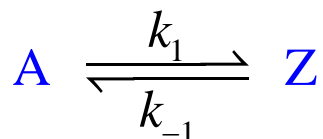


Opposing Reactions – Relaxation



At equilibrium

$$-\frac{da}{dt} = k_1 a - k_{-1} z = \frac{dz}{dt} = 0$$

$$k_1 a_{\text{eq}} = k_{-1} z_{\text{eq}} \quad \Rightarrow$$

$$K = \frac{[Z]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_{-1}}$$

If equilibrium is disturbed by an amount x , so that

$$a(t) = a_{\text{eq}} - x(t), \quad z(t) = z_{\text{eq}} + x(t), \quad \frac{dz}{dt} = \frac{dx}{dt} = -\frac{da}{dt}$$

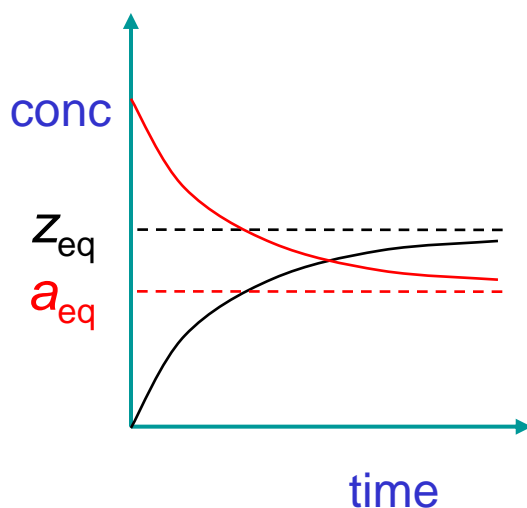
$$-\frac{da}{dt} = k_1 (a_{\text{eq}} - x) - k_{-1} (z_{\text{eq}} + x)$$

$$= -(k_1 + k_{-1}) x = \frac{dx}{dt}$$

$$x = x_0 \exp\{-(k_1 + k_{-1})t\}$$

$$(a - a_{\text{eq}}) = (a_0 - a_{\text{eq}}) e^{-(k_1 + k_{-1})t}$$

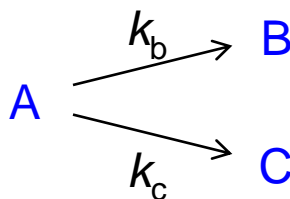
$$(z_{\text{eq}} - z) = (z_{\text{eq}} - z_0) e^{-(k_1 + k_{-1})t}$$



This exponential **relaxation** of concentrations is the basis for several **jump** methods of studying fast reaction kinetics.

Parallel Reactions – Competition

Consider a molecule that can react by two different routes:



Define $a = [A]$, $b = [B]$, $c = [C]$.

The overall decay of A depends on both reactions:

$$-\frac{da}{dt} = k_b a + k_c a = (k_b + k_c) a \quad \Rightarrow \quad a = a_0 e^{-(k_b + k_c)t}$$

The rate of formation of each product depends on both rate constants:

$$\left. \begin{aligned} \frac{db}{dt} &= k_b a = k_b a_0 e^{-(k_b + k_c)t} \\ \frac{dc}{dt} &= k_c a = k_c a_0 e^{-(k_b + k_c)t} \end{aligned} \right\} \Rightarrow \frac{b}{c} = \frac{k_b \int a dt}{k_c \int a dt} = \frac{k_b}{k_c} = \frac{db/dt}{dc/dt}$$
$$\frac{k_b}{k_c} = \frac{[B]}{[C]} = \frac{\text{yield of B}}{\text{yield of C}}$$

This is the basis for **competition kinetics**, whereby an unknown rate constant is determined from a known rate constant and the ratio of competitive products.

The above treatment assumes *kinetic control*. In contrast, at equilibrium,

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = K_b, \quad \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}} = K_c, \quad \frac{[B]_{\text{eq}}}{[C]_{\text{eq}}} = \frac{K_b}{K_c} = \frac{k_b k_{-c}}{k_c k_{-b}}$$

Consecutive Reactions

Simplest case - two first-order steps



$$\frac{da}{dt} = -k_1 a$$

$$a = a_0 e^{-k_1 t}$$

$$\frac{db}{dt} = k_1 a - k_2 b$$

$$b = a_0 \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$\frac{dc}{dt} = k_2 b$$

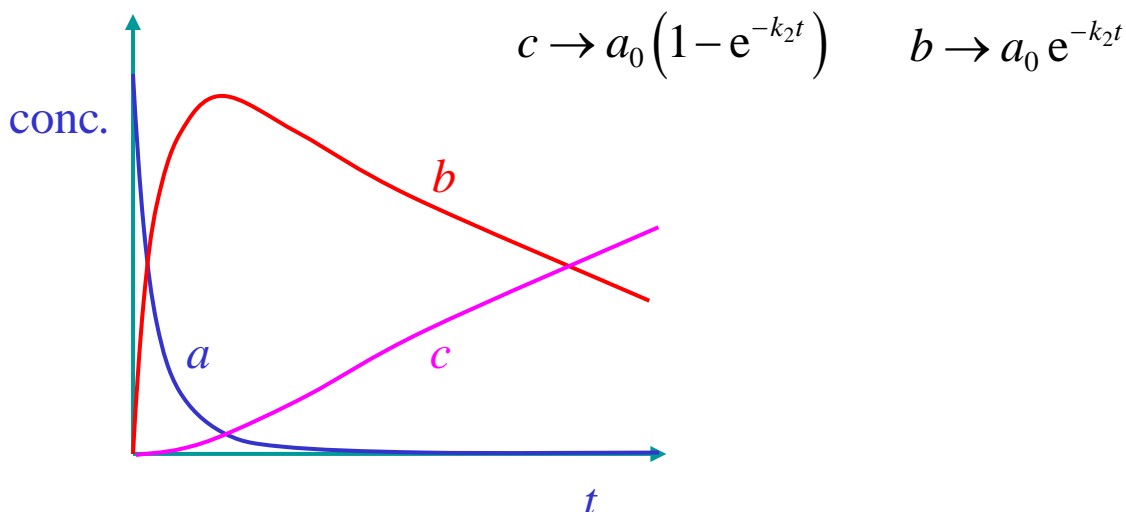
$$c = a_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

$$\frac{da}{dt} + \frac{db}{dt} + \frac{dc}{dt} = 0$$

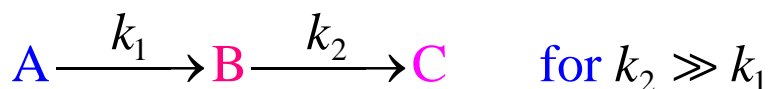
$$a + b + c = a_0$$

For $k_1 \gg k_2$ the kinetics can be considered as two steps:

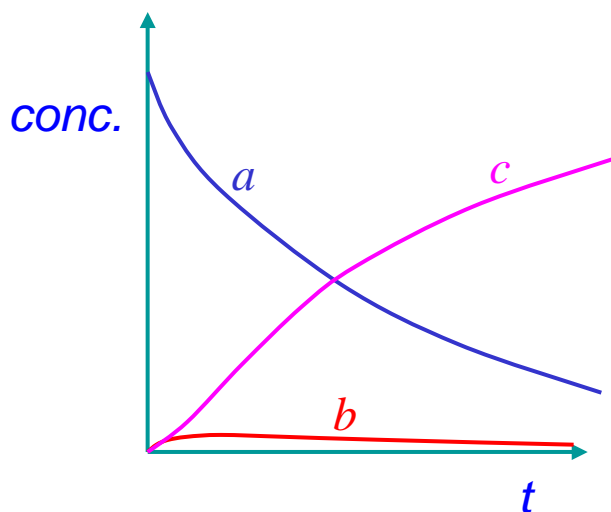
1. At short times b increases as a falls.
2. At longer times ($k_1 t \gg 0$), c increases as b falls.



The Steady-State Approximation



$$\frac{db}{dt} = k_1 a - k_2 b = k_1 a_0 e^{-k_1 t} \left[\frac{-k_1}{k_2 - k_1} + \frac{k_2}{k_2 - k_1} e^{-(k_2 - k_1)t} \right]$$



After the induction period, i.e. for $k_2 t \gg 0$,

$$\frac{da}{dt} = -k_1 a_0 e^{-k_1 t}, \quad \frac{dc}{dt} \approx k_1 a_0 e^{-k_1 t}, \quad \frac{db}{dt} \approx -k_1 a_0 e^{-k_1 t} \left[\frac{k_1}{k_2 - k_1} \right]$$

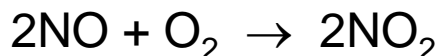
$$\left. \frac{db}{dt} \right| \ll \left. \frac{da}{dt} \right|, \left. \frac{dc}{dt} \right|$$

Although b is not constant, it changes at a much smaller rate than a or c .

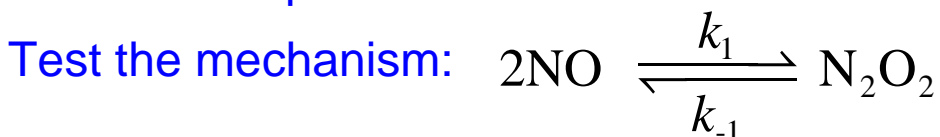
This is the essence of the **steady-state approximation**.

An Example of a Complex Mechanism

Consider the overall reaction



It is found experimentally to be third order overall, second order in NO, first order in O₂. It is much too fast to be a termolecular process



Apply the steady-state approximation to [N₂O₂]

$$\frac{d}{dt}[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2] = 0$$

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{O}_2]}$$

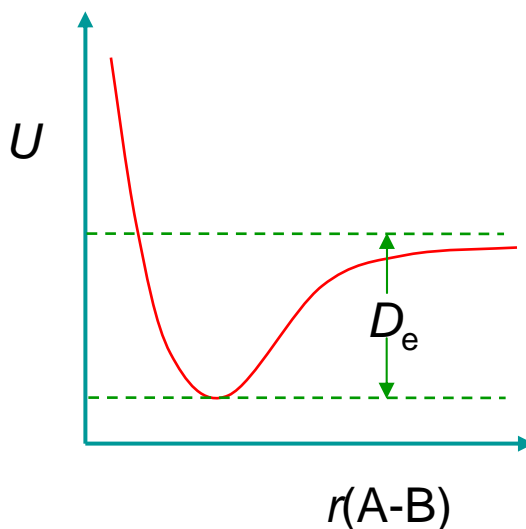
$$\text{rate} = \frac{1}{2} \frac{d}{dt}[\text{NO}_2] = k_2[\text{N}_2\text{O}_2][\text{O}_2] = \frac{k_1 k_2 [\text{NO}]^2 [\text{O}_2]}{k_{-1} + k_2 [\text{O}_2]}$$

In the limit of $k_{-1} \gg k_2 [\text{O}_2]$, $\text{rate} = \frac{k_1 k_2}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$

This is an example of a **pre-equilibrium mechanism**.

Atom/Radical Combination Reactions

In low pressure gases, atoms seem to react slower than expected because the combination product falls apart in the period of a molecular vibration ($\sim 10^{-14}$ s).



If A and B are polyatomic radicals, $(A-B)^*$ may live longer (e.g. 10^{-9} s), by distribution of D_e among different vibrational modes.

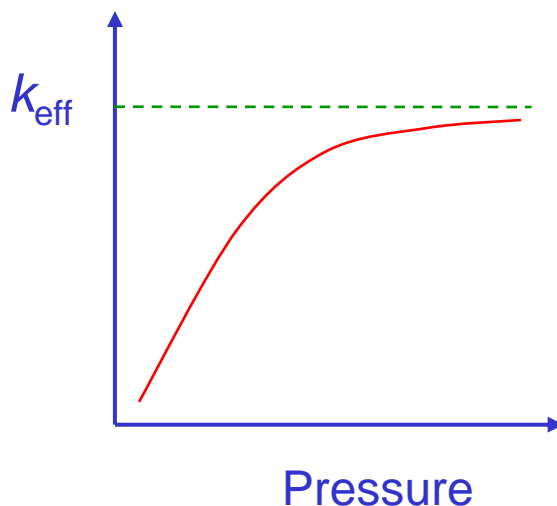
For efficient reaction a **third body** is needed:

- $A + B \rightleftharpoons AB^*$
- $AB^* + M \rightarrow AB + M$

$$\rho = \frac{d[AB]}{dt} = k_2[M][AB^*]$$

$$= k_2[M] \cdot \frac{k_1[A][B]}{k_{-1} + k_2[M]}$$

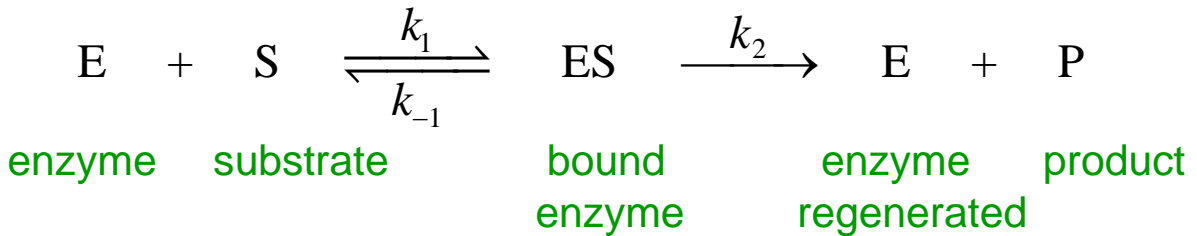
$$= \frac{k_1 k_2 [M]}{k_{-1} + k_2 [M]} \cdot [A][B]$$



The effective rate constant depends on pressure ($[M]$).

Enzyme Kinetics 1

Another example of a pre-equilibrium mechanism is one used to model the kinetics of enzyme action:



Applying the steady-state approximation to the bound state,

$$\frac{d[\text{ES}]}{dt} = k_1[\text{E}][\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0$$

$$[\text{ES}] = \frac{k_1}{k_{-1} + k_2} [\text{E}][\text{S}] = \frac{k_1}{k_{-1} + k_2} ([\text{E}]_0 - [\text{ES}])[\text{S}]$$

Rearranging:
$$[\text{ES}] = \frac{k_1[\text{E}]_0[\text{S}]}{k_{-1} + k_2 + k_1[\text{S}]}$$

Rate:
$$\rho = \frac{d[\text{P}]}{dt} = k_2[\text{ES}] = \frac{k_1 k_2 [\text{E}]_0 [\text{S}]}{k_{-1} + k_2 + k_1 [\text{S}]}$$

$$\rho = \frac{k_2 [\text{E}]_0 [\text{S}]}{K_M + [\text{S}]}$$

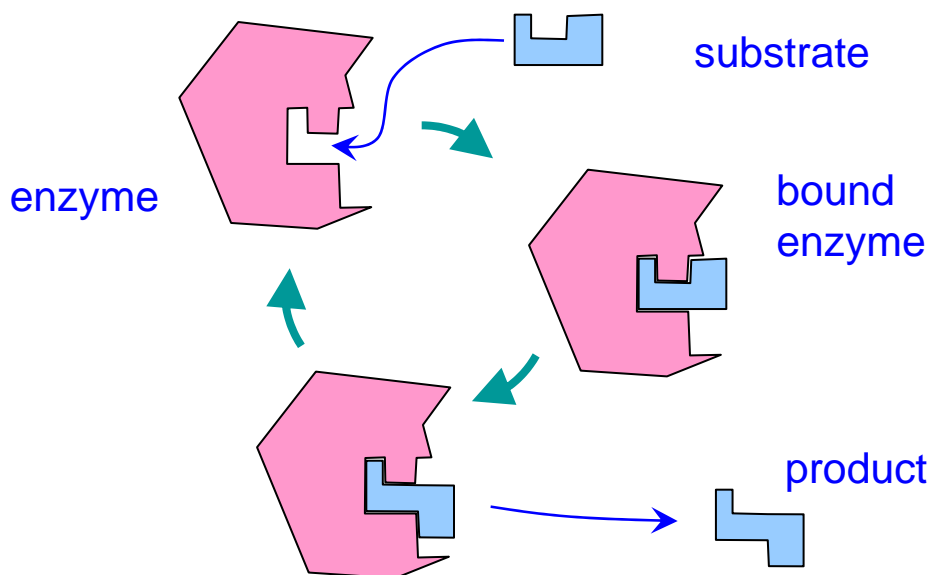
with

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

Michaelis-Menten

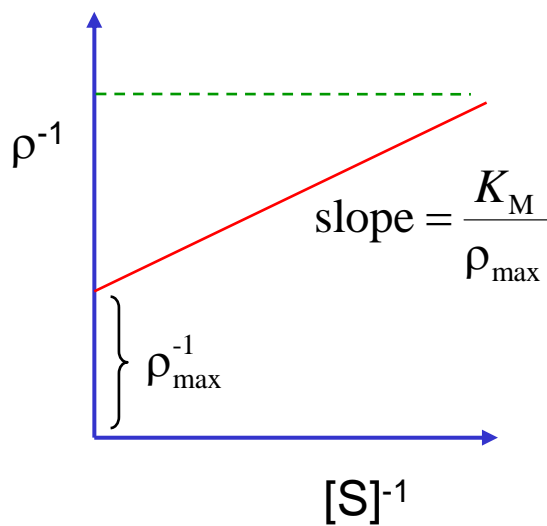
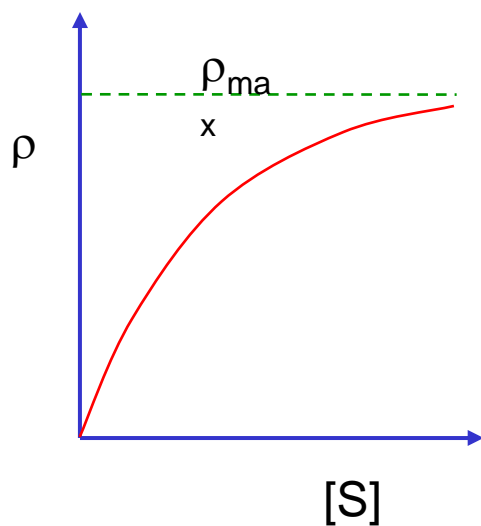
Michaelis constant

Enzyme Kinetics 2



Write the Michaelis-Menten equation in reciprocal form:

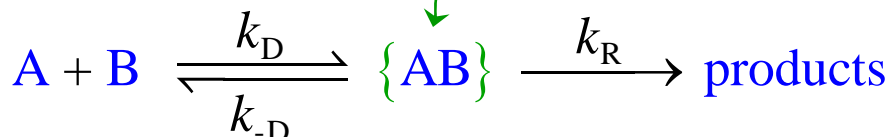
$$\frac{1}{\rho} = \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0[S]} = \frac{1}{\rho_{\max}} + \frac{K_M}{\rho_{\max}} \cdot \frac{1}{[S]}$$



Lineweaver-Burke plot

Diffusion-limited Kinetics

For fast reactions in liquids, the rate-determining step can be diffusion of the reactants to form the **encounter pair**:



Apply the steady-state approximation to $\{AB\}$:

$$\frac{d}{dt}[\{AB\}] = k_D[A][B] - (k_{-D} + k_R)[\{AB\}] = 0$$

$$\text{rate} = k_R[\{AB\}] = \frac{k_D k_R}{k_{-D} + k_R}[A][B]$$

The effective rate constant has two limits:

Slow diffusion: $k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} \rightarrow k_D$ if $k_R \gg k_{-D}$

Fast diffusion: $k_{\text{eff}} \rightarrow \frac{k_D k_R}{k_{-D}} = K_{\{AB\}} k_R = k_{\text{act}}$ if $k_{-D} \gg k_R$

Intermediate situations can be described by:

$$k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} = \frac{k_D (k_D k_R / k_{-D})}{k_D + (k_D k_R / k_{-D})} = \frac{k_D k_{\text{act}}}{k_D + k_{\text{act}}}$$

Take the inverse:

$$\frac{1}{k_{\text{eff}}} = \frac{1}{k_D} + \frac{1}{k_{\text{act}}}$$

Diffusion-limited Rate Constants

The diffusion –limited rate constant can be calculated:

Smoluchowski $k_D = 4\pi r_{AB} D_{AB}$ (m³ molecule⁻¹ s⁻¹)

$$4000\pi r_{AB} D_{AB} N_{Av} \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$$

with encounter distance $r_{AB} = r_A + r_B$

coefficient of mutual diffusion $D_{AB} = D_A + D_B$ (m²s⁻¹)

D_A, D_B can be estimated from the

Stokes-Einstein equation $D = \frac{k_B T}{\pi\beta\eta r_s}$

η is the viscosity of the solvent, r_s is the hydrodynamic radius

$\beta = 6$ for ideal Stokes diffusion (continuous medium)

$\beta = 4$ for the opposite limit (solute radius \approx solvent radius)

Assuming the hydrodynamic radius \approx reaction radius,

$$k_D = \frac{4k_B T}{\beta\eta} \left[\frac{1}{r_A} + \frac{1}{r_B} \right] (r_A + r_B) = \frac{4k_B T}{\beta\eta} \left[2 + \frac{r_B}{r_A} + \frac{r_A}{r_B} \right]$$

For reactants of similar size,

$$k_D \approx \frac{16k_B T}{\beta\eta_s} \approx 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad \text{in water at 300 K}$$

The rate constant is determined by solvent properties!

The viscosity dominates the temperature dependence.