

### isokinetic relationship

When a series of structurally related substrates undergo the same general reaction or when the reaction conditions for a single substrate are changed in a systematic way, the *enthalpies* and *entropies of activation* sometimes satisfy the relation:

$$\Delta^\ddagger H - \beta\Delta^\ddagger S = \text{constant}$$

where the parameter  $\beta$  is independent of temperature. This equation (or some equivalent form) is said to represent an 'isokinetic relationship'. The temperature  $T = \beta$  (at which all members of a series obeying the isokinetic relationship react at the same rate) is termed the 'isokinetic temperature'. Supposed isokinetic relationships as established by direct correlation of  $\Delta^\ddagger H$  with  $\Delta^\ddagger S$  are often spurious and the calculated value of  $\beta$  is meaningless, because errors in  $\Delta^\ddagger H$  lead to compensating errors in  $\Delta^\ddagger S$ . Satisfactory methods of establishing such relationships have been devised.

See also *compensation effect*, *isoequilibrium relationship*, *isoselective relationship*.

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