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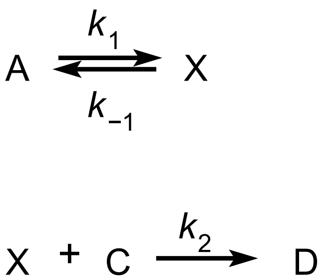
steady state (stationary state)

Also contains definition of: steady state approximation (treatment)

1. In a kinetic analysis of a complex reaction involving unstable intermediates in low concentration, the rate of change of each such intermediate is set equal to zero, so that the rate equation can be expressed as a function of the concentrations of chemical species present in macroscopic amounts. For example, assume that **X** is an unstable intermediate in the reaction sequence:



Conservation of mass requires that:

$$[\mathrm{A}] + [\mathrm{X}] + [\mathrm{D}] = [\mathrm{A}]_0$$

which, since $[\mathrm{A}]_0$ is constant, implies:

$$-\frac{\mathrm{d}\,[\mathrm{X}]}{\mathrm{d}t} = \frac{\mathrm{d}\,[\mathrm{A}]}{\mathrm{d}t} + \frac{\mathrm{d}\,[\mathrm{D}]}{\mathrm{d}t}.$$

Since [X] is negligibly small, the rate of formation of **D** is essentially equal to the rate of disappearance of **A**, and the rate of change of [X] can be set equal to zero. Applying the steady state approximation ($\frac{\mathrm{d}\,[\mathrm{X}]}{\mathrm{d}t} = 0$) allows the elimination of [X] from the kinetic equations, whereupon the rate of reaction is expressed:

$$\frac{\mathrm{d}\,[\mathrm{D}]}{\mathrm{d}t} = -\frac{\mathrm{d}\,[\mathrm{A}]}{\mathrm{d}t} = \frac{k_1\,k_2\,[\mathrm{A}]\,[\mathrm{C}]}{k_{-1} + k_2\,[\mathrm{C}]}$$

Note:
The steady-state approximation does not imply that [X] is even approximately constant, only that its absolute rate of change is very much smaller than that of [A] and [D]. Since according to the reaction scheme $\frac{\mathrm{d}\,[\mathrm{D}]}{\mathrm{d}t} = k_2\,[\mathrm{X}]\,[\mathrm{C}]$, the assumption that [X] is constant would lead, for the case in which **C** is in large excess, to the absurd conclusion that formation of the product **D** will continue at a constant rate even after the reactant **A** has been consumed.

2. In a stirred flow reactor a steady state implies a regime so that all concentrations are independent of time.

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Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1166
PAC, 1993, *65*, 2291 *(Nomenclature of kinetic methods of analysis (IUPAC Recommendations 1993))* on page 2298

See also:
PAC, 1996, *68*, 149 *(A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996))* on page 187
PAC, 1990, *62*, 2167 *(Glossary of atmospheric chemistry terms (Recommendations 1990))* on page 2216

