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 β 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 β 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

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1129