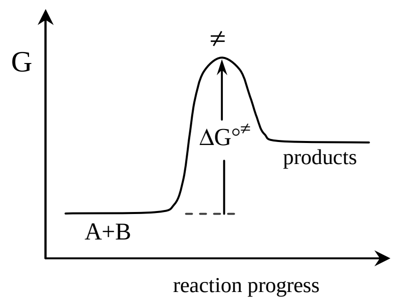
Thermodynamic Transition State Theory

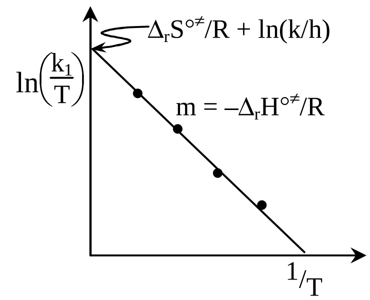
$A + B \longrightarrow [AB]^{\neq} \longrightarrow \text{products}$

$$-\frac{d[A]}{dt} = k_2\,[A][B]$$

$$K_c^{\neq} = \frac{[AB]^{\neq}}{[A][B]}$$

$$k_2 = \frac{kT}{h}\left(\frac{RT}{P^\circ}\right) K_p^{\neq}$$





$$\Delta_r G^{\circ\neq} = -RT \ln K_p^{\neq}$$

$$k_2 = \frac{kT}{h}\left(\frac{RT}{P^\circ}\right) e^{-\Delta_r G^{\circ\neq}/RT}$$

$$\Delta_r G^{\circ\neq} = \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$$

$$k_2 = \frac{kT}{h}\left(\frac{RT}{P^\circ}\right) e^{\Delta_r S^{\circ\neq}/R}\, e^{-\Delta_r H^{\circ\neq}/RT}$$

Arrhenius Law: $\left(\frac{\partial \ln k_2}{\partial T}\right)_V = \frac{E_a}{RT^2}$ $\qquad \left(\frac{RT}{P^\circ}\right) = V^\circ$

$$\left(\frac{\partial\left(\ln \frac{kT}{h} + \ln V^\circ - \frac{\Delta_r G^{\circ\neq}}{RT}\right)}{\partial T}\right)_V = \frac{E_a}{RT^2}$$

$$\frac{1}{T} + \frac{\Delta_r U^{\circ\neq}}{RT^2} = \frac{E_a}{RT^2} \qquad\qquad E_a = \Delta_r U^{\circ\neq} + RT$$

Gases: $\Delta_r H^{\circ\neq} = \Delta_r U^{\circ\neq} + \Delta_r n_g RT$ bimolecular: $\Delta_r n_g = -1$ $\quad E_a = \Delta_r H^{\circ\neq} + 2RT$

unimolecular or solution: $\Delta_r n_g = 0$ $\quad E_a = \Delta_r H^{\circ\neq} + RT$

$$k_2 = \frac{kT}{h}\left(\frac{RT}{P^\circ}\right) e^2\, e^{\Delta_r S^{\circ\neq}/R}\; e^{-E_a/RT} \qquad\qquad k_2 = A\, e^{-E_a/RT}$$

$$A = \frac{kT}{h}\left(\frac{RT}{P^\circ}\right) e^2\, e^{\Delta_r S^{\circ\neq}/R} \text{ (bimolecular)} \qquad\qquad A = \frac{kT}{h}\, e\, e^{\Delta_r S^{\circ\neq}/R} \text{ (unimolecular)}$$

"normal bimolecular" $A = 10^{10} - 10^{11}$ L mol^{-1} s^{-1} $\qquad \Delta_r S^{\circ\neq} = -80$ J K^{-1} mol^{-1}

$A_2 \longrightarrow [A\cdots A]^{\neq} \longrightarrow 2\,A$ $\qquad AB \longrightarrow [A\cdots B]^{\neq} \longrightarrow A + B$ $\qquad$ \C=C/ ⟶ [\C=C–]$^{\neq}$ ⟶ \C=C\ $\qquad \Delta_r n_g = 0$

$$k_1 = \frac{kT}{h}\, e^{\Delta_r S^{\circ\neq}/R}\, e^{-\Delta_r H^{\circ\neq}/RT} \qquad\qquad \ln\left(\frac{k_1}{T}\right) = -\frac{\Delta_r H^{\circ\neq}}{R}\left(\frac{1}{T}\right) + \frac{\Delta_r S^{\circ\neq}}{R} + \ln\left(\frac{k}{h}\right)$$