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

A + B → C
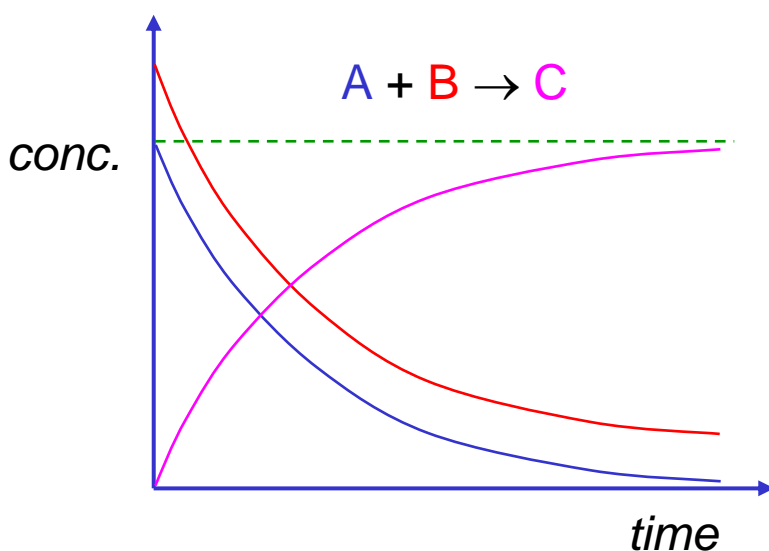
conc.

time

Empirical Chemical Kinetics

time dependence of reactant and product concentrations

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

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

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

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 $\quad dn_i = \nu_i d\xi$

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

Reaction rates usually depend on reactant concentrations,

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

rate constant $\qquad\qquad$ 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.
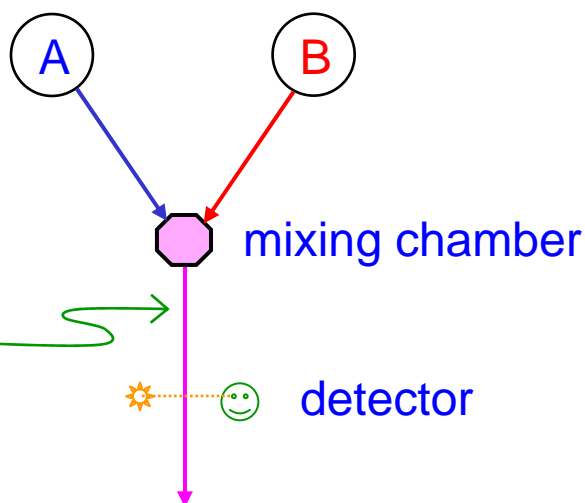

Measurement of Reaction Rates

Sampling of reaction mixture, followed by chemical analysis, chromatography, spectroscopy

Quenching of whole reaction or sample, followed by …

Matrix isolation is a particular quenching technique used to study otherwise short-lived species.

Flow

The time between mixing and measurement is varied by changing the distance or the flow rate.

mixing chamber

detector

Real time analysis involves measurement of a quantity that varies throughout the reaction. This could be:

❑ a general property of the system
   pressure, volume, conductance, optical rotation, …
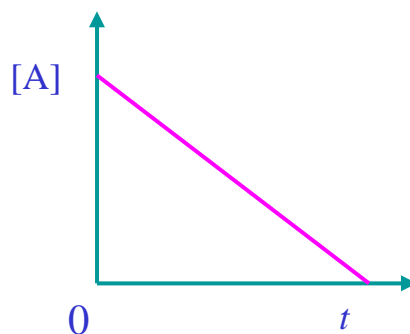
❑ a molecular property: usually by spectroscopy

Accurate initiation is necessary for real time experiments.

Simple Rate Laws

Zero order:

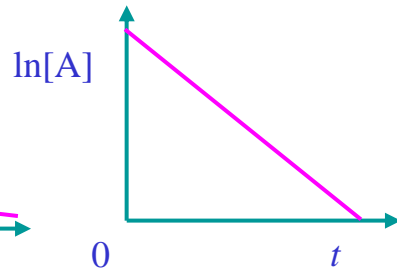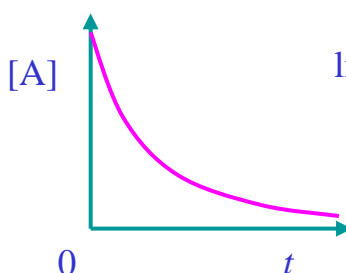$$-\frac{d[A]}{dt} = k_0$$

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

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

!st order:

$$-\frac{d[A]}{dt} = k_1[A]$$

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

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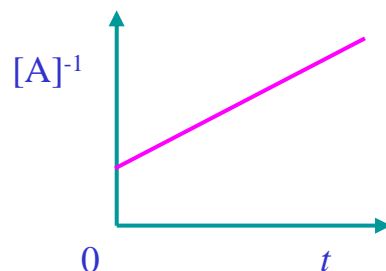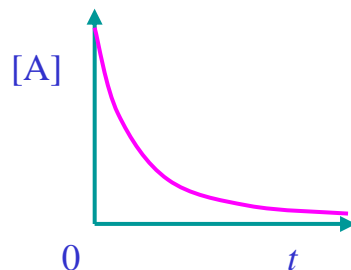
$$t_{1/2} = \frac{\ln 2}{k_1}$$
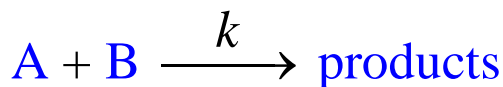
2nd order:

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

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

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

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

Second-order Kinetics: [A] ≠ [B]

$$A + B \xrightarrow{\;k\;} \text{products}$$

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

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

But since $\quad a = a_0 - x, \qquad \dfrac{dx}{dt} = -\dfrac{da}{dt}$

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

$$kt = \int_0^x \left\{ \frac{dx}{(a_0 - x)(b_0 - x)} \right\}$$

$$= \frac{-1}{(a_0 - b_0)} \int_0^x \left\{ \frac{1}{(a_0 - x)} - \frac{1}{(b_0 - x)} \right\} dx$$

$$= \frac{1}{(a_0 - b_0)} \ln \left\{ \frac{a}{a_0} \frac{b_0}{b} \right\}$$

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

Determination of Order 1

Integral Methods
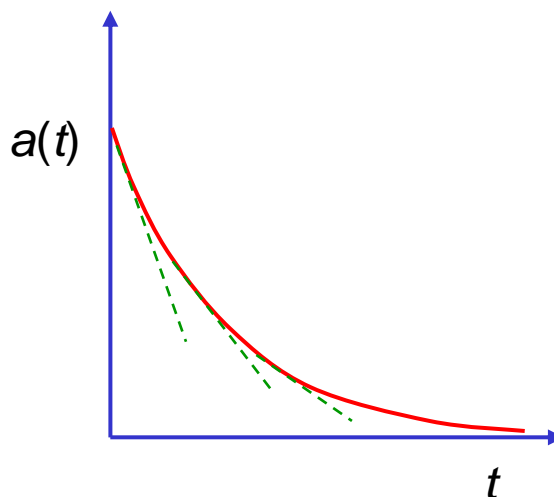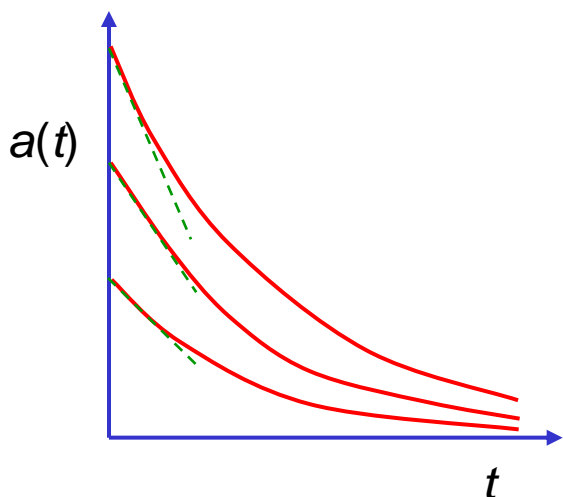
Test the data against an appropriate integral rate law.
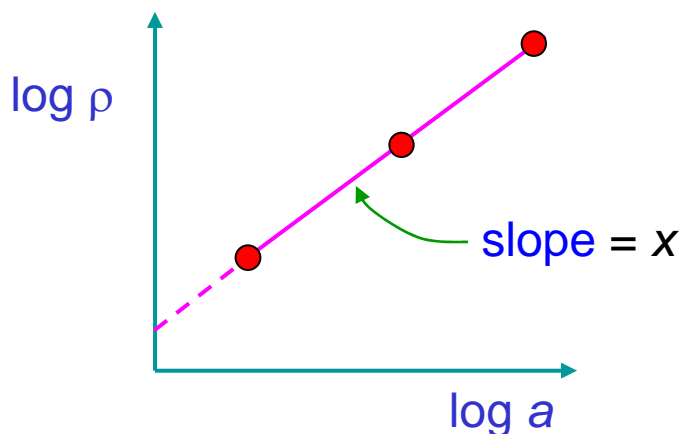e.g. ln[A] *vs t* or 1/[A] *vs t*.

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:
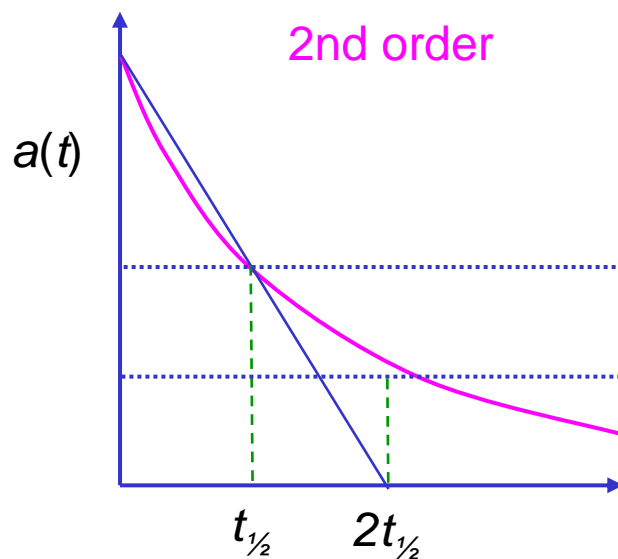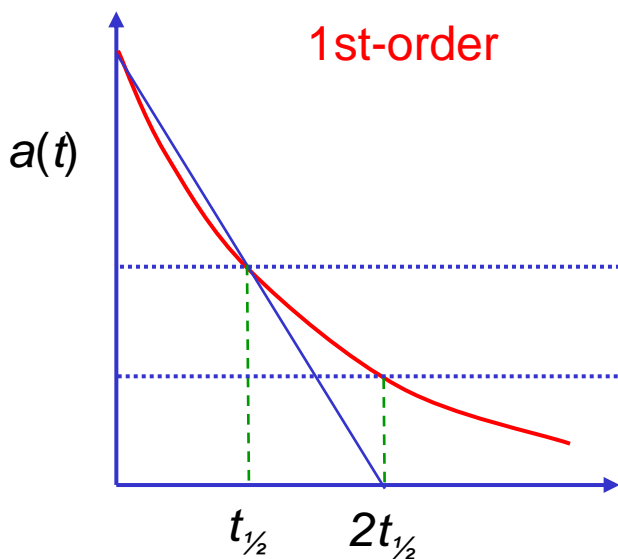

slope = *x*

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, $t_{1/2} = \dfrac{2^{n-1} - 1}{(n-1) k a_0^{n-1}}$

1st-order

$a(t)$

$t_{1/2}$ $2t_{1/2}$

2nd order

$a(t)$

$t_{1/2}$ $2t_{1/2}$

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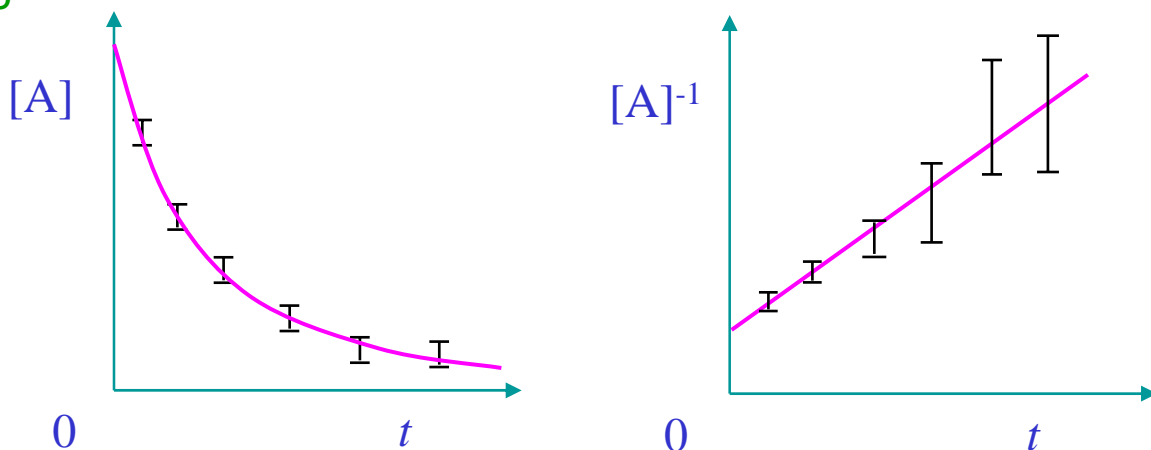
$$\rho = k_2 [A][B] = \lambda [B]   \text{for } [A] \gg [B]$$

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 $\chi^2/$(no. of degs. freedom) = 1.

Temperature Dependence

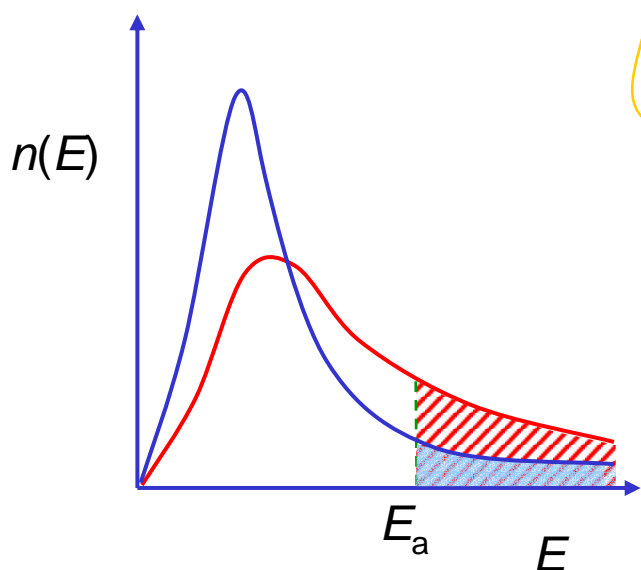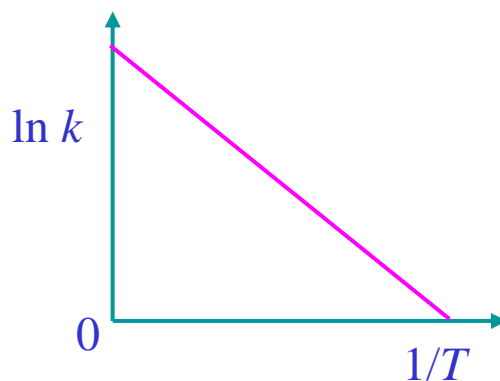The Arrhenius "law" is an empirical description of the *T* dependence of the rate constant:

$$k = A\,e^{-E_a/RT} \qquad \Rightarrow \qquad \ln k = \ln A - \frac{E_a}{RT},$$

The pre-exponential factor is often interpreted as a collision rate.

Collision theory predicts $T^{1/2}$ dependence for *A*.

The exponential factor describes the fraction of collisions with sufficient energy for reaction, as predicted by the Boltzmann distribution:

The activation energy is defined by $\quad E_a = RT^2 \dfrac{d \ln k}{dT}$

Curvature in the Arrhenius plot is often attributed to tunneling, but other reasons include complex reactions, and *T* dependence of the pre-exponential factor, which arises naturally in most theories.