ChemE 2200 – Chemical Kinetics Lecture 3

Today:

Rate Equation Nomenclature
Elementary Reactions
Reversible Reactions

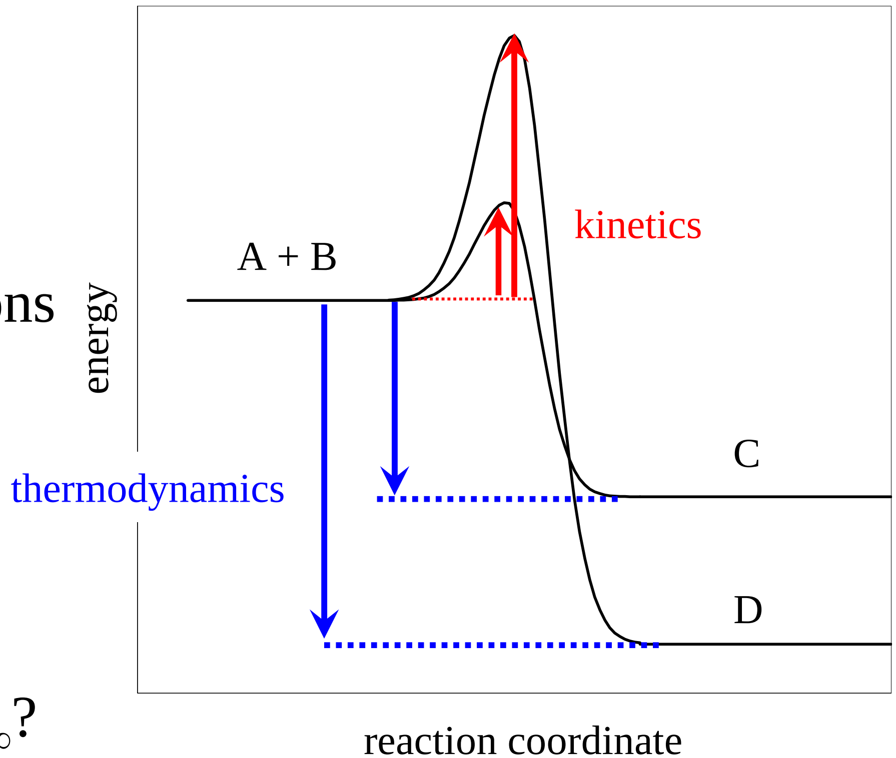
Recap:

Consider the parallel, irreversible reactions

$A + B \rightarrow C$ and $A + B \rightarrow D$

Thermodynamics favors $[D]$ over $[C]$.
Kinetics favors $[C]$ over $[D]$.

For $t \rightarrow \infty$, $[C]_\infty > [D]_\infty$ or $[D]_\infty > [C]_\infty$?



Defining Question:

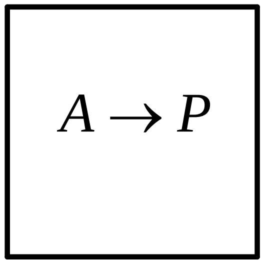
What if both reactions are reversible? For $t \rightarrow \infty$, $[C]_\infty > [D]_\infty$ or $[D]_\infty > [C]_\infty$?

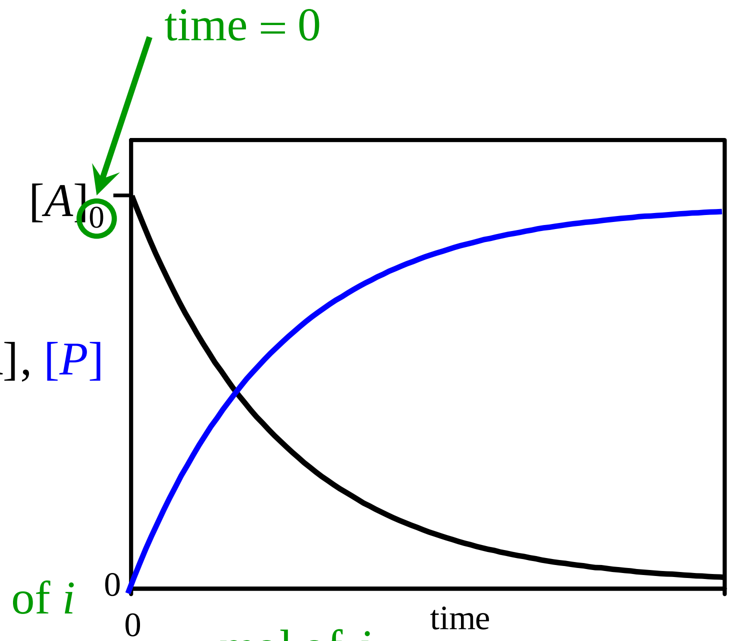
Reading for Kinetics Lecture 4:

McQuarrie & Simon, Chp 28.7.

Nomenclature for Rate Equations (aka Rate Laws)

Example: batch reactor - closed system





$$\text{Rate of Reaction of substance } i \equiv r_i = \frac{1}{V_{\text{reactor}}}\frac{dN_i}{dt} = \frac{d[i]}{dt}$$

$\frac{\text{mol}}{\text{L}\cdot\text{sec}}$ mols of i $\frac{\text{mol of } i}{\text{L}}$

$$\text{For } A \to P, \quad r_A = \frac{d[A]}{dt} < 0 \quad r_P = \frac{d[P]}{dt} > 0$$

$$\text{Rate of Reaction} \equiv r_{\text{rxn}} = \frac{1}{\nu_i} r_i$$

For $A \to P$, the chemical equation is $0 = -A + P$

$\nu_A = -1$ $\nu_P = +1$

'nu' ≡ stoichiometric coefficient of substance i

$$\text{Rate of Reaction for } A \to P = r_{\text{rxn}} = -r_A = +r_P > 0$$

Nomenclature for Rate Equations

$$\text{Rate of Reaction} \equiv r_{\mathrm{rxn}} = \frac{1}{\nu_i} r_i$$

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

$$r_{\mathrm{rxn}} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{1}{1}\frac{d[O_2]}{dt}$$

chemical equation: $0 = -2N_2O_5 + 4NO_2 + O_2$

Check: assume O_2 is produced at 1 mol/(L·sec). From the reaction stoichiometry,
NO_2 is produced at 4 mol/(L·sec), and
N_2O_5 is consumed at 2 mol/(L·sec)

$$\frac{d[O_2]}{dt} = \frac{1\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}, \qquad \frac{d[NO_2]}{dt} = \frac{4\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}, \qquad \frac{d[N_2O_5]}{dt} = -\frac{2\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}$$

$$r_{\mathrm{rxn}} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{1}\frac{d[O_2]}{dt}$$

$$r_{\mathrm{rxn}} = -\frac{1}{2}\left(-\frac{2\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}\right) = \frac{1}{4}\left(\frac{4\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}\right) = \frac{1}{1}\left(\frac{1\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}}\right)$$

$$r_{\mathrm{rxn}} = \frac{1\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}} = \frac{1\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}} = \frac{1\,\mathrm{mol}}{\mathrm{L}\cdot\mathrm{sec}} \checkmark$$

Mathematical Expressions for the Rate Equation, r_{rxn}

$1\ CH_3N{=}C \rightarrow CH_3C{\equiv}N$ $\qquad r_{rxn} = -\dfrac{d[CH_3N{=}C]}{dt} = k[CH_3N{=}C]^1$ $\qquad$ *possibly* elementary

methyl isocyanide $\qquad$ acetonitrile (aka methyl cyanide)

rate “constant”

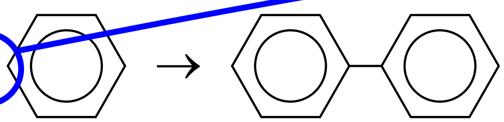
numerical value varies with reaction

numerical value varies with temperature

units vary with reaction

$1\ O_3 + 1\ {\bullet}Cl \rightarrow O_2 + ClO$ $\qquad r_{rxn} = -\dfrac{d[O_3]}{dt} = k[O_3]^1[{\bullet}Cl]^1$ $\qquad$ *possibly* elementary

ozone

2  + H_2 $\qquad r_{rxn} = -\dfrac{1}{2}\dfrac{d[C_6H_6]}{dt} = k[C_6H_6]^2$ $\qquad$ *possibly* elementary

benzene $\qquad$ phenylbenzene

Definition: Elementary Reaction

Rate equation is the product of reactant concentrations raised to the power of the stoichiometric coefficients. $\qquad$ necessary, but not sufficient.

Molecular mechanism is exactly as written. for example, O_3 and $\bullet Cl$ collide to form products. $\qquad$ necessary *and* sufficient.

Mathematical Expressions for the Rate Equation, r_{rxn}

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} \qquad r_{rxn} = -\frac{d[{}^{238}_{92}\mathrm{U}]}{dt} = k[{}^{238}_{92}\mathrm{U}]$$

elementary

$$\mathrm{CH_3CHO} \rightarrow \mathrm{CH_4} + \mathrm{CO} \qquad r_{rxn} = -\frac{d[\mathrm{CH_3CHO}]}{dt} = k[\mathrm{CH_3CHO}]^{3/2}$$

acetaldehyde

not elementary

$$2\mathrm{O_3} + \mathrm{N_2O_5} \rightarrow 3\mathrm{O_2} + \mathrm{N_2O_5} \qquad r_{rxn} = -\frac{1}{2}\frac{d[\mathrm{O_3}]}{dt} = k[\mathrm{O_3}]^{3/2}[\mathrm{N_2O_5}]^{3/2}$$

not elementary

tri-molecular collision - rarely elementary

Reversible Reactions

All reactions are reversible.

If a reaction effectively goes to completion, the reaction may be considered irreversible.

rate constant for rxn 1

$$A \xrightarrow{k_1} B$$

a rate constant written above the reaction arrow implies the reaction is elementary.

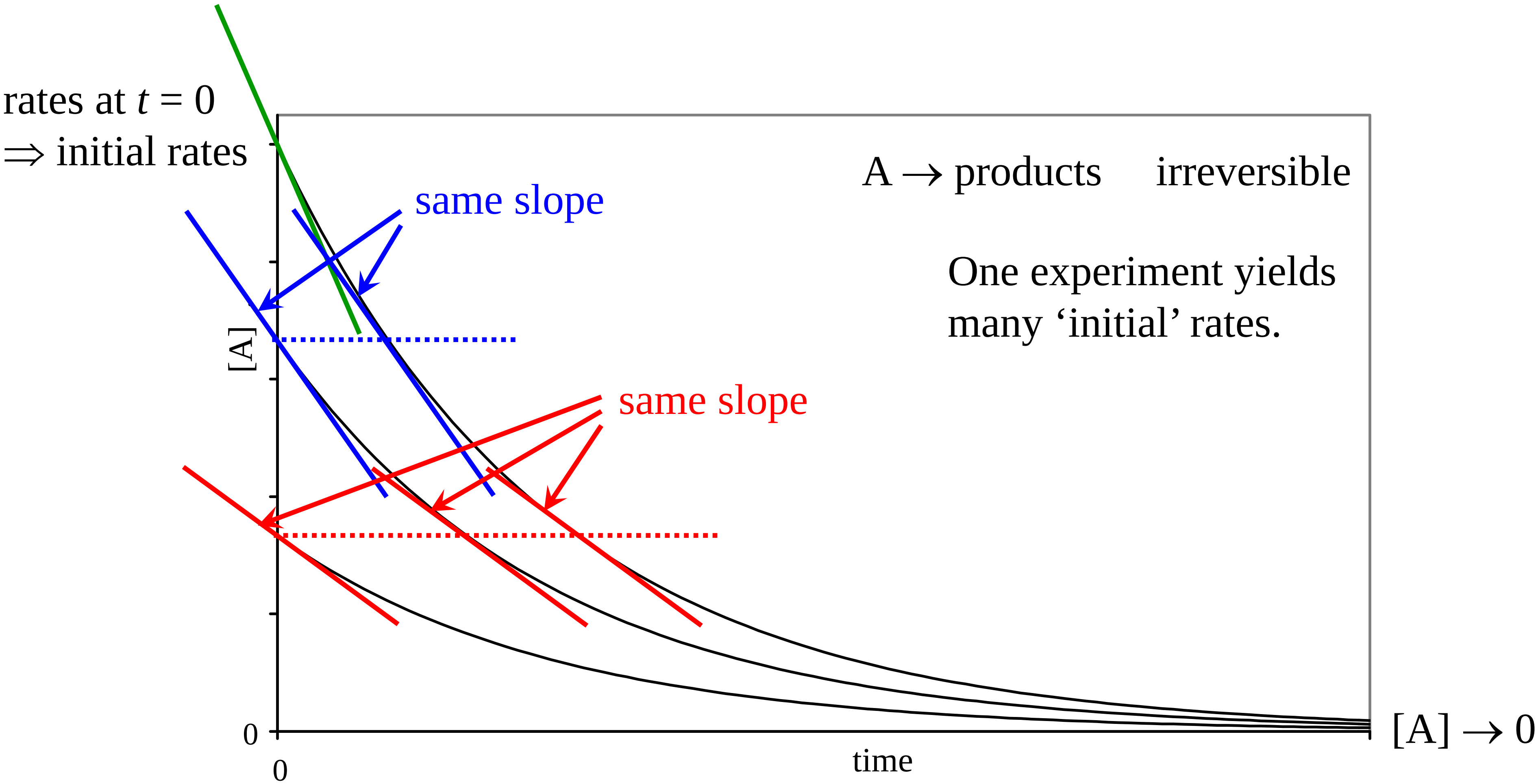
If reversible,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

rate constant for reverse of rxn 1

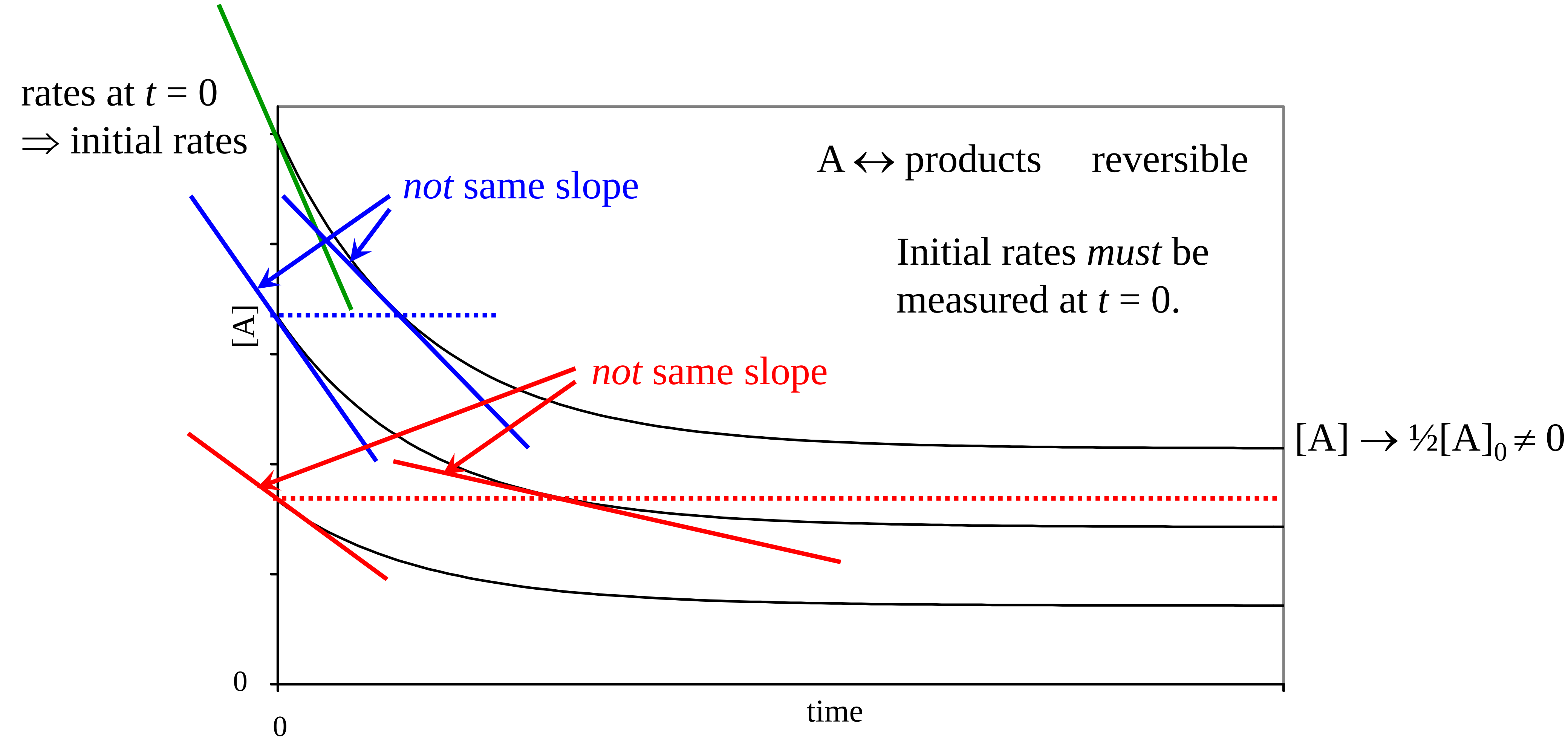
Method of Initial Rates - Revisited

Batch Reactor (closed system) initially charged with reactant(s) only.



Method of Initial Rates - Revisited

Batch Reactor (closed system) initially charged with reactant(s) only.



How to interpret slopes for $t > 0$ to calculate k_1 and k_{-1}?

We need a mathematical model for $[A] = f(t)$.

Mathematical Model for a First-Order Reversible Reaction

$$1\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 1\mathrm{B} \quad \text{or} \quad \mathrm{A} \xrightarrow{k_1} \mathrm{B} \quad \text{and} \quad \mathrm{B} \xrightarrow{k_{-1}} \mathrm{A}$$

Elementary Reactions, Batch Reactor with $[\mathrm{B}]_0 = 0$

Write the rate equation.

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}]^1 + k_{-1}[\mathrm{B}]^1 \qquad (1)$$

Must express [B] in terms of [A]. Apply a mass balance, convert to a mol balance, divide by reactor volume to convert to concentrations.

$$[\mathrm{A}]_0 + \cancel{[\mathrm{B}]_0}^{\,0} = [\mathrm{A}] + [\mathrm{B}]$$

substitute

$$[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}] \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}\left([\mathrm{A}]_0 - [\mathrm{A}]\right)$$

$$\frac{d[\mathrm{A}]}{dt} = -(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0 \qquad (3)$$

Mathematical Model for a First-Order Reversible Reaction, cont'd

Rearrange to a first-order differential equation,

These terms are the same …

$$\boxed{\frac{d[\mathrm{A}]}{dt} + (k_1 + k_{-1})[\mathrm{A}]} = k_{-1}[\mathrm{A}]_0 \qquad (4)$$

and use an integrating factor.

$$\mu(t) = \exp\left(\int_0^t (k_1 + k_{-1})\, dt \right) = e^{(k_1+k_{-1})t}$$

$$\frac{d}{dt}\left([\mathrm{A}]e^{(k_1+k_{-1})t}\right) = \frac{d[\mathrm{A}]}{dt}e^{(k_1+k_{-1})t} + [\mathrm{A}](k_1 + k_{-1})e^{(k_1+k_{-1})t}$$

$$= e^{(k_1+k_{-1})t}\boxed{\left(\frac{d[\mathrm{A}]}{dt} + (k_1 + k_{-1})[\mathrm{A}]\right)}$$

$$= e^{(k_1+k_{-1})t} k_{-1}[\mathrm{A}]_0$$

… so we can substitute these terms.

separate 'n' integrate

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]e^{(k_1+k_{-1})t}} d\left([\mathrm{A}]e^{(k_1+k_{-1})t}\right) = \int_0^t e^{(k_1+k_{-1})t} k_{-1}[\mathrm{A}]_0\, dt$$

⋮

Mathematical Model for a First-Order Reversible Reaction, cont'd

Elementary Reactions, Batch Reactor with $[\mathrm{B}]_0 = 0$

$$\frac{d[\mathrm{A}]}{dt} = -(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0 \qquad (3)$$

Alternative solution

separate 'n' integrate

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0} = \int_0^t dt$$

$$\frac{1}{-(k_1 + k_{-1})} \ln\left(-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0\right)\Bigg|_{[\mathrm{A}]_0}^{[\mathrm{A}]} = t\,\Bigg|_0^t$$

$$\ln\left(-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0\right) - \ln\left(-(k_1 + \cancel{k_{-1}})[\mathrm{A}]_0 + \cancel{k_{-1}}[\mathrm{A}]_0\right) = -(k_1 + k_{-1})t$$

$$\ln\left(\frac{-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0}{-k_1[\mathrm{A}]_0}\right) = -(k_1 + k_{-1})t$$

$$\frac{-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0}{-k_1[\mathrm{A}]_0} = e^{-(k_1 + k_{-1})t}$$

$$-(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0 = -k_1[\mathrm{A}]_0 e^{-(k_1 + k_{-1})t}$$

$$\boxed{[\mathrm{A}] = \frac{k_1 e^{-(k_1 + k_{-1})t} + k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0}$$

Mathematical Model for a First-Order Reversible Reaction, cont'd

Elementary Reactions, Batch Reactor with $[B]_0 = 0$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$\boxed{[A] = \frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{k_1 + k_{-1}}[A]_0}$$

Verify the result.

Check the dimensions. Note: $k_1 \; [=] \; k_{-1} \; [=] \; \frac{1}{\text{sec}}$ ✓

Check limits.

Okay for $k_{-1} = 0$? (irreversible reaction).

$$[A] = \frac{\cancel{k_1} e^{-(k_1+\underset{\to 0}{k_{-1}})t} + \underset{\to 0}{k_{-1}}}{\cancel{k_1} + \underset{\to 0}{k_{-1}}}[A]_0 = e^{-k_1 t}[A]_0$$ ✓

Okay at $t = 0$?

$$[A] = \frac{k_1 \underset{\to 0}{e^{-(k_1+k_{-1})t}} + k_{-1}}{k_1 + k_{-1}}[A]_0 = \frac{k_1 + k_{-1}}{k_1 + k_{-1}}[A]_0 = [A]_0$$ ✓

Mathematical Model for a First-Order Reversible Reaction, cont'd

Elementary Reactions, Batch Reactor with $[B]_0 = 0$

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

$$\boxed{[\mathrm{A}] = \frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0}$$

Check limits, continued. Okay as $t \to \infty$?

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{\cancel{k_1 e^{-(k_1+k_{-1})t}}^{\,0} + k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0 = \frac{k_{-1}}{k_{-1} + k_1}[\mathrm{A}]_0$$

Okay? Not obvious.

mol balance:

$$[\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}} = [\mathrm{A}]_0 - \frac{k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0 = \frac{k_1 + \cancel{k_{-1}} - \cancel{k_{-1}}}{k_1 + k_{-1}}[\mathrm{A}]_0$$

$$[\mathrm{B}]_{\mathrm{eq}} = \frac{k_1}{k_1 + k_{-1}}[\mathrm{A}]_0$$

Okay? Not obvious.

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{\dfrac{k_1}{k_1 + k_{-1}}[\mathrm{A}]_0}{\dfrac{k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}} \checkmark \quad !$$

Mathematical Model for a First-Order Reversible Reaction, cont'd

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{\dfrac{k_1}{k_1 + k_{-1}}[\mathrm{A}]_0}{\dfrac{k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}}$$

The rates of opposing reactions establish equilibrium concentrations.

At equilibrium: $k_1[\mathrm{A}]_{\mathrm{eq}} = k_{-1}[\mathrm{B}]_{\mathrm{eq}}$

Law of Mass Action - Cato Guldberg and Peter Waage (1864)

"The rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants."

Principle of Detailed Balance - Ludwig Boltzmann (1872)

Every elementary process has a corresponding reverse process and at equilibrium the rate of the process is equal to the rate of its reverse process.

Equilibrium is the macroscopic consequence of microscopic reversibility.

Cato Maximillian Guldberg and his brother-in-law Peter Waage