[class notes] 2/22

Half life: amt of time it takes for ½ of reactants to be used up in a reaction

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

Half life: first order reactions

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

↳ 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

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

Substitute & solve: $\frac{2}{[A]_t} - \frac{1}{[A]_1}$

$t_{1/2} = 1/(k[A]_0)$ 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 @ ↑ temps, the # of productive collisions ↑
- rule of thumb: rxn rate (& k) doubles w/ a 10°C increase in temp.

collision theory: Ea
- min. energy for rxn to occur is the activation energy, Ea
- 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

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

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

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

plot of ln k vs $^1/_T$ should be a straight line w/ slope $-Ea/R$

Ex) $E_a = 51\ kJ/mol$

k @ $310K = ?$

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

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

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

$k_2 = 38\ M^{-1}s^{-1}$

Ex) $Mn((O)_5((H_3(N)^+ + NC_5H_5 \rightarrow Mn(CO)_5(NC_5H_5)^+ + CH_3CN$

$k\ (min^{-1})$	$T\ (K)$
0.0409	298
0.0818	308

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

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

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