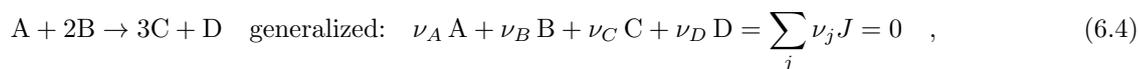


6.2 Kinetics of chemical reactions

A large variety of aspects of (transport and) kinetics can be most easily discussed for chemical reactions. In addition chemical reactions can be systematically classified according to the order of reaction.

Let us assume a reaction



with $\nu_A = -1$, $\nu_B = -2$, $\nu_C = 3$, and $\nu_D = 1$, i.e. reaction educts have a negative sign and reaction products a positive one. For the rate of consumptions we find

$$\frac{dD}{dt} = \frac{1}{3} \frac{dC}{dt} = -\frac{dA}{dt} = -\frac{1}{2} \frac{dB}{dt} \quad , \quad (6.5)$$

or in the general form we find for the rate of consumption

$$v = \frac{1}{\nu_j} \frac{d[J]}{dt} = \frac{1}{\nu_j} \frac{dn_j}{V dt} = \frac{1}{V} \frac{dn_j}{\nu_j dt} = \frac{1}{V} \frac{d\xi}{dt} \quad \text{with} \quad d\xi = \frac{dn_j}{\nu_j} \quad . \quad (6.6)$$

Here ξ is the extent of reaction.

As discussed before and holding for probabilities, the rate of consumption depends on the concentrations of the species, i.e.

$$v = k [A]^x [B]^y \dots \quad (6.7)$$

where the order of reaction $x + y$ is determined experimentally and k is a reaction constant. The following table summarizes features of such reactions. The math will be discussed in the exercises and some examples will be discussed in what follows.

order	reaction	differential form	integral form	half life time
0 th	$A \rightarrow P$	$-\frac{d[A]}{dt} = k$	$[A](t) = -k t + [A]_0$	$t_{1/2} = \frac{[A]_0}{2k}$
1 st	$A \rightarrow P$	$-\frac{d[A]}{dt} = k [A]$	$[A](t) = [A]_0 \exp(-k t)$	$t_{1/2} = \frac{\ln(2)}{k}$
2 nd	$2 A \rightarrow P$	$-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[P]}{dt} = k [A]^2$	$\frac{1}{[A](t)} = \frac{1}{[A]_0} + k t$	$t_{1/2} = \frac{1}{k [A]_0}$
2 nd	$A + B \rightarrow P$	$-\frac{d[A]}{dt} = k [A] [B] = -\frac{d[B]}{dt}$	$\frac{[A]}{[B]}(t) = \frac{[A]_0}{[B]_0} \exp(([A]_0 - [B]_0) k t)$	$t_{1/2} = \frac{1}{k [A]_0}$

As we already saw in section 6.1 concentrations $[A]$ change exponentially for linear differential equations of first order with constant coefficients. Zeroth order reactions seem somehow strange, because reactions must depend on the concentration of the reactants. However for catalytic reactions with a high concentration of $[A]$ and a small concentration of the catalyst $[B]$ the rate determining step depends on the concentration of $[B]$, which does not change. So as long as the reduction of concentration $[A]$ is connectible the process is described as a zeroth order reaction.

Mathematically challenging is only the solution of the differential equation for the last 2 nd order reaction in the above table. Left and right hand side of the differential equation imply

$$\frac{d([A] - [B])}{dt} = 0 \quad \text{i.e.} \quad [A](t) - [B](t) = [A]_0 - [B]_0 \quad (6.8)$$

Using the ratio rule and our differential equation and the result of Eq. (6.8) we now find

$$\frac{d([A]/[B])}{dt} = \frac{[B] \frac{d[A]}{dt} - [A] \frac{d[B]}{dt}}{[B]^2} = k \frac{[A]}{[B]} ([A] - [B]) = k \frac{[A]}{[B]} ([A]_0 - [B]_0) \quad (6.9)$$

which now easily give the result in the above table. As long as $[A] \neq [B]$ the Eq. (6.9) holds. If $[A] = [B]$ we either can apply a Taylor expansion or directly use the result of the first second order reaction in the above table.