

vi. Half Lives

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1. **Half life**: the amount of time it takes for $\frac{1}{2}$ of a reactant to be used up in the reaction

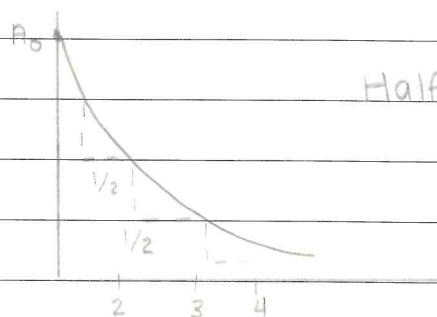
a. After 10 half lives, material is considered 'gone'

b. After one $\frac{1}{2}$ life: $\frac{[A_t]}{[A_0]} = \frac{1}{2}$

2. Integrated rate law: $\ln \frac{[A_t]}{[A_0]} = -kt$, so for half life: $\ln(\frac{1}{2}) = -kt_{\frac{1}{2}} \rightarrow$

$$\text{solve: } -0.693 = -kt_{\frac{1}{2}} \text{ or } t_{\frac{1}{2}} = \frac{0.693}{k}$$

a. Half lives are constant if first order



Half-life graph if first order

3. Smedley example: $\ln[A_0] = \ln(250\text{mg}) - (.116\text{h}^{-1} \cdot 10\text{h}) \rightarrow [A]_0 = 78\text{mg}$

4. Second Order Half Lives

a. Using integrated rate law: $\frac{1}{[A_t]} = \frac{1}{[A_0]} + kt \rightarrow t_{\frac{1}{2}} = \frac{1}{k[A_0]}$

vii. Collision Theory

1. Collision theory explains why concentration affects rate

a. Higher concentration means more molecules collide

2. It also explains why temperature affects rate

a. more energy means more collisions & reactions need sufficient energy

3. Typically if temperature increases by 10°C , then reaction rate doubles
viii. Activation Energy

1. At higher temperatures, there is a larger fraction of moles at higher energy states

2. Arrhenius, "molecules have to collide in proper orientation"

a. Arrhenius equation: incorporates effects of temperature, orientation, and frequency

$$k = A e^{-E_a/RT}$$

$\uparrow$
frequency factor, reaction specific

b. Graphically, $\ln k = -E_a/RT + \ln A$, which gives a linear line

b. Example: for a given reaction, $E_a = -51 \text{ kJ/mol}$. What is the value of k at 310K if k is $7.1 \text{ m}^{-1}\text{s}^{-1}$ at 320K ?

$$\Delta y = \ln k_2 - \ln k_1 = \ln k_2 - \ln(7.1) = \frac{-51,000 \text{ J/mol}}{8.314 \text{ J/molK}}$$

$\Delta x \quad 1/T_2 - 1/T_1 \quad 1/310\text{K} - 1/320\text{K}$

set equal
solve k $\rightarrow k_2 = 3.8 \text{ m}^{-1}\text{s}^{-1}$

c. Example 2: $\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})^+ + \text{nc}_5\text{H}_5 \rightarrow \text{Mn}(\text{CO})_5(\text{nc}_5\text{H}_5)^+ + \text{CH}_3\text{CN}$

b. $k (\text{min}^{-1})$ $T (\text{K})$

0.0409

298

0.0818

308

= 53 kJ/mol

$$\rightarrow \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}; E_a = \frac{-R \Delta y}{\Delta x} \rightarrow \ln(0.0409) \cdot -R$$

$\Delta x \quad 1/308 - 1/298$