[class notes] 2/25

CHEMICAL KINETICS, V

Reaction mechanism

- chemical mechanism: theory about which takes place at each stage of an overall chemical reaction
- pathway of bond making & bond breaking steps that show how reactants become products
- reactions may occur @ once or through several discrete steps
- each of these processes is known as an elementary step/reaction
- the molecularity of an elementary rxn tells how many molecules are involved in each step

Ex) decomposition of hydrogen peroxide

step i. $H_2O_2 + I^- \rightarrow H_2O + IO^-$ slow (limits how fast rxn occurs)

step ii. $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$ fast

☆ IO^- is an intermediate: formed & consumed during the rxn
→ catalyst

overall rxn: $2H_2O_2 \rightarrow 2H_2O + O_2$

- each elementary step constitutes a single molecular event; has its own E_a and k
- the overall rxn cannot occur faster than the slowest rxn in the mechanism
  → rate determining step (RDS)
  → the RDS determines overall rate of rxn

Requirements of a plausible mechanism

- RDS must be consistent w/ the observed rate law
- Stoichiometry must be obtained when all steps are added up
- each step must balance
- intermediates are made & used up
- catalysts are regenerated

Ex)
overall reaction: $NO_2 + CO \rightarrow NO + CO_2$
experimental RL: rate = $k[NO_2]^2$
*multistep b/c unimolecular: rate = $k[NO_2][CO]$

- If the first step is the RDS, the coefficients on the reactants side are the same as the order in the rate law
- so, the first (slow step) of the mechanism begins

$NO_2 + NO_2 \rightarrow NO + [NO_3] \rightarrow$ intermediate (slow)
$NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

2 step mechanism

Ex) $2NO_2(g) + F_2(g) \rightarrow 2FNO_2(g)$ (1 step mechanism determined by stoichiometry of the rxn)
rate law: rate = $[NO_2][F_2]$
↝ not a 1 step mechanism (rate = $[NO_2]^{(2)}[F_2]$)
① $NO_2(g) + F_2(g) \xrightarrow{K_1} FNO_2(g) + F(g)$
② $NO_2(g) + F(g) \xrightarrow{K_2} FNO_2(g)$
] F(g) = intermediate

$2NO_2(g) + F_2(g) \rightarrow 2FNO_2(g)$
Step ① is the slow step b/c it is consistent w/ overall rate law
$K_2 > K_1$ step ② is faster so rate constant is larger

presence of a catalyst
- affects rate w/ being in the overall balanced equation
- decrease activation energy, increasing rate
- increase rate of forward and back reaction
- do not affect the position of equilibrium

ratio of rate constants
$\frac{K_{cat}}{K_{uncat}}$