

### rate-controlling step

A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite reaction sequence is an *elementary reaction* the rate constant for which exerts a strong effect — stronger than that of any other rate constant — on the overall rate. It is recommended that the expressions rate-controlling, rate-determining and rate-limiting be regarded as synonymous, but some special meanings sometimes given to the last two expressions are considered under a separate heading.

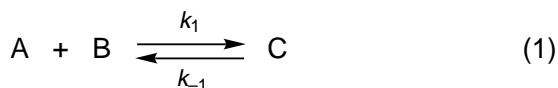
A rate-controlling step can be formally defined on the basis of a control function (or control factor) CF, identified for an elementary reaction having a rate constant  $k_i$  by:

$$CF = (\partial \ln v / \partial \ln k_i)_{K_j, k_j}$$

where  $v$  is the overall rate of reaction. In performing the partial differentiation all equilibrium constants  $K_j$  and all rate constants except  $k_i$  are held constant. The elementary reaction having the largest control factor exerts the strongest influence on the rate  $v$ , and a step having a CF much larger than any other step may be said to be rate-controlling.

A rate-controlling step defined in the way recommended here has the advantage that it is directly related to the interpretation of *kinetic isotope effects*.

As formulated this implies that all rate constants are of the same dimensionality. Consider however the reaction of A and B to give an intermediate C, which then reacts further with D to give products:



Assuming that C reaches a *steady state*, then the observed rate is given by:

$$v = \frac{k_1 k_2 [A][B][D]}{k_{-1} + k_2 [D]}$$

Considering  $k_2[D]$  a pseudo-first order rate constant, then  $k_2[D] \gg k_{-1}$ , and the observed rate  $v = k_1[A][B]$  and  $k_{\text{obs}} = k_1$ . Step (1) is said to be the rate-controlling step.

If  $k_2[D] \ll k_{-1}$ , then the observed rate:

$$v = \frac{k_1 k_2}{k_{-1}} [A][B][D]$$

$$= Kk_2 [A][B][D]$$

where  $K$  is the equilibrium constant for the pre-equilibrium (1) and is equal to  $k_1/k_{-1}$ , and  $k_{\text{obs}} = Kk_2$ . Step (2) is said to be the rate-controlling step.

See also *Gibbs energy diagram, microscopic diffusion control, mixing control, rate-determining step.*

1994, 66, 1156; see also 1996, 68, 182