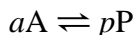


order of reaction, n

If the macroscopic (observed, empirical or phenomenological) *rate of reaction* (v) for any reaction can be expressed by an empirical differential rate equation (or rate law) which contains a factor of the form $k[A]^\alpha[B]^\beta$... (expressing in full the dependence of the rate of reaction on the concentrations $[A]$, $[B]$...) where α , β are constant exponents (independent of concentration and time) and k is independent of $[A]$ and $[B]$ etc. (rate constant, rate coefficient), then the reaction is said to be of order α with respect to A, of order β with respect to B, ... , and of (total or overall) order $n = \alpha + \beta + \dots$. The exponents α , β , ... can be positive or negative integral or rational nonintegral numbers. They are the reaction orders with respect to A, B, ... and are sometimes called 'partial orders of reaction'. Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called 'orders of reaction with respect to concentration'; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called 'orders of reaction with respect to time'.

The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence the rate of reaction) are not themselves measurable, provided it is possible to measure a *chemical flux*. For example, if there is a dynamic equilibrium according to the equation:



and if a chemical flux is experimentally found, (e.g. by NMR *line-shape analysis*) to be related to concentrations by the equation:

$$\varphi_{-A}/\alpha = k [A]^\alpha [L]^\lambda$$

then the corresponding reaction is of order α with respect to A ... and of total (or overall) order $n (= \alpha + \lambda + \dots)$. The proportionality factor k above is called the (n th order) 'rate coefficient'. Rate coefficients referring to (or believed to refer to) *elementary reactions* are called 'rate constants' or, more appropriately 'microscopic' (hypothetical, mechanistic) rate constants.

The (overall) order of a reaction cannot be deduced from measurements of a 'rate of appearance' or 'rate of disappearance' at a single value of the concentration of a species whose concentration is constant (or effectively constant) during the course of the reaction. If the overall rate of reaction is, for example, given by:

$$v = k [A]^{\alpha} [B]^{\beta}$$

but [B] stays constant, then the order of the reaction (with respect to time), as observed from the concentration change of A with time, will be α , and the rate of disappearance of A can be expressed in the form:

$$v_A = k_{\text{obs}} [A]^{\alpha}$$

The proportionality factor k_{obs} deduced from such an experiment is called the ‘observed rate coefficient’ and it is related to the $(\alpha + \beta)$ th order rate coefficient k by the equation:

$$k_{\text{obs}} = k [B]^{\beta}$$

For the common case when $\alpha = 1$, k_{obs} is often referred to as a ‘pseudo-first order rate coefficient’ (k_{ψ}).

For a simple (*elementary*) reactions a partial order of reaction is the same as the stoichiometric number of the reactant concerned and must therefore be a positive integer (see *rate of reaction*). The overall order is then the same as the *molecularity*. For *stepwise reactions* there is no general connection between stoichiometric numbers and partial orders. Such reactions may have more complex rate laws, so that an apparent order of reaction may vary with the concentrations of the *chemical species* involved and with the progress of the reaction: in such cases it is not useful to speak of orders of reaction, although apparent orders of reaction may be deducible from initial rates. In a stepwise reaction, orders of reaction may in principle always be assigned to the elementary steps.

See also *kinetic equivalence*.

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