4. Microscopic rate coefficients and unimolecular reactions

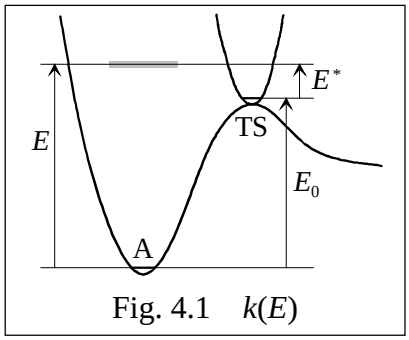

Fig. 4.1 $k(E)$

4.1 Microscopic rate coefficients

(Microcanonical form of the Transition State Theory)

[$k(E)$]

reactant transition state

$$\mathrm{A}(\underline{E}) \longrightarrow \mathrm{TS}(\underline{E^*}) \longrightarrow \textit{products}$$

excitation energy; active energy; internal energy (mostly vibrational)

$$E = E_0 + E^* \tag{4.1.1}$$

Microcanonical equilibrium: (ε_t : 1-D translational energy of TS)

$$\frac{[\mathrm{TS}(E^*, \varepsilon_t)]}{[\mathrm{A}(E)]} = \frac{\rho^*(E^* - \varepsilon_t)\rho_{trans}^{*(1\mathrm{D})}(\varepsilon_t)}{\rho(E)} \tag{4.1.2}$$

Half of TS(E^*, ε_t) passes region with length l_{TS} toward products with velocity $\sqrt{2\varepsilon_t / \mu^*}$ → rate of reaction:

$$k(E, \varepsilon_t) = \frac{1}{2}\frac{[\mathrm{TS}(E^*, \varepsilon_t)]}{[\mathrm{A}(E)]}\frac{\sqrt{2\varepsilon_t / \mu^*}}{l_{\mathrm{TS}}} = \frac{\rho^*(E^* - \varepsilon_t)}{h\rho(E)}$$

Rate coefficients for A(E):

$$k(E) = \int_0^{E^*} k(E, \varepsilon_t)\, d\varepsilon_t = \frac{W^*(E^*)}{h\rho(E)} \tag{4.1.3}$$

$$W^*(E^*) = \int_0^{E^*} \rho^*(\varepsilon)\, d\varepsilon \quad \text{[sum of states]} \tag{4.1.4}$$

by taking adiabatic rotation into account;

$$k(E) = \frac{Q_{rot}^*}{Q_{rot}}\frac{W^*(E^*)}{h\rho(E)} \tag{4.1.5}$$

$$\text{or} \quad k(E) = \frac{I^*}{I}\frac{W^*(E^*)}{h\rho(E)} \tag{4.1.5′}$$

$$Q_{rot}^{2\mathrm{D}} = \int_0^{\infty} \rho_{rot}^{2\mathrm{D}}(\varepsilon)\exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right)d\varepsilon = \frac{1}{\sigma}\frac{k_{\mathrm{B}}T}{B} \tag{4.1.6}$$

$$Q_{rot}^{3\mathrm{D}} = \int_0^{\infty} \rho_{rot}^{3\mathrm{D}}(\varepsilon)\exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right)d\varepsilon \sim \frac{\sqrt{\pi}}{\sigma}\left(\frac{k_{\mathrm{B}}T}{B_{av}}\right)^{3/2} \tag{4.1.7}$$

Problem-4.1 (OPTION)

Derive eqs. (4.1.6) and (4.1.7) from eqs. (2.2.7) and (2.2.10).

[*k*(*E*, *J*)]

· Conservation of angular momentum

$$\mathrm{A}(E, J) \longrightarrow \mathrm{TS}(E^*, J) \longrightarrow \textit{products}$$

q. n. of external rotation

$$E + BJ(J+1) = E_0 + E^* + B^* J(J+1) \qquad (4.1.8)$$

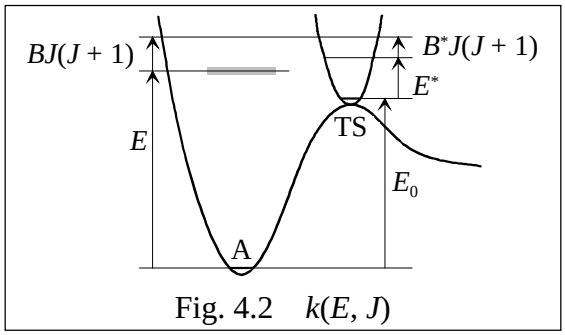

Fig. 4.2 *k*(*E*, *J*)

Microscopic rate coefficients:

$$k(E, J) = \frac{W^*(E^*)}{h\rho(E)} \qquad (4.1.9)$$

note:

For the case of similar structures of A and TS (i.e., $B \sim B^*$) → *J*-conservation may be ignored.

[Sum of states]

summation→integration (2.3.5)

$$W(E) \sim W_{cl}(E_{cl}) = \int_0^{E_{cl}} c_{vib-cl}^{(n_V)} \varepsilon_{cl}^{n_V - 1} d\varepsilon_{cl} = c_{sum-cl}^{(n_V)} E_{cl}^{n_V} \qquad (4.1.10)$$

$$E_{cl} = E + E_{ZP}, \quad c_{sum-cl}^{(n_V)} = \frac{1}{\Gamma(n_V + 1)\prod_{i=1}^{n_V} h\nu_i}$$

note:

Classical approximation [(2.3.5) , (4.1.10)] : Not good at low energy (fig. 2)

→ Whitten–Rabinovitch Approximation or Direct Count

[Whitten–Rabinovich Approximation]

$$W(E) \sim c_{sum-cl}^{(n_V)} [E + (1 - \beta\omega) E_{ZP}]^{n_V} \qquad (4.1.11)$$

$$\beta = \frac{n_V - 1}{n_V} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2}, \quad \begin{cases} \omega^{-1} = 5\varepsilon' + 2.73(\varepsilon')^{0.5} + 3.5100 & for \quad \varepsilon' = 0.1 - 1.0 \\ \log_{10}\omega = -1.0506(\varepsilon')^{0.25} & for \quad \varepsilon' = 1.0 - 8.0 \end{cases}, \quad \varepsilon' = E / E_{ZP}$$

$$\rho(E) = \frac{dW}{dE} \sim c_{viv-cl}^{(n_V)} [E + (1 - \beta\omega) E_{ZP}]^{n_V - 1} \left(1 - \beta \frac{d\omega}{d\varepsilon'}\right) \qquad (4.1.12)$$

$$\left(\frac{d\omega}{d\varepsilon'} = \begin{cases} -\dfrac{5 + 1.365(\varepsilon')^{-0.5}}{\left[5\varepsilon' + 2.73(\varepsilon')^{0.5} + 3.5100\right]^2} & for \quad \varepsilon' = 0.1 - 1.0 \\ -0.604774 \exp\left(-2.41910(\varepsilon')^{0.25}\right)(\varepsilon')^{-0.75} & for \quad \varepsilon' = 1.0 - 8.0 \end{cases} \right)$$

[Direct Count (Beyer–Swinehart algorithm)**]**

Count states in energy grains (source list 1)

Stein & Rabinovitch, *J. Chem. Phys.* 58, 2438 (1973).

Problem-4.2 ——

4.2 Unimolecular reactions

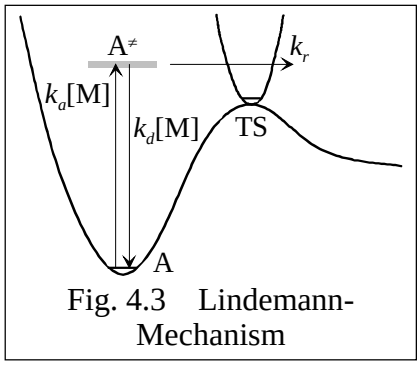

Fig. 4.3 Lindemann-Mechanism

[Lindemann Mechanism] (review)

Steady-state assumption for [$A^{\neq}$]

$$k = \frac{k_r[A^{\neq}]_{ss}}{[A]} = \frac{k_r k_a[M]}{k_r + k_d[M]} \qquad (4.2.1)$$

High-pressure limit: $k_\infty = k([M] \to \infty) = \frac{k_r k_a}{k_d}$ (4.2.2)

Low-pressure limit: $k_0 = \frac{k([M] \to 0)}{[M]} = k_a$ (4.2.3)

$$k = \frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} \qquad (4.2.4)$$

Fall-off pressure (density): $[M]_c = k_\infty / k_0$ (4.2.5)

note:

· Eq. (4.2.4) cannot reproduce the measurements (fig. 4.4) since $A^{\neq}$ is not a single state.

[Troe's formula]

· semi-empirical / reproduces measurements

[*a*] J. Troe, *J. Phys. Chem.* **83**, 114 (1979).

[*b*] R. G. Gilbert, K. Luther, and J. Troe, *Ber. Bunsenges. Phys. Chem.* **87**, 169 (1983).

$$k = \frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} F \qquad (4.2.6)$$

$$\log F \cong \frac{\log F_c}{1 + \left[\frac{\log([M]/[M]_c)}{N}\right]^2}, \quad N = 0.75 - 1.27 \log F_c \qquad [a]\ (4.2.7)$$

$$\log F \cong \frac{\log F_c}{1 + \left[\frac{\log([M]/[M]_c) + c}{N - d\{\log([M]/[M]_c) + c\}}\right]^2},$$

$$N = 0.75 - 1.27 \log F_c, \quad c = -0.4 - 0.67 \log F_c, \quad d = 0.14 \qquad [b]\ (4.2.8)$$

4.3 RRKM Theory

(4.1.5), (4.1.9) → Microcanonical form of RRKM theory

[Lindemann → RRKM]

$A^{\neq} \to A^{\#}(E)$; $k_r = k(E)$, $k_a \to k_a(E)$ [k_d : a constant independent of E]

Detailed balancing: $\frac{k_a(E)}{k_d} = \frac{\rho(E)\exp(-E/k_B T)}{Q_A}$ (4.3.1)

steady-state assumption to $A^{\#}(E)$ →

distribution function: $$g(E)=\frac{[\mathrm{A}^{\#}(E)]_{ss}}{[\mathrm{A}]}=\frac{\rho(E)\exp(-E/k_{\mathrm{B}}T)}{Q_{\mathrm{A}}\{1+k(E)/k_d[\mathrm{M}]\}} \tag{4.3.2}$$

$$k=\int_{E_0}^{\infty}k(E)g(E)dE=\frac{1}{Q_{\mathrm{A}}}\int_{E_0}^{\infty}k(E)\frac{\rho(E)\exp(-E/k_{\mathrm{B}}T)}{1+k(E)/k_d[\mathrm{M}]}dE \tag{4.3.3}$$

[High-pressure limit] = canonical average = TST (transition-state theory)

Canonical (Boltzmann) distribution of $\mathrm{A}^{\#}(E)$

$$F(E)=\frac{\rho(E)\exp(-E/k_{\mathrm{B}}T)}{Q_{\mathrm{A}}} \tag{4.3.4}$$

(4.3.2) $[\mathrm{M}]\to\infty$ ..... $g(E)=F(E)$

$$k_\infty=\int_{E_0}^{\infty}k(E)F(E)dE=\frac{k_{\mathrm{B}}T}{h}\frac{Q^*_{rot}Q^*}{Q_{rot}Q}\exp\left(-\frac{E_0}{k_{\mathrm{B}}T}\right)\ =\mathrm{TST} \tag{4.3.5}$$

Problem-4.3

Derive the eq. (4.3.5) by using $k(E)$ in eq. (4.1.5).

[Low-pressure limit] = excitation is rate-determining

(4.3.3) $[\mathrm{M}]\to 0$:

$$k_0=\frac{\lim_{[\mathrm{M}]\to 0}k}{[\mathrm{M}]}=k_d\int_{E_0}^{\infty}F(E)dE=\int_{E_0}^{\infty}k_a(E)dE \tag{4.3.6}$$

note:

· Fall-off region ~ low-pressure limit : Vibrational distribution is non-Boltzmann

[Strong-collision RRKM theory]

assumption: $\mathrm{A}^{\#}(E)$ of $E > E_0$ deactivates to $E < E_0$ by a single collision with M.

Lennard-Jones collision frequency:

$$Z_{\mathrm{LJ}}=\Omega^{(2,2)*}_{\mathrm{A-M}}\pi\sigma^2_{\mathrm{A-M}}\sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{\mathrm{A-B}}}}[\mathrm{M}] \tag{4.3.7}$$

Strong-collision deactivation rate coefficient:

$$k_d^{\mathrm{SC}}=\frac{Z_{\mathrm{LJ}}}{[\mathrm{M}]} \tag{4.3.8}$$

$k_d\to k_d^{\mathrm{SC}}$: (4.3.3)$\to k^{\mathrm{SC}}$, (4.3.6)$\to k_0^{\mathrm{SC}}$, (4.3.2)$\to g^{\mathrm{SC}}(E)$

[Weak-collision correction]

· Strong collision RRKM > measurements @ fall-off ~ low-pressure limit

$$k_d=k_d^{\mathrm{WC}}=\beta_c k_d^{\mathrm{SC}} \tag{4.3.9}$$

β_c : weak collision parameter 0.1 ~ 1 (depending on temperature, molecule, M)

$k_d \to k_d^{\mathrm{WC}}$: (4.3.3)$\to k^{\mathrm{WC}}$, (4.3.6)$\to k_0^{\mathrm{WC}}$, (4.3.2)$\to g^{\mathrm{WC}}(E)$

Problem-4.4 [OPTION] ——

[Master Equation-RRKM]

WC-RRKM :

- Satisfactory in many cases, but β_c has little physical meaning.
- Cannot describe multi-channel / multi-well problems.

Master equation system describing the problem :

$$-k_{\mathrm{uni}}\,g(E) = \omega\int_0^\infty [P(E,E')g(E') - P(E',E)g(E)]dE' - k(E)g(E) \qquad (4.3.10)$$

k_{uni} : (steady-state) unimolecular reaction rate coefficients,

ω : collision frequency; [= Z_{LJ} (4.3.7)],

$P(E,E')$ or $P(E',E)$: probability of energy transfer (from E' to E, or E to E')

By using energy grain $\to$ matrix form:

$$\mathbf{Mg} = k_{\mathrm{uni}}\mathbf{g} \qquad (4.3.11)$$

... eigenvalue problem of matrix