

Kinetics and Mechanism

to determine / describe / predict the course of reactions

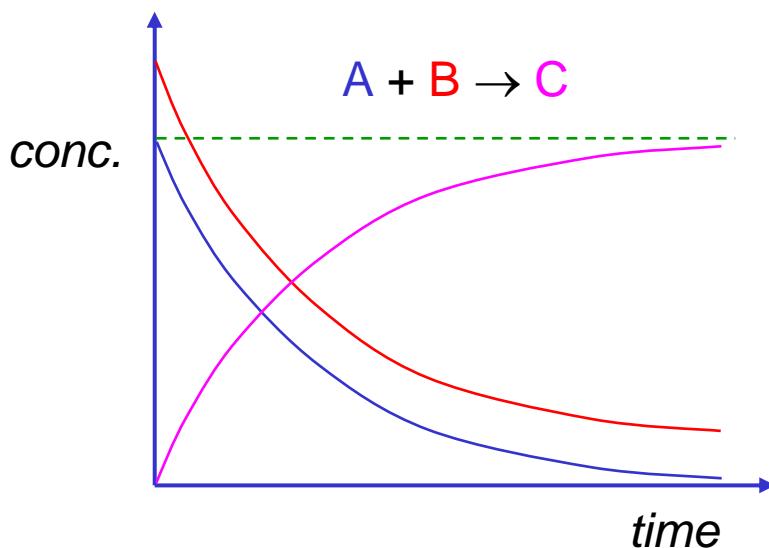
qualitatively: identify reactants, products, intermediates
identify elementary reaction steps

quantitatively: measure reaction rates \Rightarrow rate constants
explore effects of T , P , $[H^+]$, ...
relate rate constants to molecular properties
develop theories \Rightarrow make predictions

Rate data (growth of products, decay of reactants) are the basic experimental input to reaction kinetics.

The shapes of kinetic data plots depend on rate constants and concentrations.

Their functional form \Rightarrow reaction order



Empirical Chemical Kinetics

time dependence of reactant and product concentrations

e.g. for $A + 2B \rightarrow 3Y + Z$

$$\text{rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[Y]}{dt} = \frac{d[Z]}{dt}$$

In general, a chemical equation is written $0 = \sum_i \nu_i X_i$

The extent of a reaction
(the **advancement**) $\xi = \frac{n_i(t) - n_i(0)}{\nu_i}$

For an infinitesimal advancement $d\xi$ the concentration of each reactant/product changes by $dn_i = \nu_i d\xi$

By definition, $\text{rate} = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{d[X_i]}{dt}$

Reaction rates usually depend on reactant concentrations,

$$\text{rate} = k[A]^x[B]^y$$

rate constant \rightarrow k \leftarrow order in B
total order = $x + y$

In elementary reaction steps the orders are always integral, but they may be fractional in multi-step reactions.

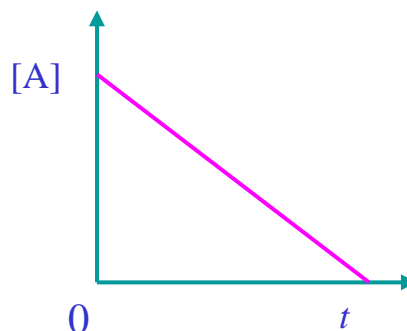
The **molecularity** is the number of molecules in a reaction step.

Simple Rate Laws

Zero order: $-\frac{d[A]}{dt} = k_0$

$$[A]_0 - [A]_t = k_0 t$$

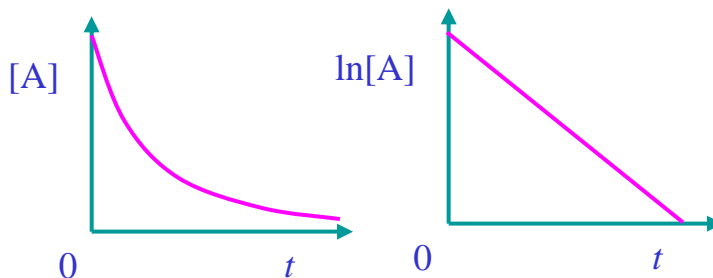
$$t_{1/2} = \frac{[A]_0}{2k_0}$$



1st order: $-\frac{d[A]}{dt} = k_1[A]$

$$[A]_t = [A]_0 e^{-k_1 t}$$

half-life $t_{1/2} = \frac{\ln 2}{k_1}$

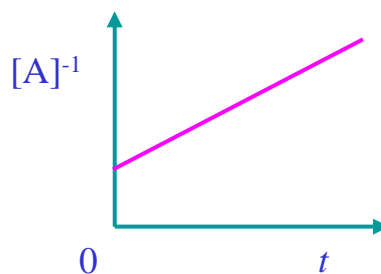
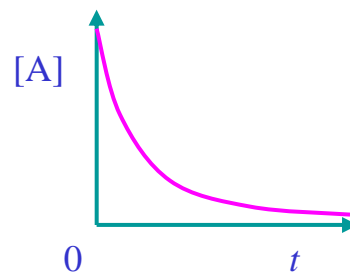


2nd order: $-\frac{d[A]}{dt} = 2k_2[A]^2$

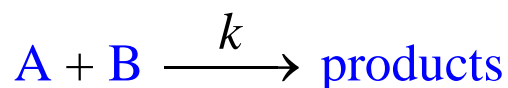
$$[A]_t = \frac{[A]_0}{1 + 2k_2[A]_0 t}$$

$$[A]_t^{-1} = [A]_0^{-1} + 2k_2 t$$

$$t_{1/2} = \frac{1}{2k_2[A]_0}$$



Second-order Kinetics: $[A] \neq [B]$



$$\text{rate} = -\frac{da}{dt} = kab \quad a = [A], \quad b = [B]$$

$$= k(a_0 - x)(b_0 - x)$$

But since $a = a_0 - x$, $\frac{dx}{dt} = -\frac{da}{dt}$

$$\therefore \frac{dx}{dt} = k(a_0 - x)(b_0 - x)$$

$$\begin{aligned} kt &= \int_0^x \left\{ \frac{dx}{(a_0 - x)(b_0 - x)} \right\} \\ &= \frac{-1}{(a_0 - b_0)} \int_0^x \left\{ \frac{1}{(a_0 - x)} - \frac{1}{(b_0 - x)} \right\} dx \\ &= \frac{1}{(a_0 - b_0)} \ln \left\{ \frac{a}{a_0} \frac{b_0}{b} \right\} \end{aligned}$$

or more usefully, $\ln\left(\frac{a}{b}\right) = \ln\left(\frac{a_0}{b_0}\right) + (a_0 - b_0)kt$

Determination of Order 1

Integral Methods

Test the data against an appropriate integral rate law.

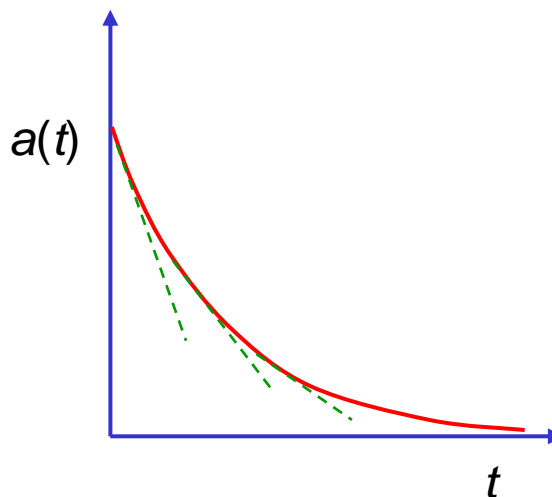
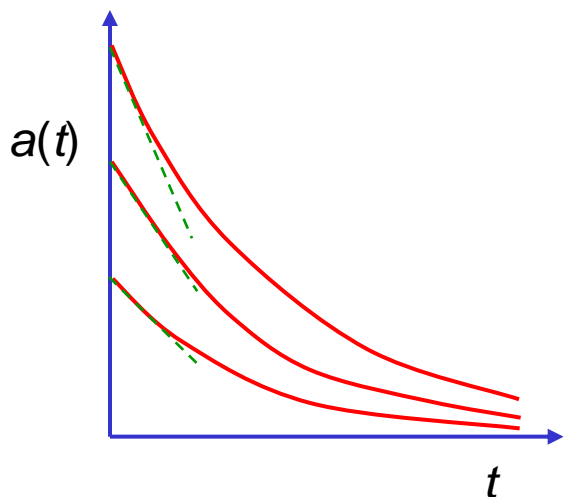
e.g. $\ln[A]$ vs t or $1/[A]$ vs t .

Differential Methods

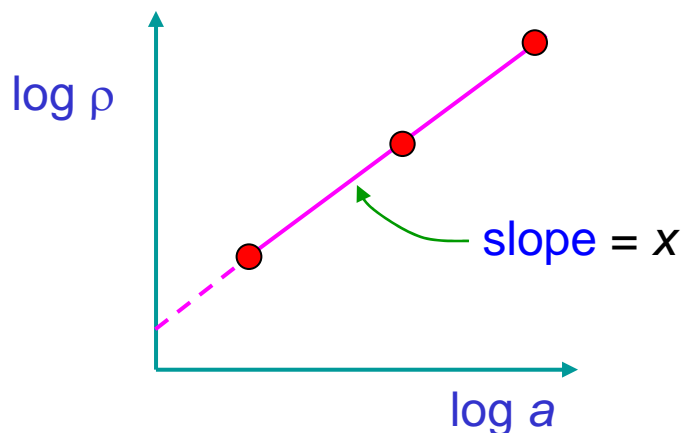
Plot the rate directly: $\rho = ka^x b^y$

$$\log \rho = \log k + x \log a + y \log b$$

Determine initial slopes or tangents from a single curve for different initial concs.



and plot versus concentration:



Determination of Order 2

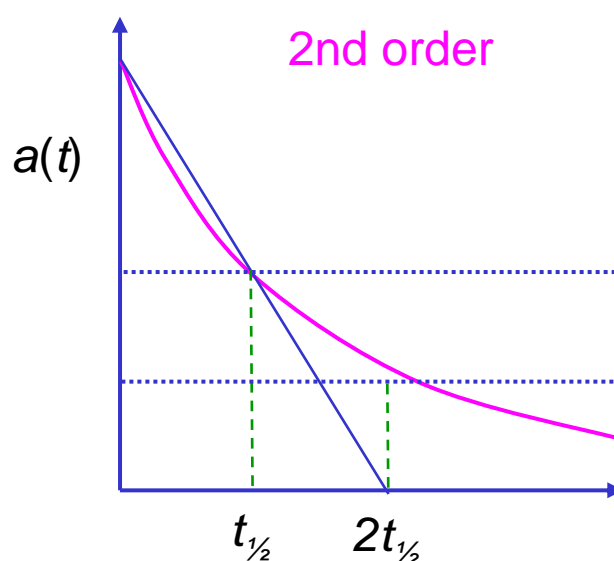
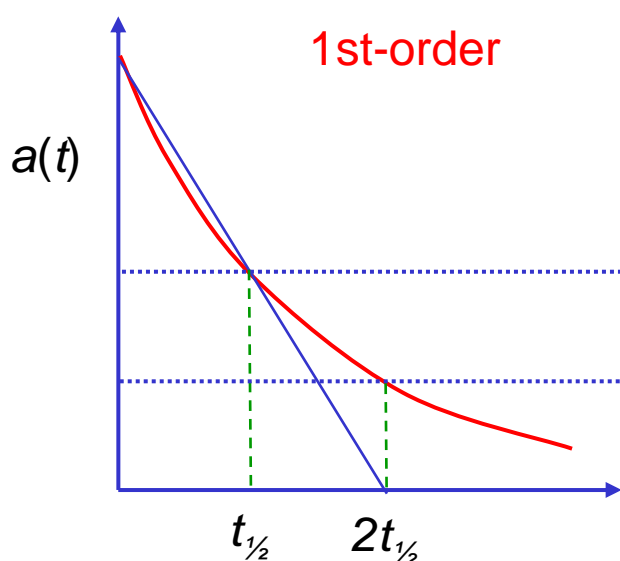
Half-life Method

Zero-order: the reactant is used up in two half-lives.

1st-order: the half-life is constant in time: $t_{1/2} = \ln 2 / k_1$

2nd order: the half-life *increases* with time

In general,
$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)ka_0^{n-1}}$$



Isolation Method together with one of the other methods

All except one reactant is added in large excess, so that their concentrations do not vary significantly. Then the other reactant has **pseudo-first order** kinetics:

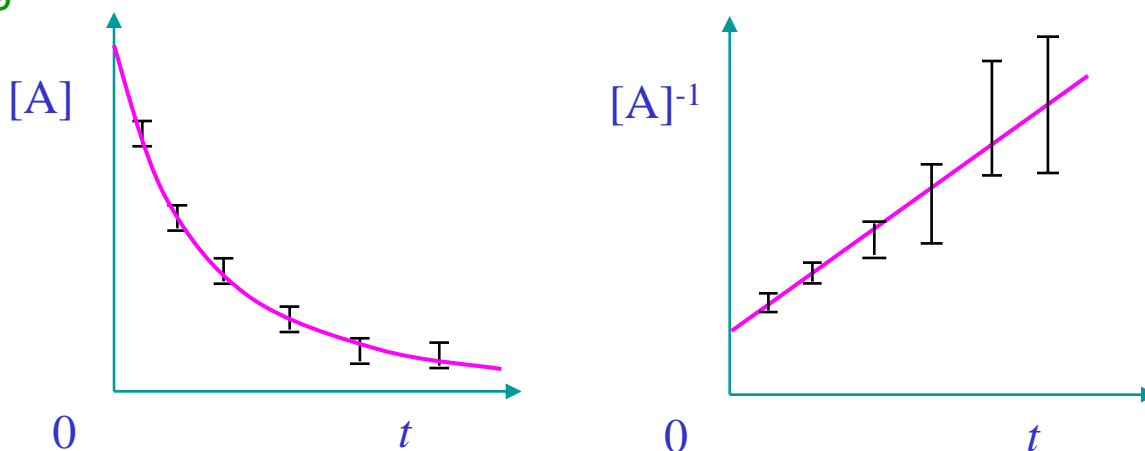
$$\rho = k_2[A][B] = \lambda[B] \quad \text{for } [A] \gg [B]$$

Data Analysis

“Classical” methods of data analysis are often useful to explore the order of reactions, or to display the results (e.g. a semi-log plot to demonstrate exponential decay).

However, these methods should be avoided for quantitative data analysis, since errors (and thus weighting) can be distorted.

e.g.

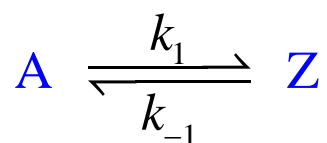


Modern data analysis uses computer methods for direct curve fitting, e.g. by chi-square minimization.

$$\chi^2 = \sum_{\text{data points}} \left(\frac{\text{expt} - \text{theory}}{\text{exptl. error}} \right)^2$$

A good fit has $\chi^2/(\text{no. of degs. freedom}) = 1$.

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

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

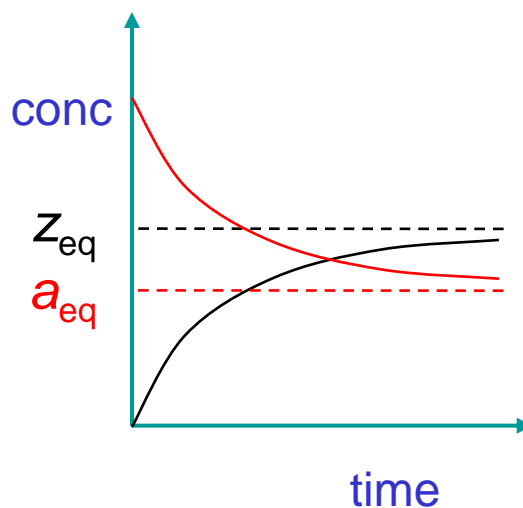
$$-\frac{da}{dt} = k_1 (a_{\text{eq}} - x) - k_{-1} (z_{\text{eq}} + x)$$

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

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

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

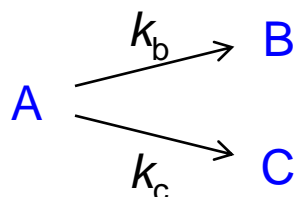
$$(z_{\text{eq}} - z) = (z_{\text{eq}} - z_0) e^{-(k_1 + k_{-1})t}$$



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:

$$\left. \begin{array}{l}
 \frac{db}{dt} = k_b a = k_b a_0 e^{-(k_b + k_c)t} \\
 \frac{dc}{dt} = k_c a = k_c a_0 e^{-(k_b + k_c)t}
 \end{array} \right\} \Rightarrow \frac{b}{c} = \frac{k_b \int a dt}{k_c \int a dt} = \frac{k_b}{k_c} = \frac{db/dt}{dc/dt}$$

$$\frac{k_b}{k_c} = \frac{[B]}{[C]} = \frac{\text{yield of B}}{\text{yield of C}}$$

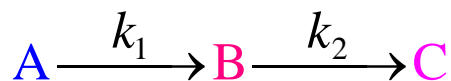
This is the basis for **competition kinetics**, whereby an unknown rate constant is determined from a known rate constant and the ratio of competitive products.

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

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

Consecutive Reactions

Simplest case - two first-order steps



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

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

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

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

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

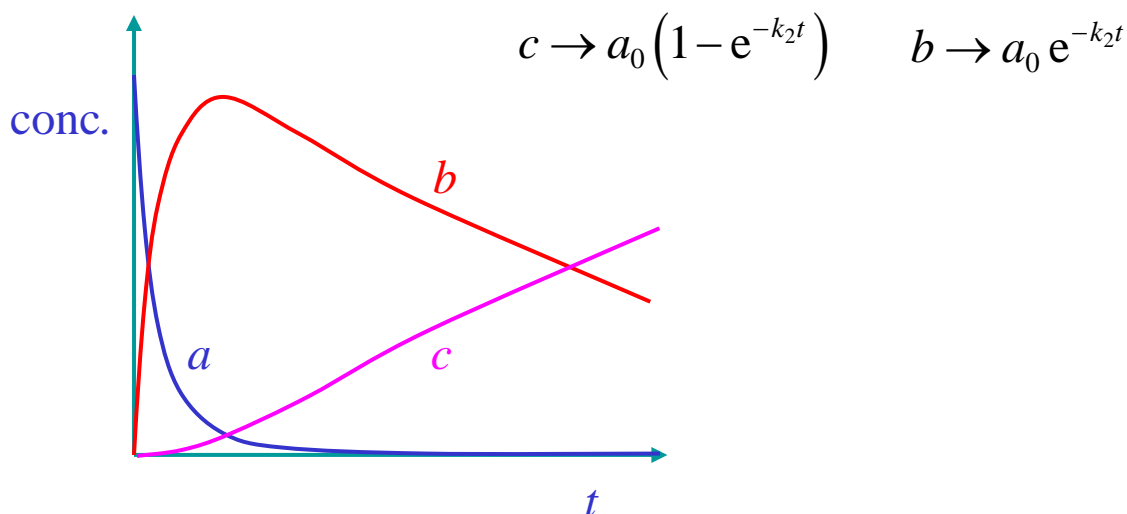
$$c = a_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

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

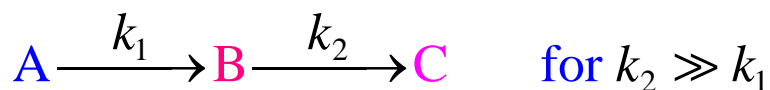
$$a + b + c = a_0$$

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

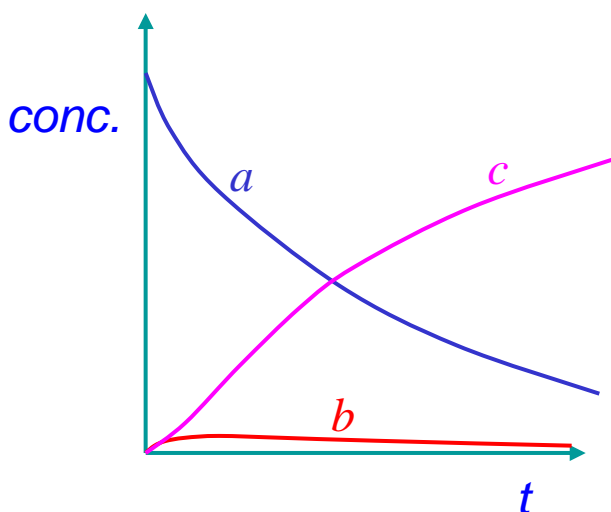
1. At short times b increases as a falls.
2. At longer times ($k_1 t \gg 0$), c increases as b falls.



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 $k_2 t \gg 0$,

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

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

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**.