensemble}} = \sum_{i} E_i = \text{const.} \)

[application] usual chemical equilibrium, transition state theory

\[ \text{Boltzmann distribution} \]
\[ P_i \propto g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) \quad (1.2) \]

[example] Distribution of fine structure of ground state oxygen atom @ 298 K
- \( \text{cm}^{-1} = 1.4388 \text{ K} \)
- \( N(3P_2) \propto 5 \exp(-0 / 298) = 5.00 \)
- \( N(3P_1) \propto 3 \exp(-158.5 \times 1.4388 / 298) = 1.40 \)
- \( N(3P_0) \propto 1 \exp(-226.5 \times 1.4388 / 298) = 0.34 \)

\[ \text{Partition function} \]
\[ P \propto Q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) \quad (1.3) \]

\[ \text{Chemical equilibrium} \]
\[ K = \frac{N(B)}{N(A)} = \frac{Q'_B}{Q'_A} \]

or
\[ K = \frac{N(B)}{N(A)} = \frac{Q_B}{Q_A} \exp\left\{ -\frac{\Delta E}{k_B T} \right\} \quad (1.4) \]

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