doi:10.1351/goldbook.E02142

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) × (reciprocal concentration), the left hand side should be read as $k\,c^{\circ}$, where c° denotes the standard concentration (usually 1 mol dm^{-3}).

$$k = \frac{k_{\mathrm{B}}\,T}{h}\,\mathrm{e}^{\frac{\Delta^{\ddagger}S^{\circ}}{R}}\,\mathrm{e}^{\frac{-\Delta^{\ddagger}H^{\circ}}{R\,T}}$$

The quantity $\Delta^{\ddagger}S^{\circ}$ is the standard entropy of activation, and care must be taken with standard states. In this equation k_{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 ° on the symbol are often omitted. The symbol is frequently (but incorrectly) written $\Delta H^{\ddagger}$, where the standard symbol is omitted and the ‡ is placed after the H.

Source:

PAC, 1996, *68*, 149 *(A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996))* on page 164
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1113
Green Book, 2nd ed., p. 56
PAC, 1993, *65*, 2291 *(Nomenclature of kinetic methods of analysis (IUPAC Recommendations 1993))* on page 2294

