16.5 Theories of Chemical Kinetics

The Effect of Temperature

– For most reactions, the reaction rate increases almost exponentially with \( T \) (rate \( \sim \) doubles for every 10°C of \( T \uparrow \))
– \( T \) affects the rate through the rate constant, \( k \)

• **Arrhenius equation** – gives the temperature dependence of \( k \)
  \[
  k = Ae^{-E_a/RT}
  \]
  \( A \) – preexponential factor; \( E_a \) – activation energy

→ Take a natural logarithm (ln) of both sides
  \[
  \ln k = \ln A - \frac{E_a}{RT}
  \]

For two different temperatures, \( T_1 \) and \( T_2 \)

\[
\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \odot
\]
\[
\ln k_1 = \ln A - \frac{E_a}{RT_1}
\]

⇒ \[
\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

→ Allows the determination of \( E_a \) by measuring \( k \) at two different \( T \)s
→ Allows the calculation of \( k \) at a given \( T \), if \( k \) is known at another \( T \) (\( E_a \) must be known too)

Example: For a given 1st order reaction, \( k \) is 2.6×10^{-10} s^{-1} at 300°C and 6.7×10^{-4} s^{-1} at 500°C. Calculate the activation energy.

\[
T_1 = 300°C = 573 K \quad k_1 = 2.6\times10^{-10} s^{-1}
\]
\[
T_2 = 500°C = 773 K \quad k_2 = 6.7\times10^{-4} s^{-1}
\]

\[
E_a = -R \left( \ln \frac{k_2}{k_1} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}
\]

\[
E_a = -8.314 \frac{J}{mol \cdot K} \left( \ln \frac{6.7\times10^{-4} s^{-1}}{2.6\times10^{-10} s^{-1}} \right) \left( \frac{1}{773 K} - \frac{1}{573 K} \right)^{-1}
\]

\[
E_a = 2.72\times10^5 J/mol = 272 kJ/mol
\]
Explaining the Effects of Concentration and Temperature

- The Arrhenius equation is empirical and it does not explain the \( T \) dependence of \( k \)

**Collision theory** – molecules must collide in order to react

- **Collision frequency** (\( Z \)) – number of collisions per unit time per unit volume (the reaction rate is proportional to \( Z \))
  
  \[ Z = Z_0[A][B] \]

  \( Z_0 \) – proportionality constant (depends on \( \sqrt{T} \))

- The reaction rate is proportional to \( Z \)
  
  \[ → \text{Rate} \propto Z \]

- The reaction rate is proportional to \( f \)
  
  \[ → \text{Rate} \propto f \]

- **Activation energy** \( (E_a) \) – the minimum collision energy required for the reaction to occur (not all collisions result in reaction)
  
  \[ f = e^{-E_a/RT} \quad 0 < f < 1 \]

  \[ T_2 > T_1 \]

  \[ f_2 > f_1 \]

  \[ T ↑ \Rightarrow f ↑ \]

- **Steric factor** \( (p) \) – the colliding molecules must have proper orientation with respect to each other in order to react
  
  \[ p \] – fraction of the total # of collisions having proper orientations (0 < \( p < 1 \))

  \[ → \text{Effective collisions} \]

  \[ \text{having } E > E_a \text{ and proper orientation} \]

- The reaction rate is proportional to \( p \)

  \[ → \text{Rate} \propto p \]

  \[ \Rightarrow k = A \times e^{-E_a/RT} \]

  \[ A \] contains the steric factor, \( p \), and part of the collision frequency, \( Z_o \) (\( Z_o \) depends weakly on \( \sqrt{T} \))
**Activated complex theory** – the reacting molecules form a high energy complex which is unstable and breaks down to form either the products or the original reactants

\[ A + B \leftrightarrow [A--B]^* \leftrightarrow \text{Products} \]

- **Activated complex or transition state**

\[ [A--B]^* \rightarrow \text{activated complex or transition state} \]

\[ E_a \] is the height of the barrier between the reactants and the transition state

\[ E_a \] is needed to weaken the bonds in the reactants so that the new bonds in the products can be formed

- Every reaction (every step in a reaction) goes through its own transition state

- Theoretically all reactions are reversible since once reached the transition state can go forward to products or back to reactants

- **Reaction energy diagrams** – show the energy profile of the reaction (\( E_{a(fwd)} \), \( E_{a(rev)} \), and \( \Delta H_{rxn} \))

**Example:** For a given reaction \( E_{a(fwd)} \) is 55 kJ/mol and \( E_{a(rev)} \) is 28 kJ/mol. Calculate \( \Delta H_{rxn} \).

\( E_{a(fwd)} > E_{a(rev)} \Rightarrow \) the reaction is endothermic

\[ \Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)} = 55 - 28 = 27 \text{ kJ/mol} \]

- Some examples of reaction energy diagrams: