Reaction Dynamics
– Advanced Statistical Theory of Chemical Reactions

1. Introduction

1.1 Statistical Theory of Canonical Ensemble (カノニカル集合; 正準集合) – *review*

· free intermolecular energy exchange under constraint: $\sum E_i = const.$

ex.) normal gas state

〈Boltzmann Statistics〉

Probability of finding a molecule in state i (energy: E_i, multiplicity: g_i)

$p_i \propto g_i \exp(-E_i / k_B T)$

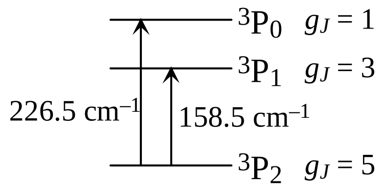
ex.) Distribution of ground triplet states of atomic oxygen;

$^3P_2$, $^3P_1$, and $^3P_0$ at 298 K (1 cm^{-1} = 1.4388 K)

$N(^3P_2) \propto 5 \exp(-0 / 298) = 5.00$

$N(^3P_1) \propto 3 \exp(-158.5\times1.4388 / 298) = 1.40$

$N(^3P_0) \propto 1 \exp(-226.5\times1.4388 / 298) = 0.34$



〈Partition Function (分配関数)〉

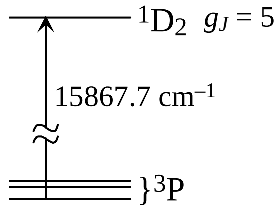
Probability of finding a molecule in a set of states A: $p_A = \sum_A p_i \propto$

$$Q_A = \sum_A g_i \exp\left(-E_i / k_B T\right) \quad \text{... partition function} \qquad (1.1.1)$$

ex.) Distribution of triplet ground states ($^3P = {}^3P_2 + {}^3P_1 + {}^3P_0$) and excited ($^1D$) state of atomic oxygen at 298 K:

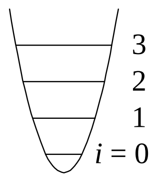
$$N(^3P) \propto Q(^3P) = \sum_{J=0}^{2} (2J+1)\exp\left(-E_J / k_B T\right) = 6.74$$

$$N(^1D) \propto 5 \exp(-15867.7\times1.4388 / 298) = 2.7\times10^{-33}$$



ex.) Vibrational partition function (harmonic approx.; $E_i = ih\nu$):

$$Q_{vib} = \sum_{i=0}^{\infty} \exp\left(-ih\nu / k_B T\right) = \left[1 - \exp\left(-h\nu / k_B T\right)\right]^{-1} \qquad (1.1.2)$$



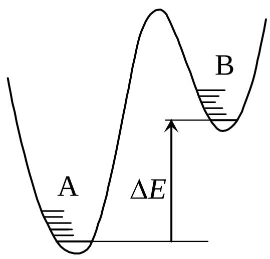
〈Chemical Equilibrium〉

Ratio of the distributions of molecule B to A:

$$K_e = \frac{[B]_e}{[A]_e} = \frac{Q'_B}{Q'_A}$$, (same energy origin for Q_A, and Q_B) or

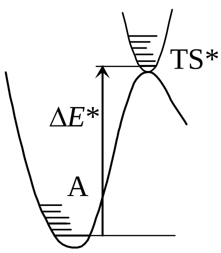
$$K_e = \frac{[B]_e}{[A]_e} = \frac{Q_B}{Q_A} \exp\left(-\frac{\Delta E}{k_B T}\right) \qquad (1.1.3)$$

(energy origin is each ground state for Q_A and Q_B)



〈Transition-State Theory (遷移状態理論)〉

$$k\,(A \to [TS^*] \to B) = \frac{k_B T}{h} \frac{Q_{TS^*}}{Q_A} \exp\left(-\frac{\Delta E^*}{k_B T}\right) \qquad (1.1.4)$$



1.2 Statistical Theory of Microcanonical Ensemble (微視的正準集合)

· free <u>intra</u>molecular energy exchange under constraint: $E_i = const.$

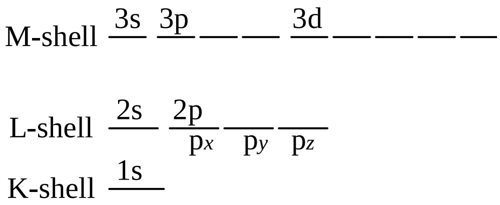
· *prior* distribution

ex.) photo-excited molecule

〈Multiplicity (多重度)〉

· $p_i : p_j = g_i : g_j$

ex.) Atomic orbitals of H: $g_n = n^2$ (n: principal q.n.), $g_l = 2l + 1$ (l: azimuthal q.n.)
K-shell ($n = 1$): 1s ($l = 0$, $g_l = 1$) only → $g_n = 1^2 = 1$
L-shell ($n = 2$): 2s ($l = 0$, $g_l = 1$), 2p ($l = 1$, $g_l = 3$) → $g_n = 2^2 = 4$
M-shell ($n = 3$): 3s ($l = 0$, $g_l = 1$), 3p ($l = 1$, $g_l = 3$), 3d ($l = 2$, $g_l = 5$) → gn = $3^2 = 9$

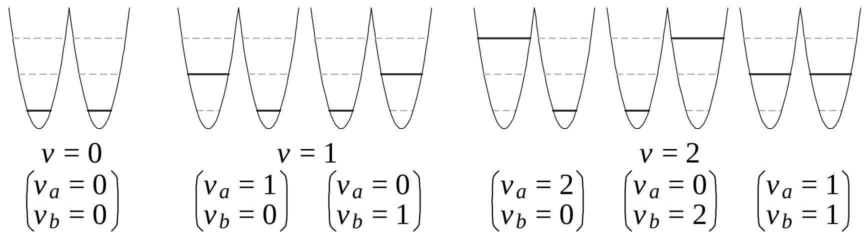


ex.) Electronic states of H-atom:
ground state: ^{2}S (1s^1) [$g = (2S + 1)(2L + 1) = 2\times1 = 2$]
excited states: ^{2}P (2p^1) [g = 2×3 = 6]
2^2S (2s^1) [g = 2×1 = 2]

total multiplicity
of K-shell states = 2
of L-shell states = 8

ex.) Bending vibration (ν_2) of CO_2 ~ 2-D harmonic oscillator

$$E(v) = h\nu\left(v + \tfrac{1}{2}\right),\quad g(v) = v + 1;\quad (v\text{: vibrational q.n.})$$



〈Density of states (状態密度)〉

· number of states per unit energy [states / cm^{-1}]

· $p_A : p_B = \rho_A : \rho_B$

ex.) Photodecomposition of HCl at 248 nm (40320 cm^{-1}):

HCl + $h\nu$(40320 cm^{-1}) → H + Cl($^2P_{3/2}$) + E_{trans} (4240 cm^{-1}) channel-*a*
→ H + Cl($^2P_{1/2}$) + E_{trans} (3359 cm^{-1}) channel-*b*

Statistical branching ratio, $P_a : P_b$
$= g[\text{Cl}(^2P_{3/2})]\rho_{\text{trans}}(4240\ \text{cm}^{-1}) : g[\text{Cl}(^2P_{1/2})]\rho_{\text{trans}}(3359\ \text{cm}^{-1})$
$= 4\times(4240)^{1/2} : 2\times(3359)^{1/2} \sim 2.25 : 1$

Problem-1

Calculate the statistical branching ratio between H + I($^2P_{3/2}$) [channel-*a*] and H + I($^2P^{1/2}$) [channel-*b*] upon the photolysis of HI at 266 nm. Use the bond dissociation energy of HI [→ H + I($^2P_{3/2}$)] = 298 kJ mol^{-1} and excitation energy of I($^2P_{1/2}$) form I($^2P_{3/2}$) (ground state) = 0.943 eV.