Chap 6. Reaction Rate Theory

- **Definition in phase space (Classical mechanics)**

Phase space : $(\mathbf{p}, \mathbf{q}) = (p_i, q_i)$, $i = 1, 2, \cdots, N$ (N degrees of freedom)

Dividing surface : $f(\mathbf{q}) = 0$ (N-1 dimension)

Flux through the div surface : $F(\mathbf{p}, \mathbf{q}) = \delta[f(\mathbf{q})] \dfrac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \dfrac{\mathbf{p}}{m}$

Characteristic function :

$$\chi(\mathbf{p}, \mathbf{q}) = \begin{cases} 1 \cdots \text{trajectory passing } (\mathbf{p}, \mathbf{q}) \text{ is } \mathbf{reactive} \\ 0 \cdots \text{else} \end{cases}$$

("reactive" = end up in the product state)

Note : to determine χ, complete info of classical trajectories is required

$\Rightarrow$ we need some approximations (e.g., TST)

Microcanonical rate $k(E)$

Constant energy E $\quad (\Rightarrow \delta[E - H(\mathbf{p}, \mathbf{q})])$

$$k(E) = \frac{h^{-N} \int d\mathbf{p} \int d\mathbf{q}\, \delta[E - H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) \chi(\mathbf{p}, \mathbf{q})}{h^{-N} \int d\mathbf{p} \int_R d\mathbf{q}\, \delta[E - H(\mathbf{p}, \mathbf{q})]}$$

- $\int_R d\mathbf{q} \equiv$ integration over the reactant configuration

- denominator $=$ density of states in reactant $\equiv \rho_R(E)$

- numerator $\times h \equiv N(E)$: cumulative reaction probability (dimensionless)

$$\Rightarrow \boxed{\; k(E) = \frac{N(E)}{h \rho_R(E)} \;}$$

(Relation with the RRKM theory will be discussed later)

Canonical rate $k(T)$

Constant temperature T ($\beta \equiv 1/k_B T$)

$$k(T) = \frac{1}{Q_R} \int dE\, k(E)\rho_R(E)e^{-\beta E} \qquad (Q_R \equiv \int dE \rho_R(E)e^{-\beta E})$$

    (Thermal average of $k(E)$)   (partition function in R)

$$\Rightarrow \boxed{ k(T) = Q_R^{-1} h^{-N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta H(\mathbf{p},\mathbf{q})} F(\mathbf{p},\mathbf{q})\chi(\mathbf{p},\mathbf{q}) }$$

- **Note** : both $k(E)$ and $k(T)$ do not depend on the choice of $f(\mathbf{p},\mathbf{q})$

  (as far as $f(\mathbf{p},\mathbf{q})$ is set to make sense...)

  - From the **Liouville's theorem** (= continuity of the phase space distribution function), the net flux in a closed surface vanishes.

  - Thus, flux across <u>any</u> two dividing surfaces $f_1(\mathbf{q}) = 0$ and $f_2(\mathbf{q}) = 0$ are the same by closing them at sufficiently far away from the relevant configuration space region

Transition state theory (TST)

Approximate the characteristic function $\chi(\mathbf{p}, \mathbf{q})$

(which is supposed to contain <u>complete info</u> of the classical trajectories)

- **Fundamental assumption of TST**
  By properly defining the dividing surface $f(\mathbf{q}) = 0$, trajectories passing through it (toward the product region) are **all "reactive"**

(ie, neglect any "recrossings" that are against this assumption)

We consider a model in which :

- $(\mathbf{p}, \mathbf{q}) \rightarrow (p_s, s, \mathbf{p}_u, \mathbf{u})$ $\begin{bmatrix} \text{reaction coordinate } s \\ \text{and other } N\text{-1 Dim coordinates} \end{bmatrix}$

- Kinetic terms in Hamiltonian are separable

$$H(p_s, s, \mathbf{p}_u, \mathbf{u}) = \frac{p_s^2}{2m_s} + T(\mathbf{p}_u) + V(s, \mathbf{u}) \qquad [\ T(\mathbf{p}_u) = \sum_{i=1}^{N-1} \frac{p_{u_i}^2}{2m_{u_i}} \ ]$$

- $f(s, \mathbf{u}) = s$ (ie, dividing surface is $s = 0$) $\Rightarrow F(\mathbf{p}, \mathbf{q}) = \delta(s)\dfrac{p_s}{m_s}$

$\Rightarrow$ $\boxed{\ \text{TST assumption is} : \ \chi(p_s, s, \mathbf{p}_u, \mathbf{u}) = \theta(p_s) \qquad \text{(step function)}\ }$

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- **<u>Microcanonical $k^{\mathrm{TST}}(E)$</u>**

Cumulative reaction probability under TST

$$
\begin{aligned}
N^{\ddagger}(E) \;&=\; \frac{1}{h^{N-1}} \int dp_s \int d\mathbf{p}_u \int ds \int d\mathbf{u}\, \delta[E - H(p_s, s, \mathbf{p}_u, \mathbf{u})]\delta(s)\frac{p_s}{m_s}\theta(p_s) \\
&=\; \frac{1}{h^{N-1}} \int_0^{\infty} dp_s \int d\mathbf{p}_u \int d\mathbf{u}\, \delta[E - \frac{p_s^2}{2m_s} - T(\mathbf{p}_u) - V(0, \mathbf{u})]\frac{p_s}{m_s}
\end{aligned}
$$

Decompose the δ-function $\qquad$ (s part and $\mathbf{u}$ part)

$$
\delta[\cdots] = \int d\varepsilon\, \delta[E - p_s^2/2m_s - \varepsilon - V(0, \mathbf{u}_0)]\delta[\varepsilon - T(\mathbf{p}_u) - V(0, \mathbf{u}) + V(0, \mathbf{u}_0)]
$$

$$(\mathbf{u}_0 : \text{potential minimum at } s = 0)$$

$$
\begin{aligned}
N^{\ddagger}(E) = \int d\varepsilon \Bigg\{ &\int_0^{\infty} dp_s \frac{p_s}{m_s}\delta[E - p_s^2/2m_s - \varepsilon - V(0, \mathbf{u}_0)] \Bigg\} \\
&\times \left\{ \frac{1}{h^{N-1}} \int d\mathbf{p}_u \int d\mathbf{u}\, \delta[\varepsilon - T(\mathbf{p}_u) - V(0, \mathbf{u}) + V(0, \mathbf{u}_0)] \right\}
\end{aligned}
$$

- 2nd $\{\}$ = density of states $\rho_{\mathbf{u}}(\varepsilon)$ for the internal energy of $(\mathbf{u}, \mathbf{p}_u)$

In 1st $\{\}$, transform the variable $p_s \rightarrow \varepsilon_s \equiv p_s^2/2m_s$

$$N^{\ddagger}(E) = \int_{-\infty}^{\infty} d\varepsilon \int_0^{\infty} d\varepsilon_s \delta[E - \varepsilon_s - \varepsilon - V(0, \mathbf{u}_0)]\rho_{\mathbf{u}}(\varepsilon)$$

$$= \int_0^{\infty} d\varepsilon_s \rho_{\mathbf{u}}(E - \varepsilon_s - V(0, \mathbf{u}_0))$$

transform the variable to $\varepsilon \equiv E - \varepsilon_s - V(0, \mathbf{u}_0)$

noting that $\rho_{\mathbf{u}}(\varepsilon)$ is defined in $\varepsilon > 0$

$$\Rightarrow \quad \boxed{\begin{array}{ll} N^{\ddagger}(E) = \displaystyle\int_0^{E-V(0,\mathbf{u}_0)} d\varepsilon \rho_{\mathbf{u}}(\varepsilon) & \left[\begin{array}{l} \text{Number of states between} \\ V(0, \mathbf{u}_0) \ (= \text{barrier top}) \text{ and } E \\ \text{for } (\mathbf{u}, \mathbf{p}_u) \text{ degrees of freedom} \end{array}\right] \\[3em] k^{\text{TST}}(E) = \dfrac{N^{\ddagger}(E)}{h\rho_R(E)} & (\textbf{RRKM} \text{ theory}) \end{array}}$$

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- **<u>Canonical $k^{\mathrm{TST}}(T)$</u>**

$$k^{\mathrm{TST}}(T) = \frac{1}{Q_R}\frac{1}{h^N}\int dp_s \int ds \int d\mathbf{p}_u \int d\mathbf{u}\, e^{-\beta H(p_s,s,\mathbf{p}_u,\mathbf{u})}\delta(s)\frac{p_s}{m_s}\theta(p_s)$$

$$= \frac{1}{Q_R}\left\{\frac{1}{h}\int_0^\infty dp_s\,\frac{p_s}{m_s}e^{-\beta p_s^2/2m_s}\right\}$$

$$\times\left\{\frac{1}{h^{N-1}}\int d\mathbf{p}_u \int d\mathbf{u}\,e^{-\beta(T(\mathbf{p}_u)+V(0,\mathbf{u}))}\right\}$$

- 1st $\{...\} = k_B T/h$ (Verify : just a Gaussian integral)

- 2nd $\{...\} \equiv Q_u^{\ddagger}e^{-\beta V(0,\mathbf{u}_0)}$

$$\left[\begin{array}{l} Q_u^{\ddagger} \equiv \frac{1}{h^{N-1}}\int d\mathbf{p}_u \int d\mathbf{u}\,e^{-\beta(T(\mathbf{p}_u)+V(0,\mathbf{u})-V(0,\mathbf{u}_0))} \\ \text{Partition function for } (\mathbf{u},\mathbf{p}_u) \text{ at the transition state} \\ (s=0, \mathbf{u}=\mathbf{u}_0) \end{array}\right]$$

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$$\Rightarrow \boxed{k^{\text{TST}}(T) = \frac{k_B T}{h} \frac{Q_u^{\ddagger}}{Q_R} e^{-\beta V(0,\mathbf{u}_0)}}$$

This is the same as the "conventional" TST derived by assuming

1. Existence of the "activation complex" $(X^{\ddagger})$, and

2. Thermal equilibrium between $X^{\ddagger}$ and the reactant R

However, as derived here, these assumptions are not essential for TST

$\Leftarrow$ The same $k^{\text{TST}}(T)$ is derived "dynamically" just from

- Separability of $p_s^2/2m_s$ in Hamiltonian H

- $\chi = \theta(p_s)$ (TST assumption)

- $F = \delta(s)\dfrac{p_s}{m_s}$ (Dividing surface : $s = 0$)

Quantum mechanical rate constant

Preface : Detailed discussion of this subject is quite involved, so we only summarize the framework/outline of the representative two theories.

1. **Flux-operator formalism** (W H Miller et al.)

$$k(T) = Q_R^{-1}\mathrm{Tr}[e^{-\beta\hat{H}}\hat{F}(\hat{\mathbf{p}}, \hat{\mathbf{q}})\hat{P}]$$

- Flux operator : $\hat{F}(\hat{\mathbf{p}}, \hat{\mathbf{q}}) \equiv \delta[f(\hat{\mathbf{q}})]\dfrac{\partial f(\hat{\mathbf{q}})}{\partial\hat{\mathbf{q}}}\dfrac{\hat{\mathbf{p}}}{m}$

- $\hat{P}$: projection operator corresponding to $\chi(\mathbf{p}, \mathbf{q})$ in the classical limit

  (For example, projection to reactant states having positive momentum toward reactive collision in gas-phase reactions)

  <div align="right">(see [SR 8.5 - 8.8] for details)</div>

Further assumptions corresponding to the classical TST, e.g., $\hat{P} \to \theta(p_s)$, would define "Quantum TST" (but seems not well-established...)

2. <u>Time correlation function formalism</u> (T Yamamoto)

Based on "linear response theory for <u>internal thermal forces</u> " (Kubo et al.)

$$k(T) = \frac{Q}{\beta Q_R} \int_0^{\Delta t} dt \int_0^\beta d\lambda \langle \dot{N}_R \dot{N}_R(t + i\hbar\lambda) \rangle$$

- N_R : projection operator defining the reactant (or product) state

  e.g., For $|\psi_R\rangle \rightarrow |\psi_P\rangle$, $N_R = |\psi_R\rangle\langle\psi_R|$ (with $\langle\psi_R|\psi_P\rangle = 0$)

- $\dot{N}_R = (i/\hbar)[H, N_R]$

- Δt (plateau time)

  microscopically long ($>$ decay time of $\int_0^\beta d\lambda \langle \dot{N}_R \dot{N}_R(t + i\hbar\lambda) \rangle$)

  macroscopically short such that $\dfrac{\langle \Delta N_R(t + \Delta t)\rangle - \langle \Delta N_R(t)\rangle}{\Delta t} \simeq \dfrac{d\langle N_R\rangle}{dt}$

Correction from TST

Especially in condensed phase, "recrossings" may become significant

Writing the exact reaction rate as $k = \kappa k^{\text{TST}}$,

$\kappa (= k/k^{\text{TST}})$ is called "transmission coefficient"

1. Grote-Hynes theory

2. Kramers limit

- **Grote-Hynes theory**

Describe the microscopic dynamics near the barrier top (TS) by GLE

$$\ddot{s}(t) = \omega_{b,eq}^2 s(t) - \int_0^t d\tau \zeta(t-\tau)\dot{s}(\tau) + R(t)$$

- $\omega_{b,na}^2 = -(\partial^2 H/\partial s^2)_{s=0}$: "non-adiabatic" barrier frequency

- $\omega_{b,eq}^2 = \omega_{b,na}^2 + \zeta(0)$: equilibrium/adiabatic barrier frequency

cf. harmonic model

$$
\begin{aligned}
H \;\; &= p_s^2/2 - \omega_{b,na}^2 s^2/2 + \sum_i (p_i^2/2 + \omega_i^2 x_i^2/2) + s \sum_i c_i x_i \\
&= p_s^2/2 - \omega_{b,na}^2 s^2/2 + \sum_i p_i^2/2 + \sum_i \omega_i^2 \underbrace{(x_i + c_i s/\omega_i^2)}^2/2 - c_i^2 s^2/2\omega_i^2
\end{aligned}
$$

If the baths $\{x_i\}$ always satisfy $x_i + c_i s/\omega_i^2 = 0$, ie, adiabatically follow
their minima along each value of s , then the "effective" potential for s
would look like $-\frac{1}{2}(\omega_{b,na}^2 + c_i^2/\omega_i^2)s^2 = -\frac{1}{2}(\omega_{b,na}^2 + \zeta(0))s^2 \equiv -\frac{1}{2}\omega_{b,eq}^2 s^2$

Laplace tr.

$$\lambda^2 \tilde{s}(\lambda) - \lambda s(0) - \dot{s}(0) = \omega_{b,eq}^2 \tilde{s}(\lambda) - \tilde{\zeta}(\lambda)(\lambda \tilde{s}(\lambda) - s(0)) + \tilde{R}(\lambda)$$

$$\tilde{s}(\lambda) = \frac{(\lambda + \tilde{\zeta}(\lambda))s(0) + \dot{s}(0) + \tilde{R}(\lambda)}{\lambda^2 - \omega_{b,eq}^2 + \lambda \tilde{\zeta}(\lambda)}$$

inverse transformation : $s(t) = \displaystyle\sum_{\text{res}\{\lambda\}} e^{\lambda t} \tilde{s}(\lambda)$

Grote-Hynes equation : $\lambda_r^2 - \omega_{b,eq}^2 + \lambda_r \tilde{\zeta}(\lambda_r) = 0$

From its solution λ_r , the transmission coefficient is given by

$$\kappa_{GH} = \frac{\lambda_r}{\omega_{b,eq}} \quad \left(= \frac{\omega_{b,eq}}{\lambda_r + \tilde{\zeta}(\lambda_r)} \right)$$

$\Big[$For details, see, eg,
Gertner, Wilson, and Hynes, J Chem Phys **90**, 3537 (1989), Appendix $\Big]$

- **<u>Kramers limit</u>** (GLE → LE)

Langevin eq limit :

$$\ddot{s}(t) = \omega_{b,eq}^2 s(t) - \zeta \dot{s}(\tau) + R(t) \qquad \zeta \equiv \int_0^\infty \zeta(\tau) d\tau = \tilde{\zeta}(\lambda = 0)$$

⇐ fast decay limit of $\zeta(t)$, or coarse-grain the time scale

Then, GH equation : $\lambda^2 + \zeta\lambda - \omega_{b,eq}^2 = 0$

$$\lambda = (-\zeta \pm \sqrt{\zeta^2 + 4\omega_{b,eq}^2})/2 \qquad (\text{take} + \text{since } \lambda > 0)$$

Further, in the strong friction case $\zeta \gg \omega_{b,eq} \qquad \Rightarrow \lambda_r \simeq \omega_{b,eq}^2/\zeta$

$$\Rightarrow \boxed{\kappa \text{ in the Kramers limit} : \kappa_{\mathrm{KR}} = \omega_{b,eq}/\zeta}$$

If we write $k^{\mathrm{TST}} = \frac{\omega_R}{2\pi} e^{-\beta\Delta G^\ddagger}$

$$\Rightarrow \boxed{k_{\mathrm{KR}} = \kappa_{\mathrm{KR}} k^{\mathrm{TST}} = \frac{1}{\zeta}\frac{\omega_R \omega_{b,eq}}{2\pi} e^{-\beta\Delta G^\ddagger} \propto \zeta^{-1}}$$

(originally, this was derived from Fokker-Planck equation)