

class notes 2/22

Half life: amt of time it takes for $\frac{1}{2}$ of reactants to be used up in a reaction

$$\text{After 1 half life } \frac{[A]_t}{[A]_0} = \frac{1}{2}$$

Half life: first order reactions

- integrated rate law: $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$

$\rightarrow$ substitute: $\ln\left(\frac{1}{2}\right) = -kt_{1/2}$

$$t_{1/2} = 0.693/k$$

successive half lives are constant. Depends only on k

Half life: second order reactions

$$-1RL \quad \frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Substitute & solve: $\frac{2}{[A]_t} = \frac{1}{[A]_0}$

$$t_{1/2} = \frac{1}{k[A]_0}$$

half life depends on starting concentration

Collision Theory

- chemical rxns can occur only when reacting particles collide with each other w/ sufficient energy
- explains why concentration affects rate
- more molecules, more collisions!

- collision theory also explains why temp affects rate
- molecules can only react if the collisions have enough energy to react
 - activation energy - minimum energy need for rxn to proceed
- molecules move faster @ ↑ temp, the # of productive collisions ↑
- rule of thumb: rxn rate (×) doubles w/ a 10°C increase in temp.

collision theory: E_a

- min. energy for rxn to occur is the activation energy, E_a
- the high energy species is called the transition state or activated complex
 - generally postulated to exist and cannot be isolated
- at higher temp's there is a larger fraction of molecules that have enough energy:
- molecules must collide in the right orientation

Arrhenius Equation

- incorporates effects of temp, orientation effects & frequency of collisions on the rate constant

$$k = Ae^{-E_a/RT}$$

- where A is the frequency factor, specific for that reaction & E_a is the activation energy
- activation energy can be determined graphically by reorganizing the equation

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

plot of $\ln k$ vs $1/T$ should be a straight line w/ slope $-E_a/R$

Ex)

$$E_a = 51 \text{ kJ/mol}$$

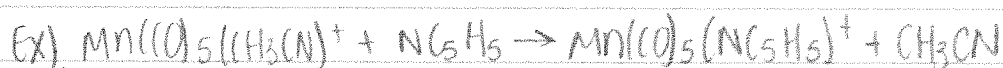
$$k @ 310 \text{ K} = ?$$

$$k @ 320 \text{ K} = 7.1 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\ln k_2 - \ln k_1}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{\ln k_2 - \ln(7.1)}{\frac{1}{310 \text{ K}} - \frac{1}{320 \text{ K}}}$$

$$\text{slope} = -E_a/R = -(51,000 \text{ J/mol}) / (8.314 \text{ J/mol} \cdot \text{K})$$

$$k_2 = 3.8 \text{ M}^{-1} \text{ s}^{-1}$$



$$k (\text{min}^{-1})$$

$$T (\text{K})$$

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

$$0.0409$$

$$298$$

$$0.0818$$

$$308$$

$$\frac{\Delta y}{\Delta x} = \frac{-E_a}{R} \rightarrow E_a = -R \cdot \frac{\Delta y}{\Delta x}$$

$$\frac{\Delta y}{\Delta x} = \frac{\ln(0.0818) - \ln(0.0409)}{\frac{1}{308} - \frac{1}{298}} \rightarrow E_a = -R \cdot \frac{\Delta y}{\Delta x} = 53 \text{ kJ/mol}$$