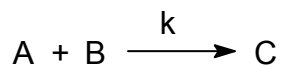


Kinetics appendix.

Mathematical derivations which are here for interest only.

Second order kinetics

(ii) Second order, irreversible reaction (two reagents, different concentrations)



Mass balance leads to:

$$[A]_0 - [A] = [B]_0 - [B] = [C] \quad (\text{assuming, as is generally the case, that } [C]_0 = 0)$$

$$\text{Then } -[B] = [A]_0 - [A] - [B]_0$$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B]$$

The rest of the derivation is given to show it can be done, but we will not be using this math any further.

In order to simplify the equation it is easier to eliminate both [A] and [B] in favor of [C], by applying the mass balance condition

$$\begin{aligned} [A] &= [A]_0 - [C] && (\text{assumes } [C]_0 = 0.0) \\ [B] &= [B]_0 - [C] \end{aligned}$$

$$\frac{d[C]}{dt} = k \{ ([A]_0 - [C])([B]_0 - [C]) \}$$

Collecting variables

$$\frac{d[C]}{\{([A]_0 - [C])([B]_0 - [C])\}} = k dt$$

This is not so straightforward: one could look at the table of integrals in the Handbook, and this leads to a solution. Or, you could apply the method of partial fractions to separate the lhs into two more manageable fractions.

Suppose that it can be factored; write in general form as

$$\frac{d[C]}{\{([A]_0 - [C])([B]_0 - [C])\}} = \frac{v d[C]}{([A]_0 - [C])} + \frac{w d[C]}{([B]_0 - [C])}$$

To evaluate v and w, recombine into a single fraction, and see if

it is possible to assign logically consistent values to v and w.

$$\begin{aligned} \frac{vd[C]}{([A]_0 - [C])} + \frac{wd[C]}{([B]_0 - [C])} &= \frac{v([B]_0 - [C])d[C] + w([A]_0 - [C])d[C]}{([A]_0 - [C])([B]_0 - [C])} \\ &= \frac{v[B]_0 + w[A]_0 - (v+w)[C]}{([A]_0 - [C])([B]_0 - [C])} d[C] \end{aligned}$$

comparison with the original form, which contains no term in [C], and a constant of unity, shows that v and w must satisfy:

$$v+w = 0 \quad v[B]_0 + w[A]_0 = 1$$

from which $v = -w$, and $w = 1/([A]_0 - [B]_0)$

Now we can write:

$$\frac{d[C]}{\{([A]_0 - [C])([B]_0 - [C])\}} = \frac{1}{([B]_0 - [A]_0)} \left\{ \frac{d[C]}{([A]_0 - [C])} - \frac{d[C]}{([B]_0 - [C])} \right\}$$

This can be integrated easily:

$$\begin{aligned} \int \frac{d[C]}{\{([A]_0 - [C])([B]_0 - [C])\}} &= \frac{1}{([B]_0 - [A]_0)} \left\{ \int \frac{d[C]}{([A]_0 - [C])} - \int \frac{d[C]}{([B]_0 - [C])} \right\} \\ &= \frac{1}{([B]_0 - [A]_0)} \left\{ -\ln([A]_0 - [C]) + \ln[A]_0 + \ln([B]_0 - [C]) - \ln[B]_0 \right\} \\ &= \frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{([B]_0 - [C])}{([A]_0 - [C])} - \ln \frac{[B]_0}{[A]_0} \right\} \\ &= \frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{[B]}{[A]} - \ln \frac{[B]_0}{[A]_0} \right\} \end{aligned}$$

Which leads to the integrated rate equation:

$$\frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{[B]}{[A]} - \ln \frac{[B]_0}{[A]_0} \right\} = kt$$

this form is convenient if both [A] and [B] can be readily measured

$$\frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{([B]_0 - [C])}{([A]_0 - [C])} - \ln \frac{[B]_0}{[A]_0} \right\} = kt$$

is convenient if [C] is readily measured

$$\frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{[B]_0 - [A]_0 + [A]}{[A]} - \ln \frac{[B]_0}{[A]_0} \right\} = kt$$

is convenient if only [A] is readily measured

$$\frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{[B]}{[A]_0 - [B]_0 + [B]} - \ln \frac{[B]_0}{[A]_0} \right\} = kt$$

is convenient if only [B] is readily measured

Which form you use depends on what is conveniently measured to follow the reaction. One thing to note is that the initial concentrations of both reactants are essential (contrast to first order).

The form of the integrated rate law for a second order equation with $[A]_0 \neq [B]_0$ looks quite different from the form when $[A]_0 = [B]_0$. How can we demonstrate that the form for $[A]_0 \neq [B]_0$ transforms into that for $[A]_0 = [B]_0$ as the two concentrations get closer and closer? There are various ways to do this; I will use one which is less elegant mathematically but shows a useful way to think about equations. The direct substitution of $[B]_0 = [A]_0$ leads to 0/0 which is indeterminate.

Suppose that A and B are at slightly different concentrations, with

$$[B]_0 = [A]_0 + \delta$$

$$[A] = [A]_0 - [C]$$

$$[B] = [B]_0 - [C] = [A]_0 + \delta - [C] = [A] + \delta$$

Then

$$\frac{1}{([B]_0 - [A]_0)} \left\{ \ln \frac{[B]}{[A]} - \ln \frac{[B]_0}{[A]_0} \right\} = kt$$

becomes

$$\frac{1}{([A]_0 + \delta - [A]_0)} \left\{ \ln \frac{[A] + \delta}{[A]} - \ln \frac{[A]_0 + \delta}{[A]_0} \right\} = kt$$

$$\frac{1}{\delta} \left\{ \ln \left(1 + \frac{\delta}{[A]} \right) - \ln \left(1 + \frac{\delta}{[A]_0} \right) \right\} = kt$$

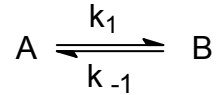
since

$$\ln(1+x) \approx x \text{ when } x \text{ is small}$$

$$\frac{1}{\delta} \left\{ \frac{\delta}{[A]} - \frac{\delta}{[A]_0} \right\} = kt$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

d) Reversible 1st order reactions



If $[A] = [A]_0$ and $[B] = [B]_0$ at $t = 0$ $[A]_e$ is the concentration of A at equilibrium, and $[B]_e$ is the concentration of B at equilibrium one finds at any time t ,

$$[A]_0 - [A] = [B] - [B]_0$$

(this assumes that $[A]_0 > [A]_e$ and $[B]_0 < [B]_e$; the alternative is possible but just means changing the sign of the definition of the progress variable).

It is convenient to define a progress variable x , with a value at equilibrium x_e ,

$$x = [A]_0 - [A] = [B] - [B]_0$$

$$x_e = [A]_0 - [A]_e = [B]_e - [B]_0$$

$$\text{and to use } a = [A]_0, \text{ and } b = [B]_0$$

The differential rate law is:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d(a-x)}{dt} = -k_1(a-x) + k_{-1}(b+x)$$

$$-\frac{dx}{dt} = -k_1a + k_{-1}b + k_1x + k_{-1}x$$

$$\frac{dx}{dt} = (k_1a - k_{-1}b) - (k_1 + k_{-1})x$$

$$\frac{dx}{(k_1a - k_{-1}b) - (k_1 + k_{-1})x} = dt$$

$$\frac{1}{(k_1 + k_{-1})} \frac{dx}{\frac{(k_1a - k_{-1}b)}{(k_1 + k_{-1})} - x} = dt$$

$$\frac{dz}{z} = -(k_1 + k_{-1})dt \quad \text{where } z = \left\{ \frac{(k_1a - k_{-1}b)}{(k_1 + k_{-1})} - x \right\}$$

at equilibrium

$$K = \frac{k_1}{k_{-1}} = \frac{[B]_e}{[A]_e} = \frac{x_e + b}{a - x_e}$$

$$x_e = \frac{k_1a - k_{-1}b}{k_1 + k_{-1}}$$

$$\int_0^t \frac{dz}{z} = \ln \left(\frac{x_e - x}{x_e} \right) = \int_0^t -(k_1 + k_{-1})dt$$

To turn an equation in x and x_e into one in $[A]$, $[A]_0$ and $[A]_e$ we replace x_e and x , using the original definitions

$$\ln\left(\frac{x_e - x}{x_e}\right) = \ln\left(\frac{([A]_o - [A]_e) - ([A]_o - [A])}{[A]_o - [A]_e}\right) = \ln\left(\frac{[A] - [A]_e}{[A]_o - [A]_e}\right)$$

$$\ln \frac{[A] - [A]_e}{[A]_o - [A]_e} = -(k_1 + k_{-1})t$$

i.e. approach to equilibrium is a first order process with the observed rate constant the sum of the forward and reverse k 's; i.e.

$$k_{\text{obs}} = k_1 + k_{-1}$$

$$\text{Since } K = \frac{[B]_e}{[A]_e} = \frac{[A]_o + [B]_o - [A]_e}{[A]_e} = \frac{k_1}{k_{-1}}$$

we may readily find k_1 and k_{-1} from k_{obs} and K , but note: If you don't know K , measuring k_{obs} will not lead to K but only to $k_1 + k_{-1}$