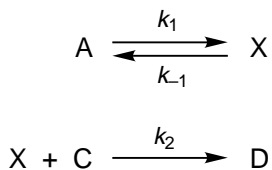


### steady state (stationary state)

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:

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

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

$$-d[\text{X}]/dt = d[\text{A}]/dt + d[\text{D}]/dt.$$

Since  $[\text{X}]$  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  $[\text{X}]$  can be set equal to zero. Applying the steady state approximation ( $d[\text{X}]/dt = 0$ ) allows the elimination of  $[\text{X}]$  from the kinetic equations, whereupon the rate of reaction is expressed:

$$d[\text{D}]/dt = -d[\text{A}]/dt = \frac{k_1 k_2 [\text{A}][\text{C}]}{k_{-1} + k_2 [\text{C}]} \quad (1)$$

Note:

1. The steady-state approximation does not imply that  $[\text{X}]$  is even approximately constant, only that its absolute rate of change is very much smaller than that of  $[\text{A}]$  and  $[\text{D}]$ . Since according to the reaction scheme  $d[\text{D}]/dt = k_2[\text{X}][\text{C}]$ , the assumption that  $[\text{X}]$  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.

1994, 66, 1166; 1993, 65, 2298; see also 1996, 68, 187; 1990, 62, 2216

