Kinetics III

Barriers / Transition State Theory

→ Kramer's Problem.

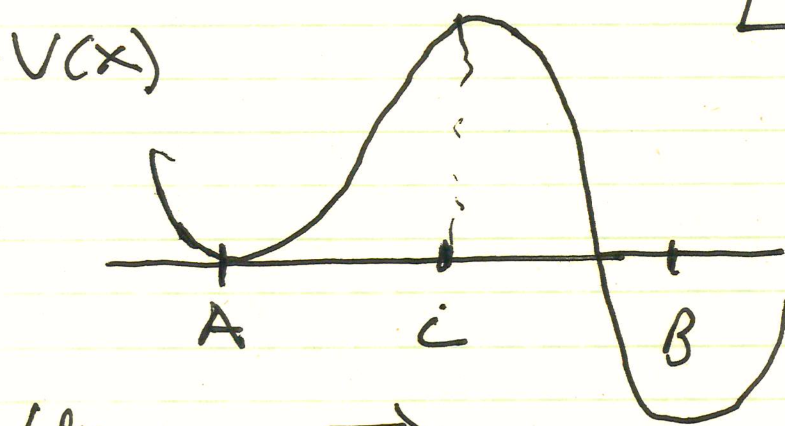
$\underline{T}$

β.

Consider:

1D

$V(x)$



$f_x = -dV(x)/dx \quad \Longrightarrow$

– Probability of escape $A \to B$

– relevance to reaction problems. (Chemistry)

Now:
$$\frac{dx}{dt} = v$$

$$\frac{dv}{dt} = -\beta v + a_{ext}(x) + \tilde{a}$$

$\Downarrow$

motion in V

or

$$\frac{dx}{dt} = \frac{a_{ext}(x)}{\beta} + \frac{\tilde{a}}{\beta}$$

So

$$\boxed{\frac{\partial n}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{q_{ext}(x)}{\beta} n - \frac{\partial}{\partial x} D_x n\right]}$$

$$D_x = \frac{1}{\beta^2} D_V = \frac{\beta V_{Th}^2}{\beta^2} = V_{Th}^2/\beta.$$

$$V = \frac{q_{ext}(x)}{\beta}$$

Now,

$$\frac{\partial n}{\partial t} + \partial_x j = 0 \qquad \underline{\text{continuity}}$$

$$j = \Gamma_n = \frac{q_{ext}(x)}{\beta} n - D_x \partial_x n$$

$\downarrow$
Current

$$= \frac{q_{ext}(x)}{\beta} n - \frac{D_V}{\beta^2} \partial_x n$$

$$q_{ext} = -\partial_x V$$

no j = const, is steady solution.

then

$$j = -\frac{D_V}{\beta^2} \exp\left(-\frac{\beta V}{D_V}\right) \partial_x\left(n \exp\left(\frac{\beta \bar{V}}{D_V}\right)\right)$$

$$= -\frac{D_V}{\beta^2}\, e^{-\frac{\beta \bar{V}}{D_V}} \left[\partial_x n\, e^{\beta \bar{V}/D_V} + n \frac{\beta}{D_V}(\partial_x \bar{V})\, e^{+\beta \bar{V}/D_V}\right]$$

$$= -\frac{D_V}{\beta^2}\left[\partial_x n + \frac{\beta}{D_V}\partial_x \bar{V}\, n\right]$$

$$= -D_x \partial_x n + \frac{a_{ext}(x)}{\beta}\, n \quad \checkmark$$

so

$$\boxed{j = -\frac{D_V}{\beta^2} \exp\left(-\frac{\beta \bar{V}}{D_V}\right) \partial_x\left(n \exp\left(\frac{\beta \bar{V}}{D_V}\right)\right)}$$

so for $j = \text{const}$

$$j \int_A^B \beta \cancel{\frac{D_V}{\beta^2}}\, e^{+\frac{\beta \bar{V}}{D_V}} = -\int_A^B \partial_x\left(n \exp\left(\frac{\beta V}{D_V}\right)\right) dx\, \frac{D_V}{\beta}$$

$$= +n\, e^{\frac{\beta \bar{V}}{D_V}} \Big|_B^A \frac{D_V}{\beta}$$

$$D_v/\beta = v_{th}^2$$ 4.

So

$$\boxed{j \int_A^B \beta\, e^{[\beta V/D_v]}\, ds = \frac{T}{m}\, n\, e^{\beta V/D_v}\Big|_B^A}$$

$$j = \frac{\frac{T}{m}\, n\, e^{\beta V/D_v}\Big|_B^A}{\int_A^B \beta\, e^{[\beta V/D_v]}\, ds}$$

j ↓ current over barrier

Can re-write as:

$$\boxed{j = \frac{\frac{T}{m\beta}\, n \exp\left[mV/T\right]\Big|_B^A}{\int_A^B \exp\left[mV(x)/T\right] dx}}$$

→ current over barrier.

$j_{A,B}$

Now, at A

n_A

$V \cong 0$

at B

$n_B \ll n_A \rightarrow 0$

$V \simeq -|V_B|$

$\Rightarrow$

$$\boxed{j \cong \frac{T}{m\beta} n_A \left[\int_A^B dx \, e^{mV/T} \right]^{-1}}$$

Now, for:

$p \rightarrow$ rate of escape

$p \cong j / \nu_A$

$\nu_A \rightarrow$ # near A

$\left[\begin{array}{l} \nu \rightarrow \# \\ n \rightarrow \text{density} \end{array} \right.$

$d\nu_A = n_A e^{-mV/T} dx$

$V \cong (1/2) \omega_A^2 x^2$ (parabolic approx.)

$$r_A = n_A \int_{-\infty}^{+\infty} \exp\left[-m\omega_A^2 x^2/2T\right] dx$$

$$\boxed{r_A = \left(\frac{n_A}{\omega_A}\right)\left(2\pi T/m\right)^{1/2}}$$

So

$$\rho = \frac{j}{r_A} = \frac{\frac{T}{m\beta} n_A \left[\quad\right]^{-1}}{\frac{n_A}{\omega_A}\left(2\pi T/m\right)^{1/2}}$$

$$\boxed{\rho = \frac{\omega_A}{\beta}\left(\frac{T}{m}\right)^{1/2}\left\{\int_A^B e^{mV/T}\right\}^{-1}}$$

For integral:

- main contribution near peak C (largest V)

- there $V = Q - \frac{1}{2}\omega_C^2 (x - x_C)^2$

So

$$\int_A^B e^{mV/T} \cong e^{mQ/T}\int_{-\infty}^{+\infty} \exp\left[-m\omega_C^2 (x-x_0)^2/2T\right] dx$$

$$= e^{mQ/T}\left(2\pi T/m\omega_C^2\right)^{1/2}$$

So Finally:

$$\boxed{P = \left(\omega_A \omega_C / 2\pi B\right) e^{-mQ/T}}$$

– Probability of transition

Transition rate

Aside: Another approach to F-P.
Averaging (a la' QLT)

Consider dynamical variables $\underline{a}$

Seek $f(\underline{a},t)$, where:

$$\frac{d\underline{a}}{dt} = \underbrace{\underline{V}(\underline{a})}_{\text{determ.}} + \underbrace{\underline{F}(t)}_{\text{noise}}$$

$$\langle \underline{F}(t)\,\underline{F}(t')\rangle = 2\underline{\underline{B}}\,\delta(t-t')$$

then

consider
$\nabla_a \cdot V_a = 0.$

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \underline{a}}\cdot\left(\frac{d\underline{a}}{dt} f\right) = 0$$

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \underline{a}}\cdot\left(\left(\underline{V}(a) + \underline{F}(t)\right) f\right) = 0$$

$$\frac{\partial f}{\partial t} + \underbrace{\frac{\partial}{\partial \underline{a}}\cdot\left(\underline{V}(a)\, f(a)\right)}_{\text{drift}} + \underbrace{\frac{\partial}{\partial \underline{a}}\cdot\left(\underline{F}(t) f\right)}_{\text{noise}} = 0$$

Now close noise term by
$f \to \frac{\delta f}{\delta F} F$, a la' quasilinear theory.

Now, $L\underline{\Phi} \equiv \frac{\partial}{\partial \underline{q}}\cdot\left(\underline{v}(q)\,\underline{\Phi}\right)$

so, sans noise, f satisfies:

$$\frac{\partial f}{\partial t} = -Lf$$

&

$$f(q,t) = e^{-tL} f(\underline{q},0)$$

with noise:

$$\frac{\partial f}{\partial t} = -Lf - \frac{\partial}{\partial \underline{q}}\cdot\left(\underline{F}(t)\, f\right)$$

&

$$f(\underline{q},t) = e^{-tL} f(\underline{q},0) - \int_0^t ds\, e^{-(t-s)L} \frac{\partial}{\partial \underline{q}}\cdot \underline{F}(s) f(\underline{q},s)$$

Now, plug in – iteratively:

$$\frac{\partial f}{\partial t} = -Lf - \frac{\partial}{\partial \underline{q}}\cdot\left[\underline{F}(t)\, e^{-tL} f(\underline{q},0)\right]$$

$$+ \frac{\partial}{\partial \underline{q}}\cdot\left[\underline{F}(t) \int_0^t ds\, e^{-(t-s)L} \frac{\partial}{\partial \underline{q}}\cdot \underline{F}(s)\, f(\underline{q},s)\right]$$

Note now: $\langle \ \rangle_F$

→ average over noise.

$$\left\langle \frac{\partial f}{\partial t} \right\rangle_F = \langle -Lf \rangle_F \cancel{- \left\langle \frac{\partial}{\partial \underline{q}} \cdot \left[\underline{F}(t)\, e^{-tL} f(\underline{q},0) \right] \right\rangle_F} \to 0$$

$$+ \left\langle \frac{\partial}{\partial \underline{q}} \cdot \left[\underline{F}(t) \int_0^t ds\, e^{-(t-s)L} \frac{\partial}{\partial \underline{q}} \cdot \underline{F}(s)\, f(\underline{q},s) \right] \right\rangle_F$$

$$\langle \underline{F}(t)\, \underline{F}(s) \rangle = 2 \underline{\underline{B}}\, \delta(t-s)$$

(F indep $\underline{q}$!)

Diffn tensor in $\underline{q}$

↓

so

$$\frac{\partial \langle f \rangle}{\partial t} = -L \langle f \rangle + \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{B}} \cdot \frac{\partial}{\partial \underline{q}} \langle f \rangle$$

$\langle f \rangle \equiv \langle f(q,t) \rangle$ → understood noise averaged.

So

$$\boxed{\frac{\partial f}{\partial t} + \frac{\partial}{\partial \underline{q}} \cdot \left(\underline{v}(q) f \right) = \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{B}} \cdot \frac{\partial}{\partial \underline{q}} f}$$

Alternatively, $f = \langle f \rangle + \tilde{f}$

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \underline{a}} \cdot \left(v(\varepsilon)\, f(\varepsilon) \right) + \frac{\partial}{\partial \underline{a}} \cdot \left(\underline{E}(t)\, f \right) = 0$$

$$\frac{\partial \tilde{f}}{\partial t} + L \tilde{f} = -\frac{\partial}{\partial a} \cdot \left[\underline{E}(t) \langle f \rangle \right]$$

so

$$(-i\omega + L)\, \tilde{f} = -\frac{\partial}{\partial \underline{a}} \cdot \left[\underline{E}_\omega \langle f \rangle \right]$$

$$\tilde{f} = \frac{1}{-i\omega + L} - \left(\frac{\partial}{\partial \underline{a}} \cdot \underline{E}(t) \langle f \rangle \right)$$

$$\frac{\partial \langle f \rangle}{\partial t} + L \langle f \rangle = -\frac{\partial}{\partial \underline{a}} \cdot \sum_\omega \tilde{\underline{E}}_\omega \tilde{f}_\omega$$

$$= +\frac{\partial}{\partial \underline{a}} \cdot \sum_\omega \tilde{\underline{E}}_\omega \frac{1}{-i\omega + L} \left(\frac{\partial}{\partial \underline{a}} \cdot \tilde{\underline{E}}_\omega \langle f \rangle \right)$$

$$= \frac{\partial}{\partial \underline{a}} \cdot \underline{\underline{D}} \cdot \frac{\partial}{\partial \underline{\varepsilon}} \langle f \rangle .$$

$$\underline{\underline{D}} = \sum_\omega |E_\omega|^2 \frac{1}{\left[-i\omega + L \right]} .$$

Assumes: – $\tilde{F}$ fast relative $\langle f \rangle$.

– not nec. Gaussian,
delta correl.

– conv. orbits.

$$\boxed{\begin{aligned} &\partial_t \langle f \rangle + \left\langle \frac{\partial}{\partial \underline{q}} \cdot \left[\underline{v}(\underline{q}) f \right] \right\rangle \\ &\quad = \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{D}} \cdot \frac{\partial \langle f \rangle}{\partial \underline{q}} \\ &\underline{\underline{D}} = \sum_\omega |F_\omega|^2 \frac{1}{(-i\omega + L)} \end{aligned}}$$

Finally,

$$\frac{\partial \cdot \underline{v}(\underline{q})}{\partial \underline{q}} = 0 \qquad \text{(Hamiltonian)}$$

$\Rightarrow$

$$\partial_t \langle f \rangle + \underline{v}(\underline{q}) \cdot \underline{\nabla} \langle f \rangle$$

$$= \frac{\partial}{\partial \underline{q}} \cdot \underline{\underline{D}} \cdot \frac{\partial \langle f \rangle}{\partial \underline{q}}$$

$$\underline{\underline{D}} = \sum_{\omega} |E_\omega|^2 \frac{1}{-i(\omega - k \cdot \underline{V}(\epsilon))}$$

ala' QL.

τ_{ac} set by resonance
and spectral width