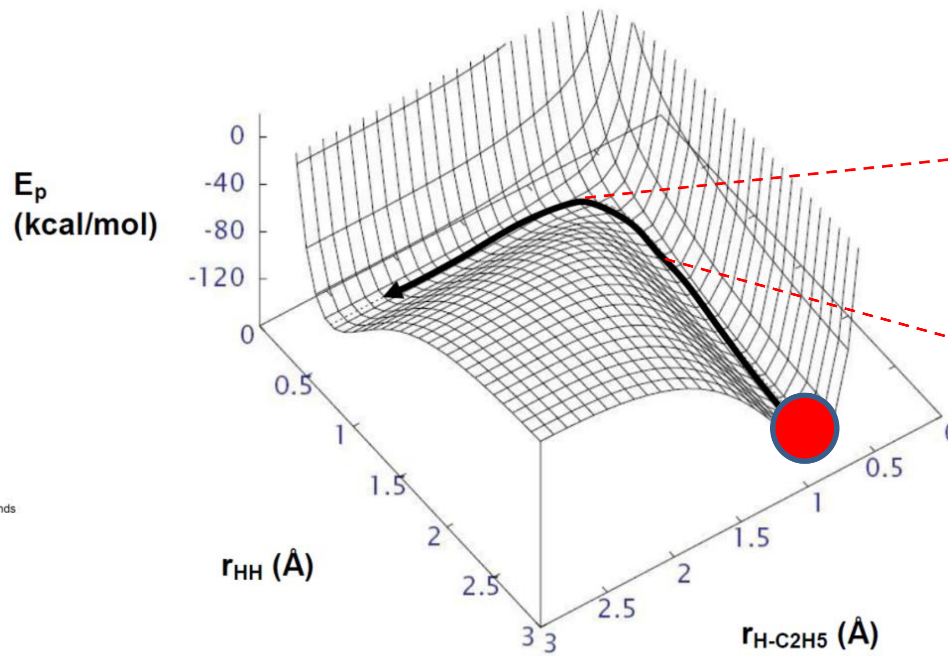
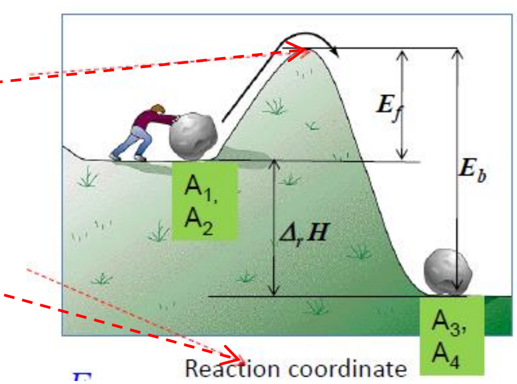
2. Elementary reaction. Transition state theory.

- **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.**

$$H^{\bullet} + H\text{-}C_2H_5 \rightleftarrows H\text{-}H + {}^{\bullet}C_2H_5$$





Reaction coordinate is the most "economical" path in terms of the energy required for reaction.

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Transition State Theory = Theory of absolute reaction rates

(S. Glasstone, K.J. Laidler, H. Eyring, 1941)

$$A_1 + A_2 \Leftrightarrow Z \rightarrow \text{products}$$

Transition state (Activated complex) in equilibrium with reactants

$$r_V = f_o c_Z$$

$$f_o = \frac{k_B T}{h}$$ characteristic frequency of activated complex decomposition

$$f_o(500\,K) \cong 10^{13}\,s^{-1}$$

kinetic equation (see next slide)

$$r_V = A_o . \exp\left(-\frac{E}{RT}\right) . c_{A_1} c_{A_2}$$

$k_B = 1{,}38054.10^{-23}$ J.K^{-1} (Boltzmann's constant)

h = $6{,}6256.10^{-34}$ J.s (Planck's constant)

Justification of kinetic equation

$$K_Z^{eq} = \frac{a_Z}{a_{A_1} a_{A_2}} = \frac{\gamma_Z}{\gamma_{A_1}\gamma_{A_2}} \frac{c_Z}{c_{A_1} c_{A_2}}$$

$$\exp\left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R}\right] = \frac{\gamma_Z}{\gamma_{A_1}\gamma_{A_2}} \frac{c_Z}{c_{A_1} c_{A_2}}$$

$$c_Z = \frac{\gamma_{A_1}\gamma_{A_2}}{\gamma_Z} \exp\left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R}\right] c_{A_1} c_{A_2}$$

$$r_V = \frac{\mathrm{k_B} T}{\mathrm{h}} c_Z = \frac{\mathrm{k_B} T}{\mathrm{h}} \frac{\gamma_{A_1}\gamma_{A_2}}{\gamma_Z} \exp\left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R}\right] c_{A_1} c_{A_2}$$

$$r_V = A_o . \exp(-\frac{E}{RT}) . c_{A_1} c_{A_2}$$

$$A_o = \frac{k_B T}{h} \exp\left[\frac{\Delta S_Z^o}{R}\right] \frac{\gamma_{A_1}\gamma_{A_2}}{\gamma_Z}, \qquad E = \Delta H_Z^o$$

$E = \Delta H_Z^o$ – standard enthalpy of active complex formation (J.mol^{-1})

ΔS_Z^o – standard entropy of active complex formation (J.mol^{-1}.K^{-1})

$\gamma_{A_1}, \gamma_{A_2}, \gamma_Z$ – activity coefficients of reactants and activated complex, resp.

Kinetics and thermodynamic equilibrium of elementary reaction

$$\nu_1 A_1 + \nu_2 A_2 + \ldots.\nu_{N_1-1} A_{N_1-1} \underset{r_b}{\overset{r_f}{\rightleftarrows}} \nu_{N_1} A_{N_1} + \nu_{N_\nu+1} A_{N_\nu+1} + \ldots.\nu_N A_N$$

$$A_1, A_2, \ldots..A_{N_1-1} - \text{reactants} \qquad A_{N_1}, A_2, \ldots..A_N - \text{products}$$

$$r = r_f - r_b = k_f \prod_{i=1}^{N_1-1} c_i^{m_{f,i}} - k_b \prod_{j=N_1}^{N} c_j^{m_{b,j}} =$$

$$= \underbrace{A_{of}.\mathrm{T}^{n_1}.\exp(-\frac{E_f}{RT})}_{k_f} \prod_{i=1}^{N_1-1} c_i^{m_{f,i}} - \underbrace{A_{ob}.\mathrm{T}^{n_2}.\exp(-\frac{E_b}{RT})}_{k_b} \prod_{j=N_1}^{N} c_j^{m_{b,j}}$$

The orders of reaction relative to given component ($m_{f,i}$, $m_{b,j}$)

In the thermodynamic equilibrium:

$$r = 0$$

$$r_f = r_b$$

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

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

From classical thermodynamics it follows:

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

$$\frac{\prod_{j=N_1}^{N} c_{j,eq}^{\nu_j}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{|\nu_i|}} = \exp\left(\frac{\Delta_r S^o}{R}\right)\exp\left(\frac{-\Delta_r H^o}{RT}\right)$$

By comparison of kinetic and thermodynamic expressions:

$$K_{eq} = \frac{k_f}{k_b} \Rightarrow \frac{\prod_{j=N_1}^{N} c_{j,eq}^{\nu_j}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{|\nu_i|}} = \frac{\prod_{j=N_\nu}^{N} c_{j,eq}^{m_{b,j}}}{\prod_{i=1}^{N_\nu-1} c_{i,eq}^{m_{f,i}}} \Rightarrow \begin{matrix} m_{b,j} = \nu_j \\ m_{f,i} = |\nu_i| \end{matrix} \Rightarrow \begin{matrix} \dfrac{A_{of}}{A_{ob}} = \exp\left(\dfrac{\Delta_r S^o}{R}\right) \\ E_f - E_b = \Delta_r H^o \end{matrix}$$

Using above developed relations , we get :

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

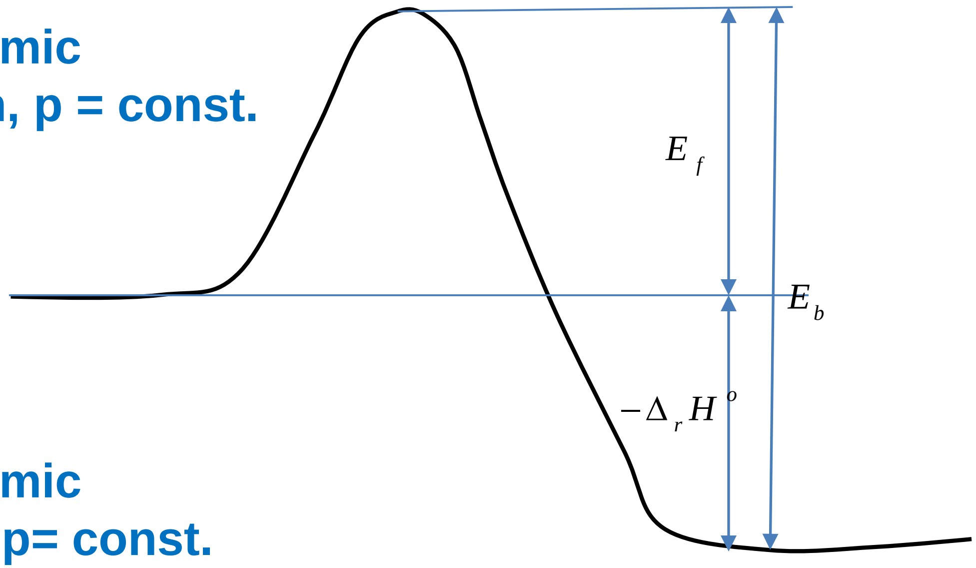
$$= r_f \left[1 - \frac{1}{K_{eq}} \frac{\prod_{j=N_1}^{N} c_j^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_i^{m_{f,i}}} \right] = r_f \left[1 - \beta \right] \qquad \beta = \frac{1}{K_{eq}} \frac{\prod_{j=N_1}^{N} c_j^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_i^{m_{f,i}}}$$

In the thermodynamic equilibrium

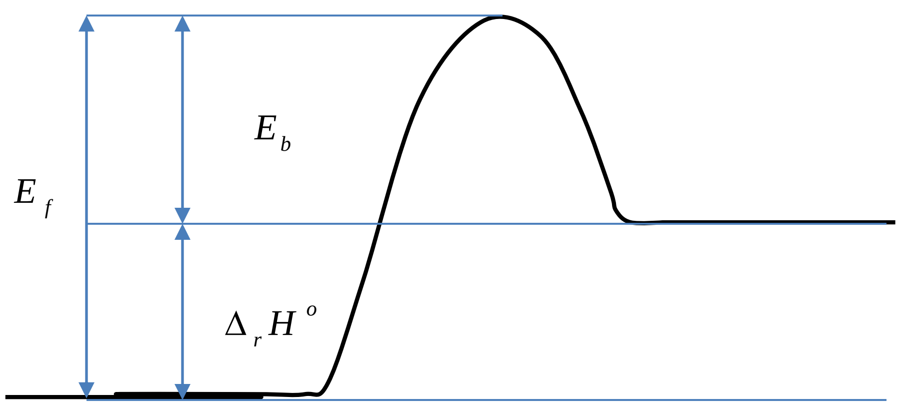
$$\beta \to 1 \Rightarrow r \to 0$$

Elementary reactions energy diagrams

Exothermic reaction, p = const.



Endothermic reaction, p= const.



Examples of complex reactions

$$2\ NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$$

$$r_V = k_1 c_{NO}^2 c_{O_2} - k_2 c_{NO_2}^2$$

$$CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$$

$$r_V = k c_{CO} c_{Cl_2}^{\frac{3}{2}}$$

$$2\ N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$$

$$r_S = \frac{k_1 c_{N_2O}}{1 + k_2 c_{O_2}}$$