

L.3.9 Chemical kinetics

Name	Symbol	Definition	SI unit	Notes
rate of change of quantity X	\dot{X}	$\dot{X} = dX/dt$	(varies)	(1)
rate of conversion	$\dot{\xi}$	$\dot{\xi} = d\xi/dt$	mol s^{-1}	(2)
rate of concentration change (due to chemical reaction)	r_B, ν_B	$r_B = dc_B/dt$	$\text{mol m}^{-3} \text{s}^{-1}$	(3),(4)
rate of reaction (based on amount of concentration)	ν	$\nu = \dot{\xi} / V$ $= \nu_B^{-1} dc_B/dt$	$\text{mol m}^{-3} \text{s}^{-1}$	(2), (4)
partial order of reaction	n_B, m_B	$\nu = k \prod c_B^{n_B}$	1	(5)
overall order of reaction	n, m	$n = \sum n_B$	1	

(1) E.g. rate of change of pressure $\dot{p} = dp/dt$, for which the SI unit is Pa s^{-1} .

(2) The reaction must be specified for which this quantity applies.

(3) The symbol and the definition apply to entities B.

(4) Note that r_B and ν can also be defined on the basis of partial pressure, number concentration, surface concentration etc., with analogous definitions. If necessary differently defined rates of reaction can be distinguished by a subscript, e.g. $\nu_p = \nu_B^{-1} dp_B/dt$, etc. Note that the rate of reaction can only be defined for a reaction of known and time-independent stoichiometry, in terms of a specified reaction equation; also the second equation for the rate of reaction follows from the first only if the volume V is constant. The derivatives must be those due to the chemical reaction considered; in open systems, such as flow systems, effects due to input and output processes must also be taken into account.

(5) The symbol applies to reactant B. The symbol m may be used when confusion with n for amount of substance occurs.

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
rate constant, rate coefficient	k	$v = k \Pi c_B^{n_b}$	$(\text{m}^3 \text{mol}^{-1})^{n-1} \text{s}^{-1}$	(6)
Boltzmann constant	k, k_B		J K^{-1}	
half life	$t_{1/2}$	$c(t_{1/2}) = c(0)/2$	s	
relaxation time	τ		s	(7)
(Arrhenius) activation energy	E_a, E_A	$E_a = RT^2 d \ln k / dT$	J mol^{-1}	(8)
pre-exponential factor, frequency factor	A	$k = A \exp(-E_a/RT)$	$(\text{m}^3 \text{mol}^{-1})^{n-1} \text{s}^{-1}$	
volume of activation	$\Delta^\ddagger V, \Delta V^\ddagger$	$\Delta^\ddagger V = -RT(\partial \ln k / \partial T)$	$\text{m}^3 \text{mol}^{-1}$	

- (6) Rate constants k and pre-exponential factors A are usually quoted in either $(\text{dm}^3 \text{mol}^{-1})^{n-1} \text{s}^{-1}$ or on a molecular scale in $(\text{cm}^3)^{n-1} \text{s}^{-1}$ or $(\text{cm}^3 \text{molecule}^{-1})^{n-1} \text{s}^{-1}$. Note that 'molecule' is not a unit, but is often included for clarity. Rate constants are frequently quoted as decadic logarithms.

Example For a second order reaction
 $k = 10^{8.2} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ or $\lg(k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = 8.2$
or alternatively
 $k = 10^{-12.6} \text{cm}^3 \text{s}^{-1}$ or $\lg(k/\text{cm}^3 \text{s}^{-1}) = -12.6$

- (7) τ is defined as the time in which a concentration perturbation falls to 1/e of its initial value.
- (8) Note that the term Arrhenius activation energy is to be used only for the empirical quantity defined in the table. Other empirical equations with different 'activation energies', such as $k(T) = A'T^n \exp(-E_a'/RT)$, are also being used.

<i>Name</i>	<i>Symbol</i>	<i>SI unit</i>	<i>Notes</i>
standard enthalpy of activation	$\Delta^\ddagger H^\circ, \Delta H^\ddagger$	J mol^{-1}	(9)
standard internal energy of activation	$\Delta^\ddagger U^\circ, \Delta U^\ddagger$	J mol^{-1}	(9)
standard entropy of activation	$\Delta^\ddagger S^\circ, \Delta S^\ddagger$	$\text{J mol}^{-1} \text{K}^{-1}$	(9)
standard Gibbs energy of activation	$\Delta^\ddagger G^\circ, \Delta G^\ddagger$	J mol^{-1}	(9)
quantum yield, photochemical yield	ϕ, Φ	1	(10)

- (9) The quantities $\Delta^\ddagger H^\circ$, $\Delta^\ddagger U^\circ$, $\Delta^\ddagger S^\circ$ and $\Delta^\ddagger G^\circ$ are used in the transition state theory of chemical reaction. They are normally used only in connection with elementary reactions. The relation between the rate constant k and these quantities is

$$k = \kappa(k_B T/h) \exp(-\Delta^\ddagger G^\circ/RT),$$

where k has the dimensions of a first-order rate constant and is obtained by multiplication of an n th-order rate constant by $(c^\circ)^{n-1}$, κ is a transmission coefficient, and $\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$. Unfortunately the standard symbol $^\circ$ is usually omitted, and these quantities are usually written ΔH^\ddagger , ΔU^\ddagger , ΔS^\ddagger and ΔG^\ddagger .

- (10) The quantum yield ϕ is defined in general as follows:

$$\phi = \frac{\text{number of defined events}}{\text{number of photons absorbed}}$$

For a photochemical reaction it can be defined as

$$\phi = \frac{\text{rate of conversion}}{\text{rate of photon absorption}} = \frac{d\xi/dt}{dn_\gamma/dt}$$