16.5 Theories of Chemical Kinetics

The Effect of Temperature

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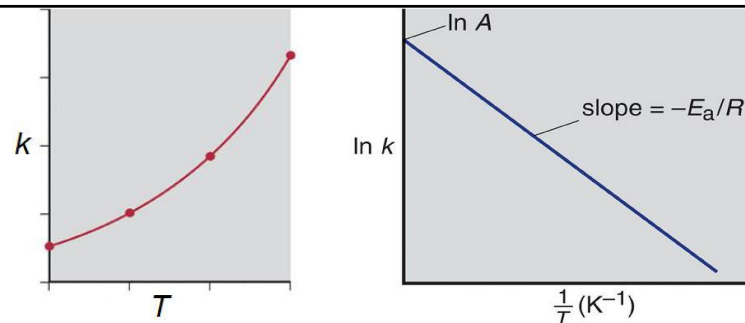- T affects the rate through the rate constant, k

• **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

$$\ln k = \ln A - E_a/RT$$

$$k = Ae^{-E_a/RT}$$
$$\uparrow T \Rightarrow \uparrow k \Rightarrow \uparrow Rate$$

$$\ln k = \ln A - (E_a/R)(1/T)$$
$$y \;=\; b \;+\; m\,x$$

- E_a is the minimum energy the molecules must have in order to react (E_a can be determined by measuring k at different T from the slope of a plot of $\ln k$ versus $1/T$)

➢ For two different temperatures, T_1 and T_2

→ $\ln k_2 = \ln A - E_a/RT_2$ $\Big|_{\ominus}$
→ $\ln k_1 = \ln A - E_a/RT_1$

$$\Rightarrow \; \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

→ Allows the determination of E_a by measuring k at two different Ts
→ 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 $k_1 = 2.6\times10^{-10}$ s^{-1}
$T_2 = 500°C = 773$ K $k_2 = 6.7\times10^{-4}$ 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)

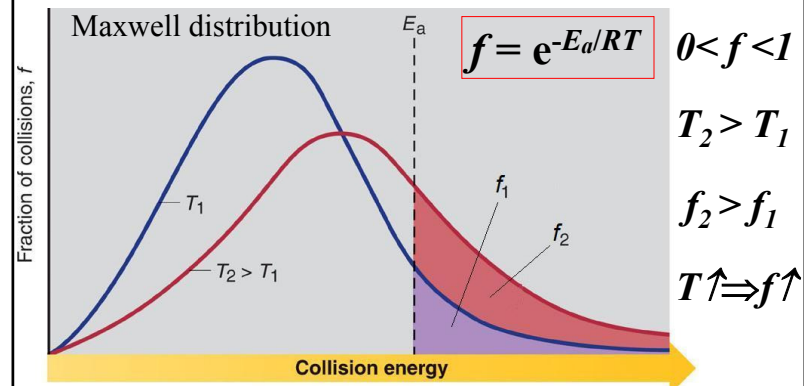→ Z is proportional to the concentration of the reactants

→ For a 2nd order reaction (A + B → Products)

$$Z = Z_o[A][B]$$

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

➢ **Activation energy** (E_a) – the minimum collision energy required for the reaction to occur (not all collisions result in reaction)

→ f – fraction of collisions with energy $E > E_a$ (only collisions with $E > E_a$ can lead to reaction)

Maxwell distribution

$f = e^{-E_a/RT}$ $0 < f < 1$

$T_2 > T_1$

$f_2 > f_1$

$T\uparrow \Rightarrow f\uparrow$
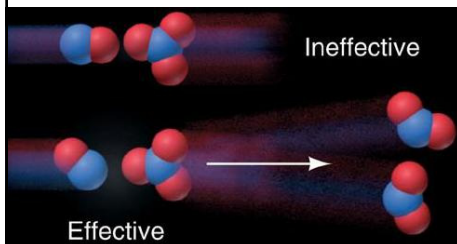

→ The reaction rate is proportional to f

$\Rightarrow \uparrow T \Rightarrow \uparrow f \Rightarrow \uparrow Rate$
$\Rightarrow \uparrow E_a \Rightarrow \downarrow f \Rightarrow \downarrow Rate$

$f = e^{-E_a/RT}$

➢ **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 ($0 < p < 1$)

Ineffective

Effective

→ The reaction rate is proportional to p
→ **Effective collisions** – having $E > E_a$ and proper orientation

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➢ The reaction rate is proportional to the collision frequency (Z), the fraction of collisions (f) with $E > E_a$, and the fraction of collisions (p) with proper orientations

→ For a 2nd order reaction (A + B → Products)

$Rate = p \times f \times Z = p \times e^{-E_a/RT} \times Z_o[A][B]$ (From theory)

$Rate = k[A][B]$ (From exper.)

$\Rightarrow k = p \times Z_o \times e^{-E_a/RT}$ ($p \times Z_o = A$)

$$\Rightarrow \quad k = A \times e^{-E_a/RT}$$

→ The equation is the same as the Arrhenius equation

→ 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

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

➤ $[A\text{---}B]^* \rightarrow$ **activated complex** or **transition state**
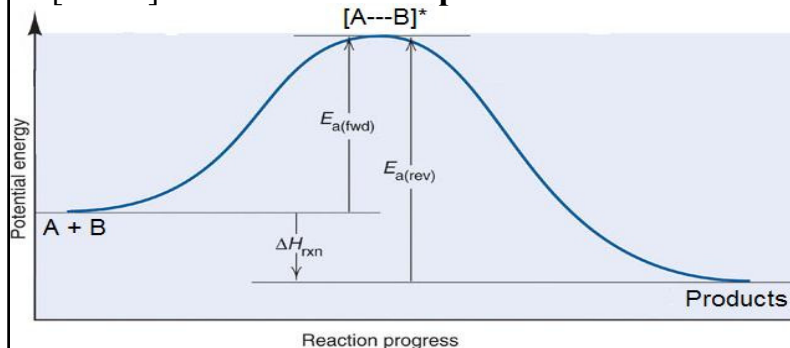
- E_a is the height of the barrier between the reactants and the transition state
- E_a is needed to weaken the bonds in the reactants so that the new bonds in the products can be formed
- Every reaction (every step in a reaction) goes through its own transition state
- Theoretically all reactions are 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 ΔH_{rxn})

Example: For a given reaction $E_{a(fwd)}$ is 55 kJ/mol and $E_{a(rev)}$ is 28 kJ/mol. Calculate ΔH_{rxn}.

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

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

➤ Some examples of reaction energy diagrams: