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:

\[
A \quad \xrightarrow{k_1} \quad X \quad \xleftarrow{k_{-1}}
\]

\[X + C \quad \xrightarrow{k_2} \quad D\]

Conservation of mass requires that:

\[[A] + [X] + [D] = [A]_0\]

which, since \([A]_0\) is constant, implies:

\[-\frac{d[X]}{dt} = \frac{d[A]}{dt} + \frac{d[D]}{dt}.\]

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 (\(\frac{d[X]}{dt} = 0\)) allows the elimination of \([X]\) from the kinetic equations, whereupon the rate of reaction is expressed:

\[\frac{d[D]}{dt} = -\frac{d[A]}{dt} = \frac{k_1 k_2 [A] [C]}{k_{-1} + k_2 [C]}\]

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 \(\frac{d[D]}{dt} = k_2 [X] [C]\), 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.
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