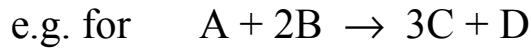


Empirical Chemical Kinetics

time dependence of reactant and product concentrations



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

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

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

For an infinitesimal advancement $d\xi$ each reactant/product concentration changes by $d[R_i] = \nu_i d\xi$.

By definition, the rate $= \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{d[R_i]}{dt}$

Reaction rates usually depend on reactant concentrations,

e.g., $\text{rate} = k[A]^x[B]^y$ order in B
total order = $x+y$
rate constant

In elementary reaction steps the orders are always integral, but they may not be so in multi-step reactions.

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

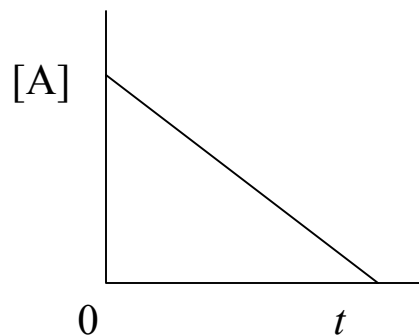
Rate Laws

Zero order:

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

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

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

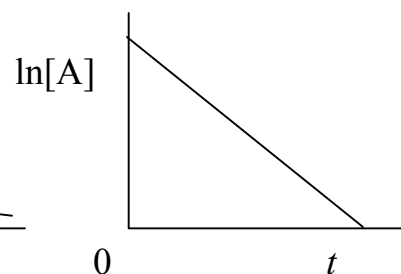
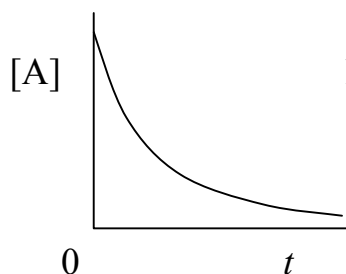


First order:

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

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

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



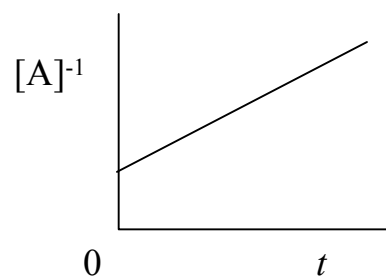
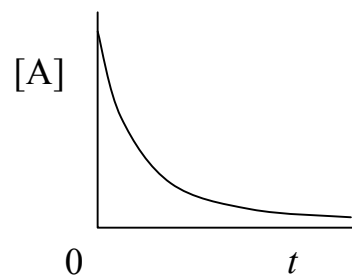
Second order:

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

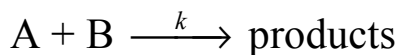
$$[A]_t = \frac{[A]_0}{1 + 2k_2[A]_0 t}$$

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

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



Second-order Kinetics: Two Reactants



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

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

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

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

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

or more usefully,

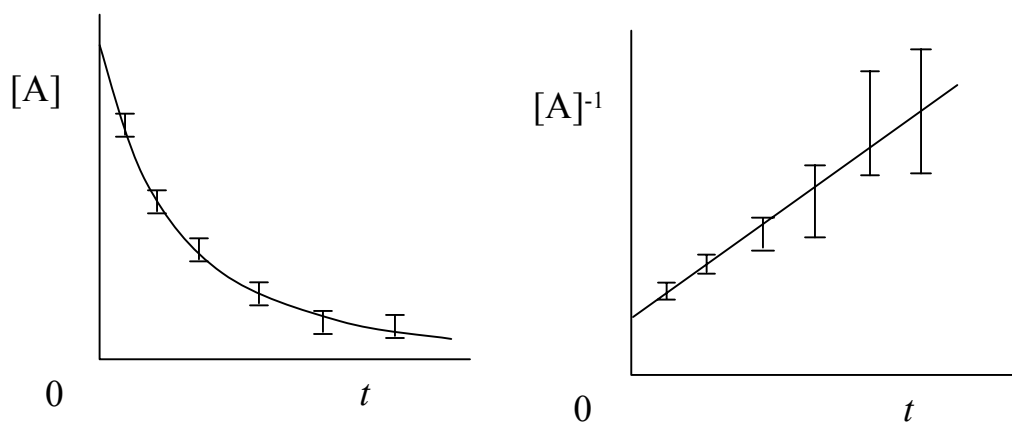
$$\ln \frac{a}{b} = \ln \frac{a_0}{b_0} + (a_0 - b_0)kt$$

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 for direct curve fitting, e.g. by chi-square minimization.

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

A good fit has $\chi^2 / \text{degs. freedom} = 1$

The errors in model parameters are found by taking each in turn and finding the variation necessary to change χ^2_{\min} to $\chi^2_{\min} + 1$.

To avoid correlation the fit must be re-optimized with *all the other* adjustable parameters variable.

Temperature Dependence of Complex Reactions

Assume some complex reaction $A + B \xrightarrow{k_1} C + D \xrightarrow{k_2} \dots$
for which the overall reaction rate constant can be expressed in terms of the elementary steps:

$$k_{\text{overall}} = \frac{k_1^{n_1} k_2^{n_2} \dots}{k_3^{n_3} \dots}$$

If each rate constant obeys the Arrhenius expression, $k_i = A_i e^{-E_i/RT}$

$$k_{\text{overall}} = \left(\frac{A_1^{n_1} A_2^{n_2} \dots}{A_3^{n_3} \dots} \right) \exp \left\{ -(n_1 E_1 + n_2 E_2 - n_3 E_3 - \dots) / RT \right\}$$

i.e. The Arrhenius parameters are

$$k_{\text{overall}} = \prod_i A_i^{n_i}$$

$$E = \sum_i n_i E_i$$

The overall “activation energy” may be negative, if n_i is negative and the corresponding E_i is large enough.

Temperature Dependence of Rate Constants

The Arrhenius expression, $k = A e^{-E_a/RT}$, often expressed as

$$\ln k = \ln A - \frac{E_a}{RT}, \quad \text{is empirical.}$$

Curvature in the Arrhenius plot is sometimes attributed to tunnelling, but other reasons include complex reactions, non-equilibrium kinetics, and temperature dependence of the pre-exponential factor, which arises naturally in most theories.

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

Various theories predict an expression of the form

$$k = A_{\text{th}} T^m e^{-E_{\text{th}}/RT}$$

whence $\ln k = \ln A_{\text{th}} + m \ln T - \frac{E_{\text{th}}}{RT}$

The empirical parameters are then related to theory by:

$$E_a = E_{\text{th}} + mRT$$

$$A = A_{\text{th}} T^m \exp\{(E_a - E_{\text{th}})/RT\}$$

Theoretical T Dependence of Rate Constants

Simple Collision Theory

$$A \propto T^{1/2}$$

$$k = p Z(T) e^{-E_{\min}/RT} = p (\pi \sigma^2) \sqrt{\frac{8RT}{\pi \mu}} e^{-E_{\min}/RT}$$

Transition State Theory

$$A \propto T$$

$$k = \frac{RT}{Lh} K_c^\ddagger = \frac{RT}{Lh} \frac{1}{c_0} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

This gives

$$E_a = \Delta U^\ddagger + RT = \Delta H^\ddagger - \Delta \nu RT + RT \text{ for gases}$$

Unimolecular gas reaction

$$E_a = \Delta H^\ddagger + RT$$

$$A = \frac{eRT}{hL} e^{\Delta S^\ddagger/R}$$

Bimolecular gas reaction

$$E_a = \Delta H^\ddagger + 2RT$$

$$A = \frac{e^2 RT}{hLc_0} e^{\Delta S^\ddagger/R}$$

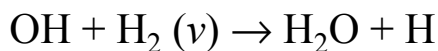
Liquid phase reaction

$$E_a = \Delta H^\ddagger + RT$$

$$A = \frac{eRT}{hLc_0} e^{\Delta S^\ddagger/R}$$

T Dependence of State to State Reactants

Rate constants have been determined for the reaction of OH with different vibrational states of H_2 .



$$k_{v=0} = 9.3 \times 10^{-12} \exp(-18000 / RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{v=1} = 6.0 \times 10^{-11} \exp(-11000 / RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The Boltzmann populations for these states of H_2 are

$$f_{v=0} = 1 / Q_{\text{vib}} \quad \text{and} \quad f_{v=1} = \exp(-\Delta E / RT) / Q_{\text{vib}}$$

$$\text{where } Q_{\text{vib}} = [1 - \exp(-\Delta E / RT)]^{-1} \quad \text{and} \quad \Delta E = 49.6 \text{ kJ mol}^{-1}$$

and the thermal rate constant can be expressed as

$$k(T) = f_{v=0} k_{v=0} + f_{v=1} k_{v=1}$$

