Lecture 22 - Intro to kinetics and reaction rates

Consider the reaction

$$A \rightleftarrows B$$

Detailed balance, at Eq

$$[A]_{Eq} \cdot k_{A \to B} = [B]_{Eq} k_{B \to A}$$

where $k_{A \to B}$ is rate const

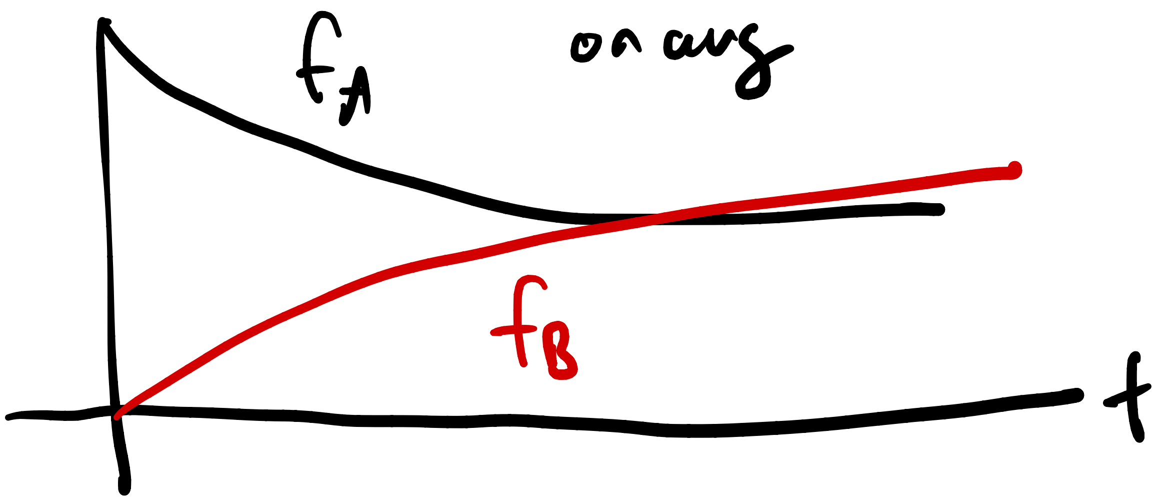
$$\Rightarrow K_{eq} \equiv \frac{[B]_{Eq}}{[A]_{Eq}} = \frac{k_{A \to B}}{k_{B \to A}}$$

$$\text{Frac } A = \frac{N_A}{N_A + N_B} \times \frac{1/V}{1/V} = \frac{[A]}{[A]+[B]}$$

$$= \frac{1}{1 + [B]/[A]} = \frac{1}{1 + K_{eq}}$$

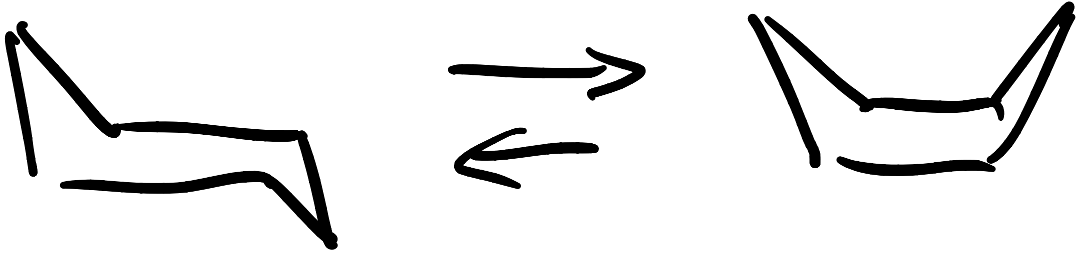
@ Eq

If start 100% A

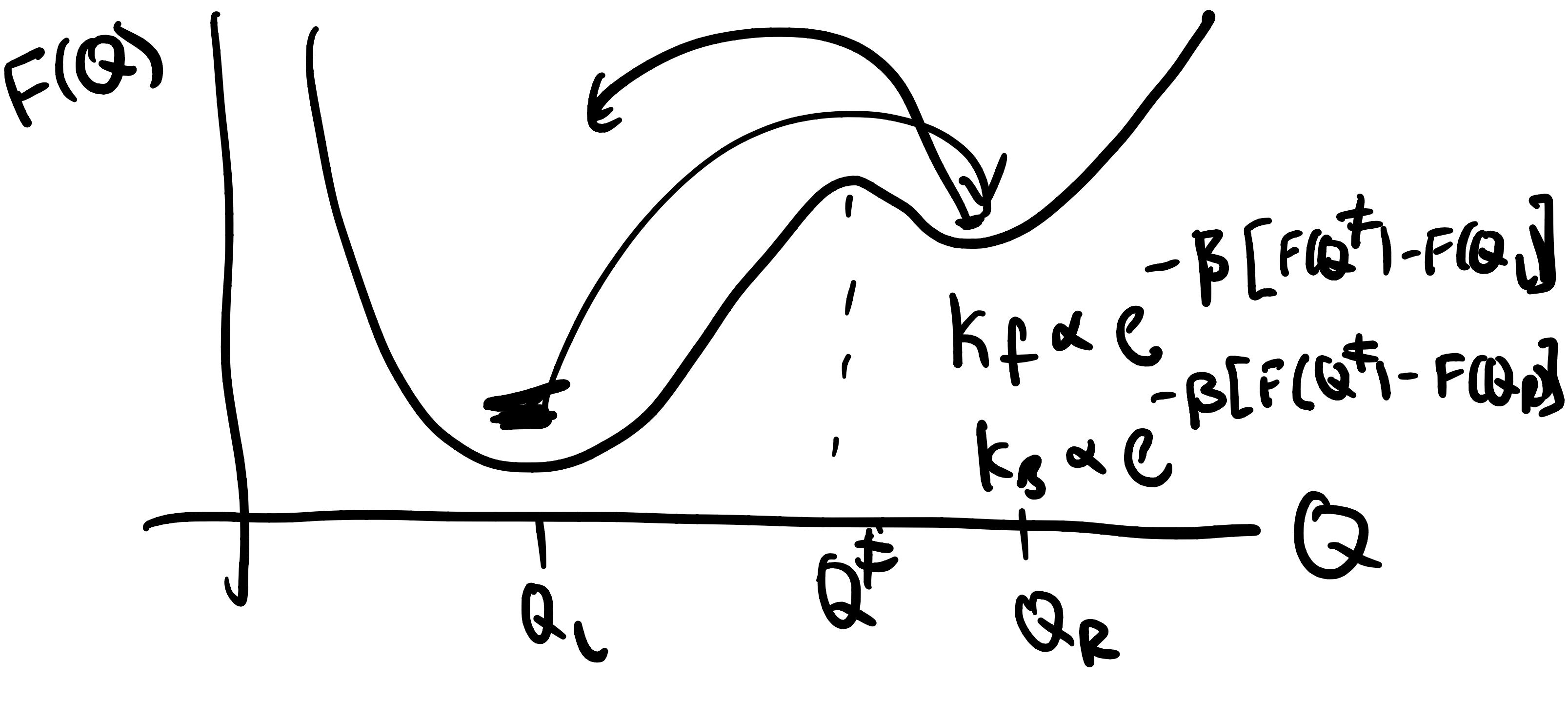


For a single molecule, not an avg, can't be this smooth & simple

Eg



99.99% @ Eq



$$F(Q') = -k_B T \ln \int dx\, \delta(Q(x) - Q')$$

$k_f \propto e^{-\beta[F(Q^\ddagger)-F(Q_i)]}$

$k_b \propto e^{-\beta[F(Q^\ddagger)-F(Q_f)]}$

$K_{eq} = \dfrac{k_f}{k_b}$

$$\Rightarrow K_{eq} \propto e^{-\beta[F(Q_f)-F(Q_i)]}$$

$$\Rightarrow \Delta F = -k_B T \ln K_{eq}$$

$$[\Delta G = -k_B T \ln K_{eq} \text{ @ const } T, P]$$

Now we can return to the dynamics

Can define a progress <u>variable</u>

$$C = \delta A = A - A_{eq} = -\delta B$$

$$A + B = N = A_{eq} + B_{eq}$$

so $A - A_{eq} = B_{eq} - B = -\delta B$

$$\frac{dA}{dt} = \frac{d(\cancel{A_{eq}}+C)}{dt} = k_{B\to A}B - k_{A\to B}A$$

$$\frac{dB}{dt} = \frac{d(\cancel{B_{eq}}-C)}{dt} = k_{A\to B}A - k_{B\to A}B$$

$$\Rightarrow 2\frac{dC}{dt} = 2\left[k_{B\to A}B - k_{A\to B}A\right]$$

$$\Rightarrow \frac{dC}{dt} = \left[k_{B\to A}\left[B_{eq}-C\right] - k_{A\to B}\left[A_{eq}+C\right]\right]$$

use d.b.

$$= -\left(k_{B\to A} + k_{A\to B}\right)C$$

$$\Rightarrow C(t) = C(0)\,e^{-(k_{B\to A}+k_{A\to B})t}$$

or $\tau_{rxn} = \dfrac{1}{k_{B\to A}+k_{A\to B}}$

But what about fluctuations?

Onsager regression hypothesis (1931)

Small microscopic fluctuations at equilibrium decay on average the same as macro deviations decay

$$\Rightarrow \langle C(t)\,C(t')\rangle = \langle c^2\rangle_{eq}\, e^{-(k_f+k_b)|t-t'|}$$

To maintain Var(C), require something like Langevin equation

$$\frac{dC}{dt} = -(k_f+k_b)C + \underbrace{\delta F}_{\text{"force" related to random jumping over barrier}}$$

$$\langle \delta F(t)\,\delta F(t')\rangle = 2(k_1+k_2)\langle c^2\rangle_{eq}\,\delta(t-t')$$

What is $\langle C^2 \rangle_{eq} = \langle \delta A^2 \rangle_{eq}$?

And what is the microdynamics of the reaction on the surface

Define $H_A[Q] = \begin{cases} 1 & Q < Q^{\ddagger} \\ 0 & Q \geq Q^{\ddagger} \end{cases}$

$$f_A = \int dQ \, H_A[Q] \, e^{-\beta F(Q)} / Z \equiv \chi_A$$

$$\langle H_A^2 \rangle = \langle H_A \rangle = \chi_A$$

$$\mathrm{Var}\, C = \langle \delta H_A^2 \rangle = \langle H_A^2 \rangle - \langle H_A \rangle^2$$

$$= \chi_A - \chi_A^2 = \chi_A(1 - \chi_A)$$

$$= \chi_A \chi_B$$

$$\langle C(t) C(0) \rangle = \mathrm{Var}(C) e^{-t/\tau_{rxn}}$$

$$\parallel$$

$$\langle \delta H_A(t) \delta H_A(0) \rangle = \chi_A \chi_B e^{-t/\tau_{rxn}}$$

$$\Downarrow \quad \text{deriv}$$

$$\langle \delta \dot{H}_A(t) \delta H_A(0) \rangle = \chi_A \chi_B \cdot -\frac{1}{\tau_{rxn}} e^{-t/\tau_{rxn}}$$

$$\Downarrow \qquad \text{for } t \sim \tau_{rxn}$$

$$-\frac{\langle \delta \dot{H}_A(t) \delta H_A(0) \rangle}{\chi_A \chi_B} \approx K_{rxn}$$

$$\parallel$$

$$\langle \delta H_A(t) \delta \dot{H}_A(0) \rangle \quad \text{by parts}$$

and $\delta H_A = -\delta H_B$

$$\frac{d H_A[Q]}{dt} = -\frac{dQ}{dt} \delta(Q - Q^{\ddagger})$$

$$\Rightarrow K_{rxn} = \left\langle \frac{dQ}{dt} \delta(Q - Q^{\ddagger}) \delta H_B(t) \right\rangle / \chi_A \chi_B$$

$$\chi_B(k_f+k_b) = \frac{1}{\chi_A}\langle \dot{Q}\,\delta(Q-Q(0))\,\delta H_B(Q(t))\rangle$$

$$\parallel$$

$$\frac{B}{A+B}(k_f+k_b) = \frac{B/A}{1+B/A}(k_f+k_b) \qquad \text{db}$$

$$= \frac{k_f/k_b}{1+k_f/k_b}(k_f+k_b)$$

$$= \frac{k_f}{k_f+k_b}(k_f+k_b) = k_f$$

so $$k_f = \frac{1}{\chi_A}\langle \dot{Q}\,\delta(Q-Q(0))\,\delta H_B(Q(t))\rangle$$

$t \sim$ frxn

fraction of time on barrier plus chance

Q vel going forward

Transition State theory