

### enthalpy of activation, $\Delta^\ddagger H^\circ$

The standard enthalpy of activation  $\Delta^\ddagger H^\circ$  is the enthalpy change that appears in the thermodynamic form of the rate equation obtained from conventional *transition state theory*. This equation is only correct for a first order reaction, for which the rate constant has the dimension reciprocal time. For a second order reaction, for which the rate constant has the dimension (reciprocal time)  $\times$  (reciprocal concentration), the left hand side should be read as  $kc^\circ$ , where  $c^\circ$  denotes the standard concentration (usually  $1 \text{ mol dm}^{-3}$ ).

$$k = (k_{\text{B}}T/h) \exp(\Delta^\ddagger S^\circ/R) \exp(-\Delta^\ddagger H^\circ/RT)$$

The quantity  $\Delta^\ddagger S^\circ$  is the standard *entropy of activation*, and care must be taken with standard states. In this equation  $k_{\text{B}}$  is the Boltzmann constant,  $T$  the absolute temperature,  $h$  the Planck constant, and  $R$  the gas constant. The enthalpy of activation is approximately equal to the *activation energy*; the conversion of one into the other depends on the molecularity.

The enthalpy of activation is always the standard quantity, although the word standard and the superscript  $^\circ$  on the symbol are often omitted. The symbol is frequently (but incorrectly) written  $\Delta H^\ddagger$ , where the standard symbol is omitted and the  $\ddagger$  is placed after the  $H$ .

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