2. Elementary reaction. Transition state theory.

- The rearrangement of atoms occurs through the motion of nuclei in the continuous potential field set up by the rapid motion of the electrons of the system.
- For the elementary reaction there exists a single potential energy surface on which the system will move to go from reactants to products and back, e.g.

\[ \text{H}^* + \text{H} - \text{C}_2\text{H}_5 \rightleftharpoons \text{H} - \text{H} + \cdot \text{C}_2\text{H}_5 \]

Reaction coordinate is the most “economical” path in terms of the energy required for reaction.
Transition State Theory = Theory of absolute reaction rates
(S. Glasstone, K.J. Laidler, H. Eyring, 1941)

\[ A_1 + A_2 \rightleftharpoons Z \rightarrow \text{products} \]

Transition state (Activated complex) in equilibrium with reactants

\[ r_v = f_0 c_Z \]

\[ f_0 = \frac{k_B T}{h} \quad \text{characteristic frequency of activated complex decomposition} \]

\[ f_0 (500\text{K}) \approx 10^{13} \text{s}^{-1} \]

\[ r_v = A_o \cdot \exp\left(-\frac{E}{RT}\right) c_{A_1} c_{A_2} \]

\[ k_B = 1.38054 \times 10^{-23} \text{J.K}^{-1} \quad \text{(Boltzmann's constant)} \]

\[ h = 6.6256 \times 10^{-34} \text{J.s} \quad \text{(Planck's constant)} \]
\[ K_{Z}^{eq} = \frac{a_{Z}}{a_{A_1} a_{A_2}} = \frac{\gamma_{Z}}{\gamma_{A_1} \gamma_{A_2}} \frac{c_{Z}}{c_{A_1} c_{A_2}} \]

\[
\exp\left[-\frac{\Delta H_{Z}^o}{RT} + \frac{\Delta S_{Z}^o}{R}\right] = \frac{\gamma_{Z}}{\gamma_{A_1} \gamma_{A_2}} \frac{c_{Z}}{c_{A_1} c_{A_2}}
\]

\[ c_{Z} = \frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_{Z}} \exp\left[-\frac{\Delta H_{Z}^o}{RT} + \frac{\Delta S_{Z}^o}{R}\right] c_{A_1} c_{A_2} \]

\[ r_{v} = \frac{k_{B}T}{h} c_{Z} = \frac{k_{B}T}{h} \frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_{Z}} \exp\left[-\frac{\Delta H_{Z}^o}{RT} + \frac{\Delta S_{Z}^o}{R}\right] c_{A_1} c_{A_2} \]

\[ r_{v} = A_{o} \cdot \exp\left(-\frac{E}{RT}\right) c_{A_1} c_{A_2} \]

\[ A_{o} = \frac{k_{B}T}{h} \exp\left[\frac{\Delta S_{Z}^o}{R}\right] \frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_{Z}} \text{,} \quad E = \Delta H_{Z}^o \]

\[ E = \Delta H_{Z}^o - \text{standard enthalpy of active complex formation (J.mol}^{-1}) \]
\[ \Delta S_{Z}^o - \text{standard entropy of active complex formation (J.mol}^{-1}.K^{-1}) \]
\[ \gamma_{A_1}, \gamma_{A_2}, \gamma_{Z} - \text{activity coefficients of reactants and activated complex, resp.} \]
Kinetics and thermodynamic equilibrium of elementary reaction

\[ \nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_{N_1-1} A_{N_1-1} \rightleftharpoons r_f \rightarrow r_b \nu_{N_1} A_{N_1} + \nu_{N_v+1} A_{N_v+1} + \ldots + \nu_N A_N \]

\( A_1, A_2, \ldots, A_{N_1-1} \) – reactants  \( A_{N_1}, A_2, \ldots, A_N \) – products

\[ r = r_f - r_b = k_f \prod_{i=1}^{N_1-1} c_i^{m_f,i} - k_b \prod_{j=N_1}^{N} c_j^{m_b,j} = \]

\[ = A_{of}.T^{n_1}.\exp(-\frac{E_f}{RT}) \prod_{i=1}^{N_1-1} c_i^{m_f,i} - A_{ob}.T^{n_2}.\exp(-\frac{E_b}{RT}) \prod_{j=N_1}^{N} c_j^{m_b,j} \]

The orders of reaction relative to given component

\( k_f \)  \( k_b \)
In the thermodynamic equilibrium:

\[ r = 0 \]

\[ r_f = r_b \]

\[ A_{of} \cdot T^{n_1} \cdot \exp\left(-\frac{E_f}{RT}\right) \cdot \prod_{i=1}^{N_1-1} c_{i,eq}^{m_{f,i}} = A_{ob} \cdot T^{n_2} \cdot \exp\left(-\frac{E_b}{RT}\right) \cdot \prod_{j=N_1}^{N} c_{j,eq}^{m_{b,j}} \]

\[ \frac{k_f}{k_b} = \frac{A_{of} \cdot T^{n_1}}{A_{ob} \cdot T^{n_2}} \exp\left[-\frac{(E_f - E_b)}{RT}\right] \equiv \frac{A_{of}}{A_{ob}} \exp\left[-\frac{(E_f - E_b)}{RT}\right] = \frac{\prod_{j=N_1}^{N} c_{j,eq}^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{m_{f,i}}} \]
From classical thermodynamics it follows:

\[
K_{eq} = \frac{\prod_{j=N_1}^{N} c_{j,eq}^{|v_j|}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{|v_i|}} = \exp\left(-\frac{\Delta_r G^o}{RT}\right) = \exp\left(-\frac{\Delta_r H^o - T \Delta_r S^o}{RT}\right) = \exp\left(\frac{\Delta_r S^o}{R}\right) \exp\left(-\frac{\Delta_r H^o}{RT}\right)
\]

\[
\prod_{j=N_1}^{N} c_{j,eq}^{|v_j|} = \exp\left(\frac{\Delta_r S^o}{R}\right) \exp\left(-\frac{\Delta_r H^o}{RT}\right)
\]

By comparison of kinetic and thermodynamic expressions:

\[
K_{eq} = \frac{k_f}{k_b} \Rightarrow \frac{\prod_{j=N_1}^{N} c_{j,eq}^{|v_j|}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{|v_i|}} \Rightarrow \frac{\prod_{j=N_1}^{N} c_{j,eq}^{|v_j|}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{|v_i|}} \Rightarrow m_{b,j} = |v_j| \Rightarrow A_{of} = \exp\left(\frac{\Delta_r S^o}{R}\right) \Rightarrow A_{ob} = \exp\left(\frac{\Delta_r S^o}{R}\right) \Rightarrow E_f - E_b = \Delta_r H^o
\]
Using above developed relations, we get:

\[ r = r_f - r_b = k_f \prod_{i=1}^{N_1-1} c_i^{m_f,i} - k_b \prod_{j=N_1}^{N} c_j^{m_b,j} = k_f \left[ \prod_{i=1}^{N_1-1} c_i^{m_f,i} - \frac{1}{K_{eq}} \prod_{j=N_1}^{N} c_j^{m_b,j} \right] = \]

\[ = r_f \left[ 1 - \frac{1}{K_{eq}} \prod_{j=N_1}^{N} c_j^{m_b,j} \right] = r_f \left[ 1 - \beta \right] \quad \beta = \frac{1}{K_{eq}} \prod_{j=N_1}^{N} c_j^{m_b,j} \]

In the thermodynamic equilibrium

\[ \beta \to 1 \Rightarrow r \to 0 \]
Elementary reactions energy diagrams

Exothermic reaction, $p = \text{const}$. 

Endothermic reaction, $p = \text{const}$. 

$E_f$, $E_b$, $-\Delta_r H^\circ$, $\Delta_r H^\circ$
Examples of complex reactions

\[ 2 \text{NO}(g) + \text{O}_2(g) \leftrightarrow 2\text{NO}_2(g) \]

\[ r_V = k_1 c^2_{\text{NO}} c_{\text{O}_2} - k_2 c^2_{\text{NO}_2} \]

\[ \text{CO}(g) + \text{Cl}_2(g) \rightarrow \text{COCl}_2(g) \]

\[ r_V = k c_{\text{CO}} c^2_{\text{Cl}_2} \]

\[ 2 \text{N}_2\text{O}(g) \rightarrow 2\text{N}_2(g) + \text{O}_2(g) \]

\[ r_S = \frac{k_1 c_{\text{N}_2\text{O}}}{1 + k_2 c_{\text{O}_2}} \]