2012-2

Chemical reactions

$$\nu_1 X_1 + \ldots + \nu_k X_k \rightleftharpoons \nu_{k+1} X_{k+1} + \ldots + \nu_m X_m$$

ν_α - stoichiometric coefficients (order)

standard chemical potential

chemical potential $\mu_\alpha = -T \left.\frac{dS}{dN_\alpha}\right|_{E, N_{\beta \neq \alpha}} = k_B T \ln \frac{c_\alpha}{c_0} + \mu^0(\varepsilon_\alpha, T)$

$\Delta G \equiv -\nu_1 \mu_1 - \ldots - \nu_k \mu_k + \nu_{k+1} \mu_{k+1} + \ldots + \nu_m \mu_m$ "chemical force

$-\Delta G$ free energy change for forward step

$\Delta G < 0 \Rightarrow$ forward reaction ΔG:

$\Delta G > 0 \Rightarrow$ backward reaction isolated Entropy

Helmholtz Free E

$\Delta G = 0 \Rightarrow$ equilibrium open Gibbs Free Energy

Standard free energy change ΔG^0

$$\Delta G^0 \equiv -\nu_1 \mu_1^0 - \ldots + \ldots + \nu_m \mu_m^0$$

at equilibrium ($\Delta G = 0$)

$$\boxed{\frac{[X_{k+1}]^{\nu_{k+1}} \cdots [X_m]^{\nu_m}}{[X_1]^{\nu_1} \cdots [X_k]^{\nu_k}} = K_{eq} = e^{-\Delta G^0 / k_B T}}$$

Mass action rule

μ_α^0 ΔG^0 found in tables

$\Delta G'^0$ at room temperature

$[X] = c_\alpha / c_0$ where $c_0 = 1\,M$

Units (exercise)

$\frac{\Delta G^0}{k_B T}$ J $\Longleftrightarrow$ $\frac{\Delta G^0}{RT}$ J/mole

$R = N_A k_B$

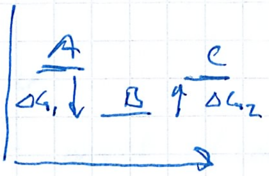
$k_B = 1.38 \cdot 10^{-23}$ J/K

$N_A = 6 \cdot 10^{23}$

$R = 8.32$ J/mole·K

Multiple reactions

$$A \underset{k_{1-}}{\overset{k_{1+}}{\rightleftarrows}} B \underset{k_{2-}}{\overset{k_{2+}}{\rightleftarrows}} C$$



equilibrium $\quad \frac{c_B}{c_A} = K_{eq1} = e^{-\Delta G_1^0/k_BT}$

$$\frac{c_C}{c_B} = K_{eq2} = e^{-\Delta G_2^0/k_BT}$$

$$\frac{c_C}{c_A} = \frac{c_B\,K_{eq2}}{c_B/K_{eq1}} = K_{eq1}\cdot K_{eq2} = K_{eq} = e^{-\overset{\Delta G_1^0+\Delta G_2^0}{\Delta G_{AC}^0}/k_BT}$$

∴ Details of the intermediate steps are immaterial for overall equilibrium

Note‼ May change kinetics (how to reach equilibrium)

Are reactions in equilibrium?

$\boxed{\text{example 1}}$ $2H_2 + O_2 \rightleftarrows 2H_2O$ at room temp (must be heated)

$\boxed{\text{example 2}}$ our bodies ⟹ energy from sun

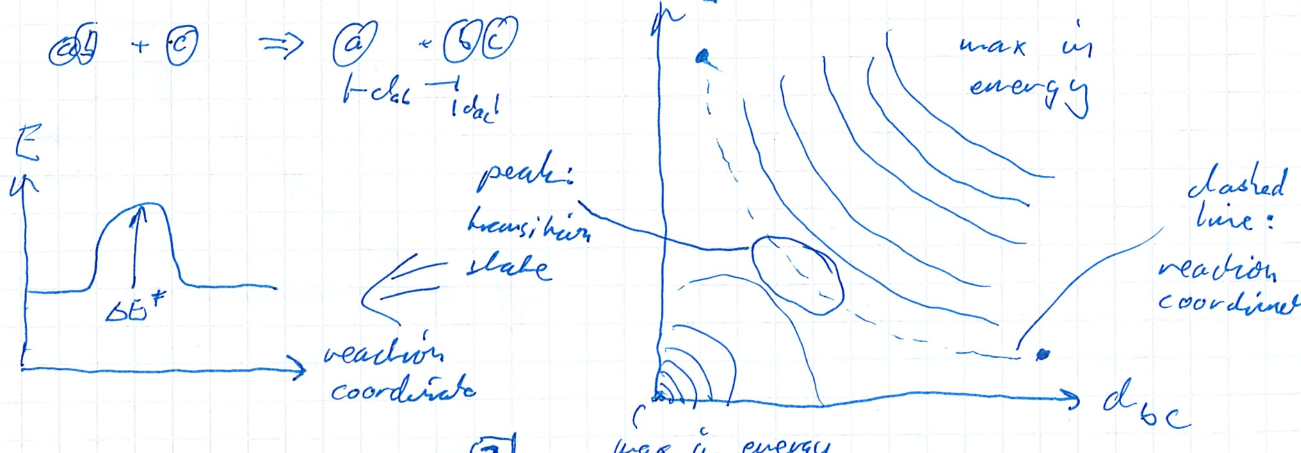
(H_2 to fuel cars, food for our work)

Reaction rates 3.2.4, 6.6.2, 10.3.2

Reaction coordinate

- chemical reactions reflect random walk on a free energy landscape of molecular configurations
- assume a valley in the landscape ⟹ reaction coordinate
- transition state: highest point along reaction path

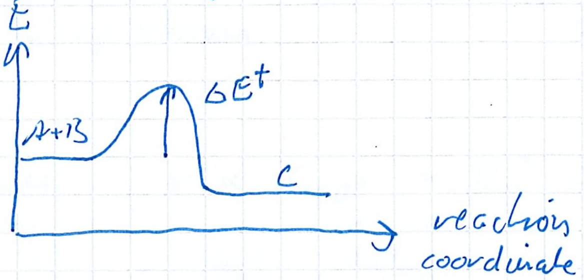
$\boxed{\text{example}}$ $H_2 + H^+ \rightarrow H^+ + H_2$



Collision theory

For a reaction $A + B \xrightarrow{k} C$ to occur

- an A and a B molecule must meet (collide)
- the kinetic energy of the molecules must exede an energy barrier $\Delta E^{\ddagger}$

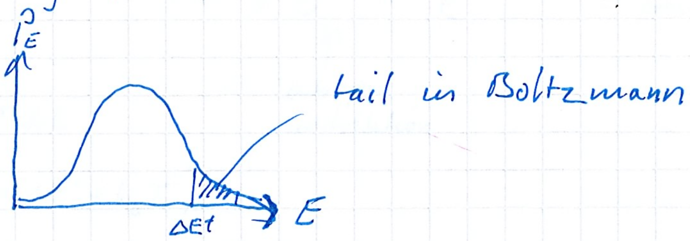


- probability that A and B meet per time

$$P_{col} \propto c_A \, c_B$$

- fraction of colliding particles with $E > \Delta E^{\ddagger}$

$$e^{-\Delta E^{\ddagger}/k_BT}$$



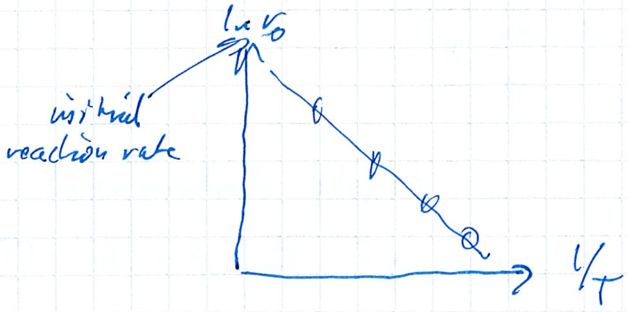
- other "constant" factors, e.g. steric factor

reaction rate $A+B \xrightarrow{k} C$ $\quad r = k \, c_A \, c_B \quad \left(\frac{dc_A}{dt} = \frac{dc_B}{dt} = -\frac{dc_C}{dt} = -k c_A c_B \right)$

$$\boxed{k = A \, e^{-\Delta E^{\ddagger}/k_BT}}$$

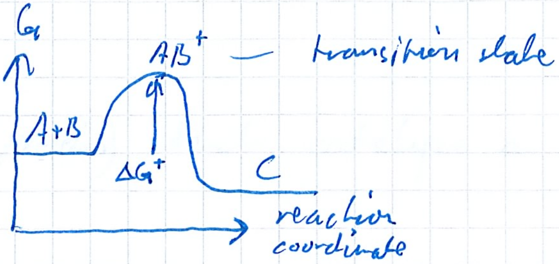
Arrhenius rate law

often seen in experiments (not only for simplistic reactions)



Transition state theory

$$A + B \xrightarrow{k_{obs}} C$$



$$\underbrace{A + B \rightleftarrows AB^{\ddagger}}_{\text{in equilibrium}} \longrightarrow C$$

$$K_{eq}^{\ddagger} = \frac{c_{AB^{\ddagger}}}{c_A\, c_B}$$

$$\text{rate} \quad r \propto c_{AB^{\ddagger}} = K_{eq}^{\ddagger}\, c_A\, c_B = e^{-\Delta G_0^{\ddagger}/k_BT}\, c_A\, c_B$$

$$\boxed{k_{obs} = \frac{k_BT}{h} e^{-\Delta G^{\ddagger}/k_BT}}$$

Eyring equation

$k_B = 1.4 \cdot 10^{-23}$ J/

$h = 6.6 \cdot 10^{-34}$ J·

$T_r \sim 300$ K

$\Delta G^{\ddagger}$ vs $\Delta E^{\ddagger}$

$$e^{-\Delta G^{\ddagger}/k_BT} = e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/k_BT} = e^{\Delta S^{\ddagger}/k_B}\, e^{-\Delta H^{\ddagger}/k_BT} = \text{const} \cdot e^{\Delta S^{\ddagger}/k_B}\, e^{-\Delta E^{\ddagger}/k_BT}$$

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

(enthalpy $\Delta H^{\ddagger} = \Delta E^{\ddagger} + k_BT$)

entropic contribution

'Problematic' example

$$X_2 + Y_2 \underset{k_-}{\overset{k_+}{\rightleftarrows}} 2XY \qquad \text{1st order in } X_2\ Y_2$$

theory $\begin{cases} \text{forward rate} & v_+ = k_+\, c_{X_2}\, c_{Y_2} \\ \text{backward rate} & v_- = k_-\, c_{XY}^2 \end{cases}$

experiments

$c_{X_2} \rightarrow 2\, c_{X_2} \Longrightarrow v_+ \rightarrow 4\, v_+$ (2nd order)

$c_{Y_2} \rightarrow 2\, c_{Y_2} \Longrightarrow v_+ \rightarrow v_+$ (0th order)

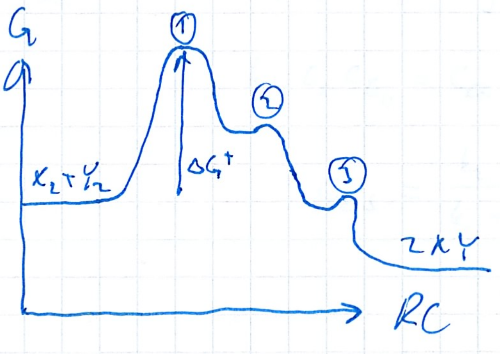
?

Intermediate steps:

① $X_2 + X_2 \rightleftarrows 2X + X_2$

② $X + Y_2 \rightleftarrows XY_2$

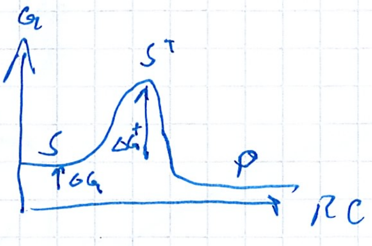
③ $X + XY_2 \rightleftarrows 2XY$

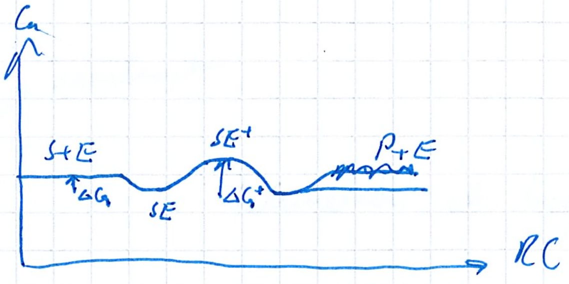


⊛ Enzymes (10.3.3, 10.4.1)

- Molecules created by cells (proteins) that catalyze a reaction i.e. increase the rate
- Is not used up in the reaction (cyclic machine)
- Effect from lowering activation barrier

example





$\Delta G^{\ddagger}$ decreased while ΔG unchanged!

Michaelis-Menten rule

- Describes kinetics of simple enzymatic reactions

$$S+E \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SE \xrightarrow{k_2} P+E$$

Assume: $\left\{\begin{array}{l} \text{- second reaction rate limiting} \\ \quad \text{(SE in quasi equilibrium)} \\ \text{- fixed amount of enzyme } c_{E_0} = c_E + c_{SE} \end{array}\right.$

Goal: describe production of P by c_S

$$\frac{dc_S}{dt} = -k_1 c_S c_E + k_{-1} c_{SE}$$

$$\frac{dc_E}{dt} = -k_1 c_S c_E + (k_{-1}+k_2) c_{SE}$$

quasi eq

$c_{E_0} = c_E + c_{SE}$

$$\frac{dc_{SE}}{dt} = k_1 c_S c_E - (k_{-1}+k_2) c_{SE} = 0 = k_1 c_S (c_{E_0} - c_{ES}) - (k_{-1}+k_2) c_{ES}$$

$$\frac{dP}{dt} = k_2 c_{ES}$$

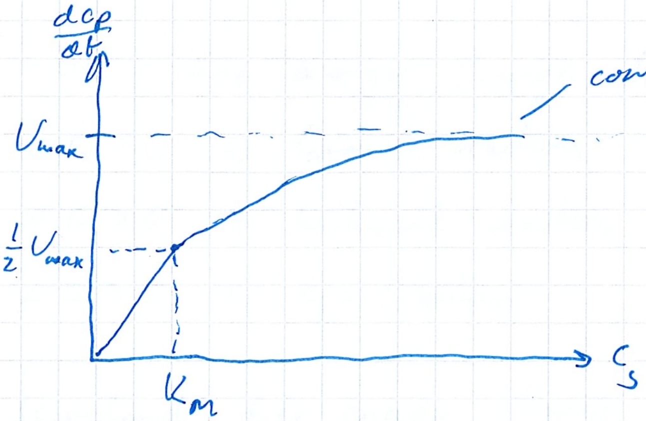
$$k_1 c_S c_{E_0} = c_{ES} (k_1 c_S + k_{-1} + k_2)$$

$$c_{ES} = \frac{k_2 c_S c_{E_0}}{k_{-1}+k_2+k_1 c_S}$$

$$\frac{dc_p}{dt} = \frac{k_2 c_s c_{E_0}}{\frac{k_{-1}+k_2}{k_1} + c_s} \qquad \left\{ \begin{array}{l} V_{max} = k_2 c_{E_0} \\ K_M = \frac{k_{-1}+k_2}{k_1} \end{array} \right\}$$

$$\boxed{\frac{dc_p}{dt} = \frac{V_{max}\, c_s}{K_M + c_s}}$$

Michaelis Menten equation



constant

Saturation at high c_s

e.g. gene transcription

$2TF + DNA \rightleftarrows DNA^t \rightarrow mRNA$

mediated ~~st~~transport