Can determine rate laws for chemical reactions

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

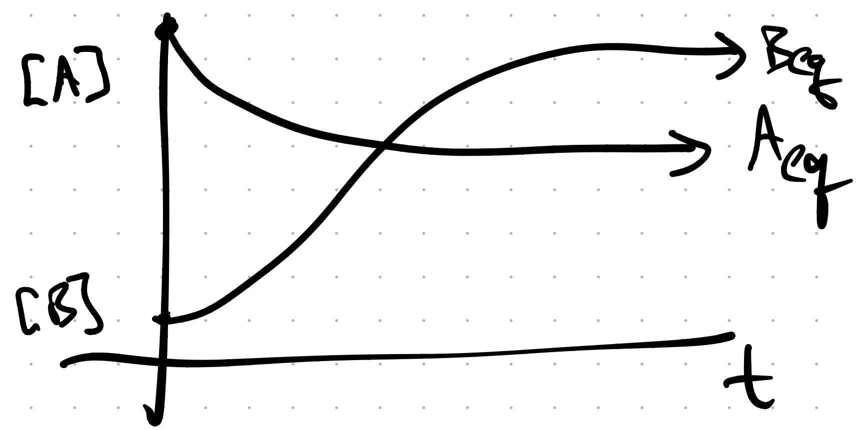
$$v_f(t) = k[A]^{m_A}[B]^{m_B}$$

Does not work (initial rate method) when reaction is faster than mixing

Relaxation Method

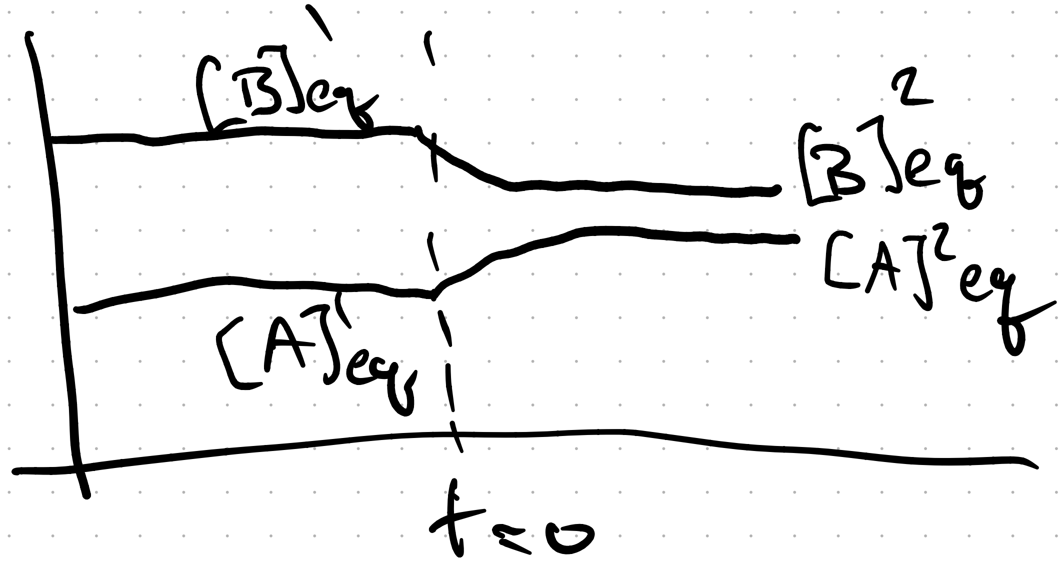
- Start @ Equilibrium
- Change conditions
- Watch system "relax" to a new Equilibrium

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$



Last time, we showed

$$[A]-[A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k_f+k_b)t}$$



increase temp

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$K_{eq} = e^{-\Delta \bar{G}^\circ/RT} = e^{-\Delta \bar{H}^\circ/RT}\, e^{\Delta \bar{S}^\circ/R}$$

$$\Delta G^\circ = \Delta \bar{H}^\circ - T\Delta \bar{S}^\circ$$

$$K_{eq} = e^{-\Delta \bar{G}^\circ/RT} = e^{-\Delta \bar{H}^\circ/RT} e^{\Delta \bar{S}^\circ/R}$$

$$\Delta G^\circ = \Delta \bar{H}^\circ - T\Delta \bar{S}^\circ$$

Is the reaction exothermic [releases heat]
or endothermic [absorbs heat]

- $\Delta \bar{H}^\circ < 0$ energy in the molecules goes down in the reaction

heat released, exothermic case

$$A \rightleftharpoons B + q$$

Increasing $T\uparrow$ adding heat, reaction shift to the left

$$K_{eq}(T) = e^{-\Delta \bar{H}^\circ / RT} (\;) = \frac{[B]_{eq}}{[A]_{eq}}$$

positive

$\Delta \bar{H}^\circ < 0$

$e^{a/T}$, $a > 0$

$T\uparrow \Rightarrow e^{a/T}\downarrow \Rightarrow B_{eq}\downarrow, A_{eq}\uparrow$

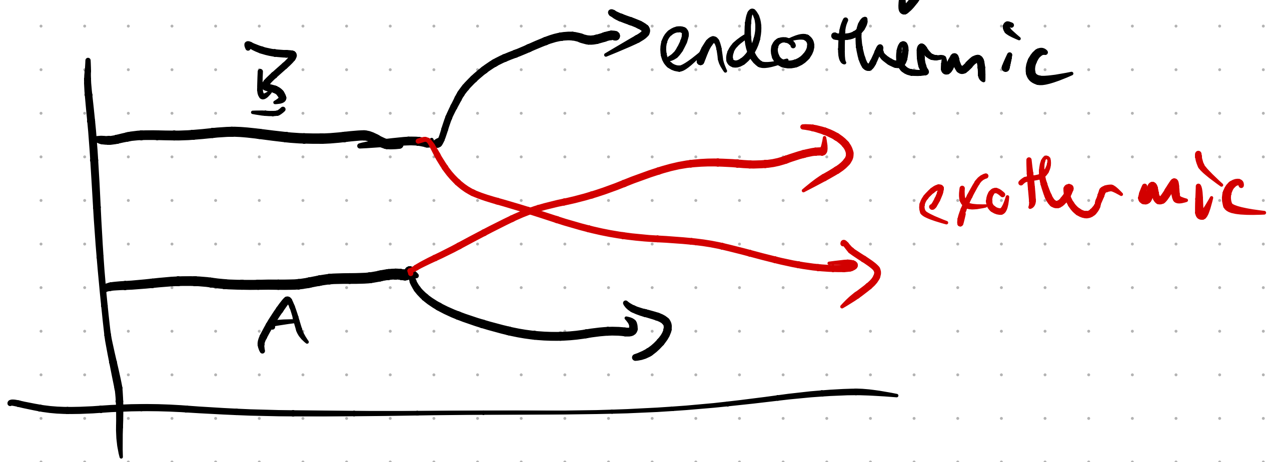
$$q + A \rightleftharpoons B$$

$\Delta H > 0$

$$\frac{[B]_{eq}}{[A]_{eq}} = e^{-\Delta \bar{H}^{\circ}/RT}\, e^{\Delta S^{\circ}/R}$$

all negative

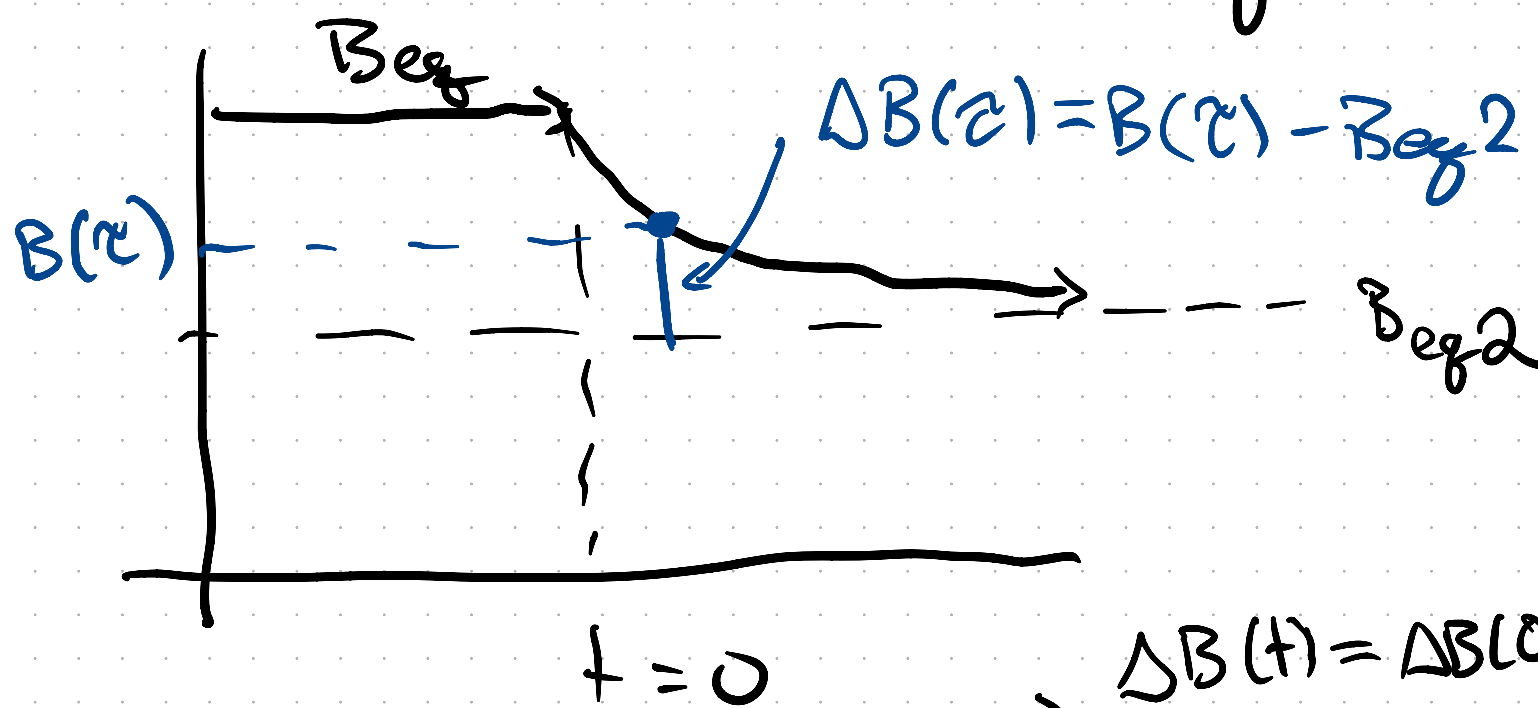
heat drives reaction to the right



Consider exothermic

$$\Delta A(t) = [A](t) - [A]_{eq2}$$

$$\Delta B(t) = [B](t) - [B]_{eq2}$$



$$\Delta B(t) = \Delta B(0) e^{-t/\tau}$$

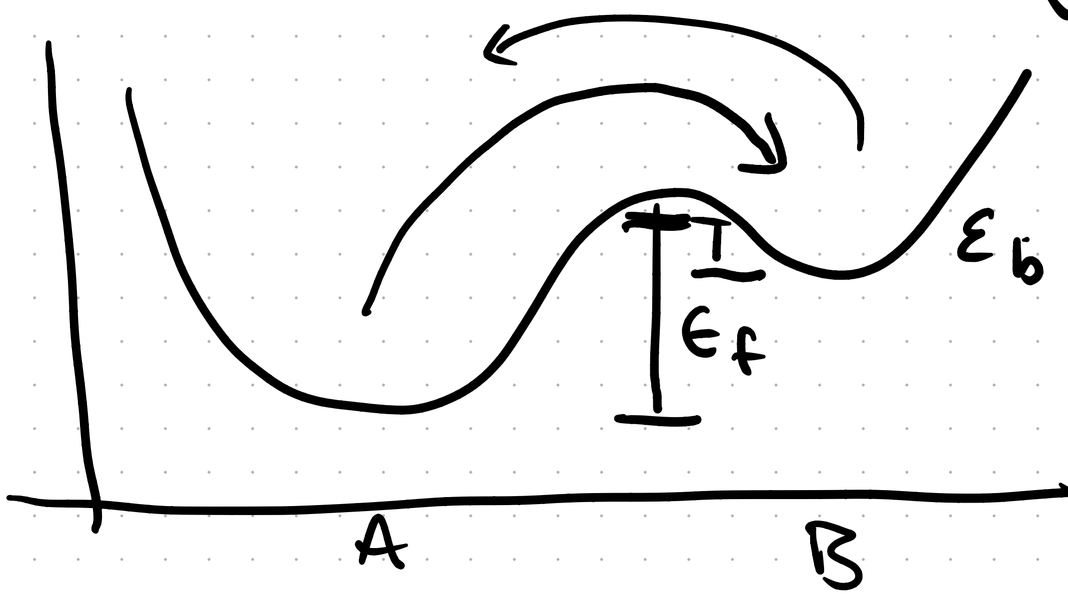
$$d\Delta B/dt = -(k_f + k_b)\Delta B \Rightarrow$$

$$\tau = (k_f + k_b)^{-1}$$

Temperature dependence of rate constants

Rate of a reaction slows down at low temperature

- How often collide & how much energy

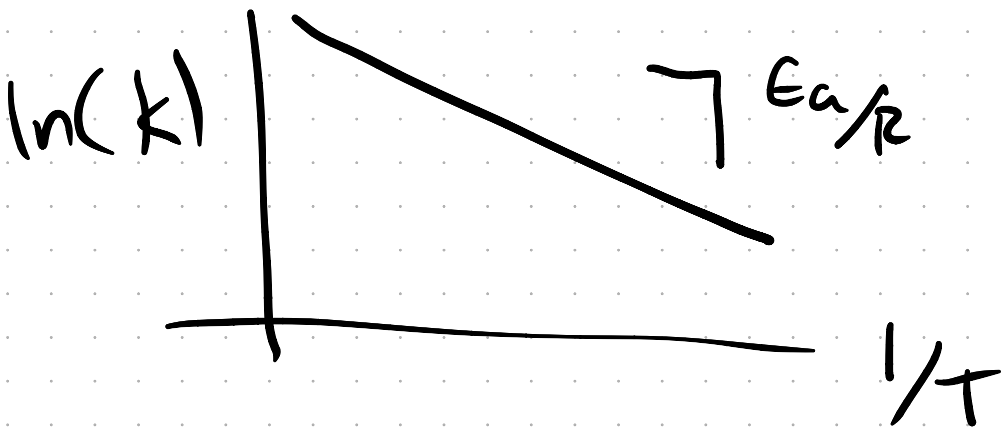


$$K = A e^{-\varepsilon_a/RT}$$

"high barrier" relative to RT or $k_B T$

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = \underline{\ln(A)} - \underline{E_a/R}\,T$$



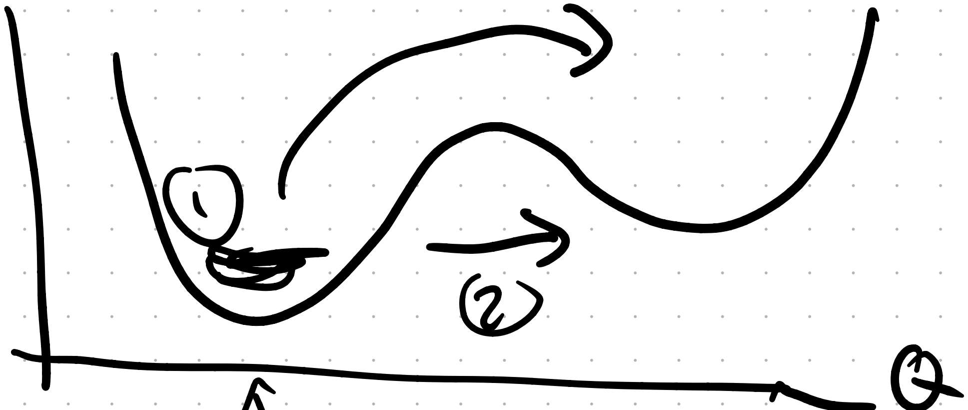
Sometimes — is not linear

$\Rightarrow A(T)$ and / or $E_a(T)$

Many reactions follow

McQuarrie (28-8)

$$k = aT^m e^{E'/RT}$$



① how long in basin

② how fast does it cross

diffusion in reactant basin

"Kramer's theory"

McQuarrie Ch 29 – Reaction Mechanism

Mechanism: Sequence of single step elementary reactions

Reactants → Intermediates

Intermediates → Products

Elementary Reactions

- we don't think has intermediates
- involves direct collision/interaction

$$aA + bB \Rightarrow \text{products}$$

↖ elementary

$aA + bB \Rightarrow$ products

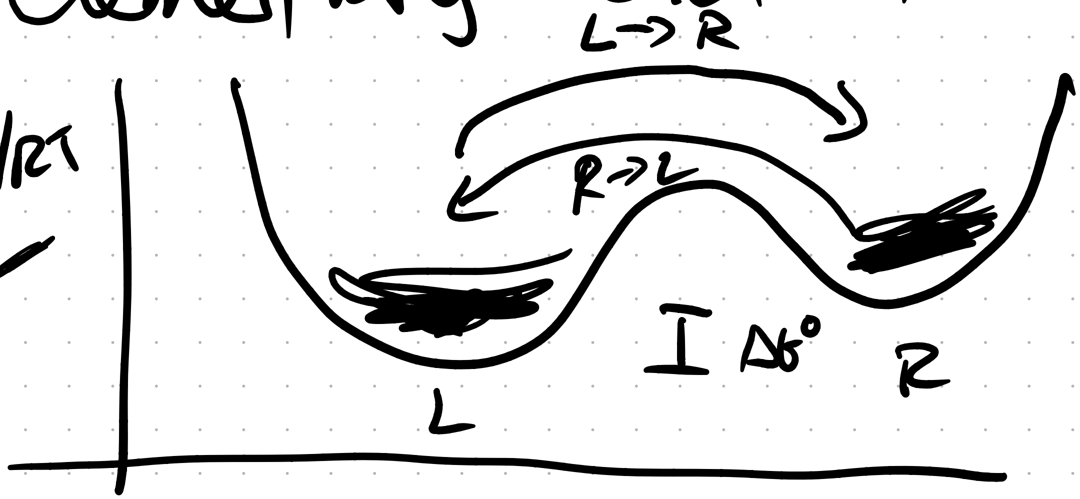
rate law $v(t) = k[A]^a[B]^b$

Principle of Detailed Balance

@ Equilibrium forward rate & backward rate of every elementary reaction are equal

$K_{eq} = e^{-\Delta G^\circ/RT}$

$\nwarrow \frac{[R]}{[L]}$



flux

L→R = R→L

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

$$v_f = k_f [A]^a [B]^b \qquad v_b = k_b [C]^c [D]^d$$

Detailed balance means $v_f = v_b$ @ eq

$$k_f [A]_{eq}^a [B]_{eq}^b = k_b [C]_{eq}^c [D]_{eq}^d$$

$$k_f / k_b = \frac{[C]_{eq}^c [D]_{eq}^d}{[A_{eq}]^a [B]_{eq}^b} = K_{eq}$$

for each elementary reaction

$$K_{eq}^{i} = k_f^{i} / k_b^{i}$$

- Detailed Balance links steps in a reaction mechanism

$$A \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} B \quad (1)$$

$$A + C \underset{k_b^2}{\overset{k_f^2}{\rightleftharpoons}} B + C \quad (2)$$

$$A \rightleftharpoons B \quad (1)$$

$$A + C \rightleftharpoons B + C \quad (2)$$

detailed balance

$$v_f^1 = v_b^1$$

$$v_f^2 = v_b^2$$

@ Eq

$$k_f^1 [A]_{eq}^1 = k_b^1 [B]_{eq}^1 \quad (1)$$

$$k_f^2 [A]_{eq} [C]_{eq} = k_b^2 [B]_{eq} [C]_{eq} \quad (2)$$

$$\frac{k_f^1}{k_b^1} \overset{(1)}{=} \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f^2}{k_b^2} \leadsto \boxed{\frac{k_f^1}{k_b^1} = \frac{k_f^2}{k_b^2}}$$

Aside Sum of reactions

$$v_f^1 = v_b^1$$

$$+ \quad v_f^2 = v_b^2$$

$$v_f^1 + v_f^2 = v_b^1 + v_b^2$$

Next: How do we know if a reaction is elementary

$$A \overset{k_f^1}{\Longrightarrow} I \overset{k_f^2}{\Longrightarrow} P$$