

[[class NOTES]] 2/25

CHEMICAL KINETICS, V

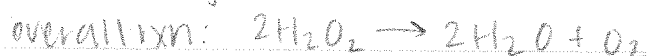
Reaction mechanism

- 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



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



- 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 not consumed

Ex)

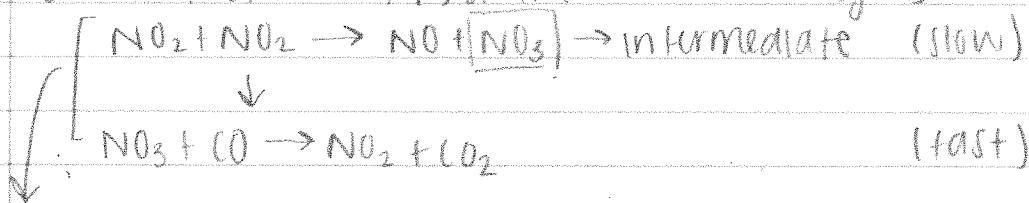
overall reaction: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

experimental PL: rate = $k[\text{NO}_2]^2$

* multistep b/c unimolecular: rate = $k[\text{NO}_2][\text{CO}]$

- 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



2 step mechanism

Ex) $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{FNO}_2(\text{g})$ 1 step mechanism determined by stoichiometry of the rxn

rate law: rate = $[\text{NO}_2]^2[\text{F}_2]$

✓ not a 1 step mechanism (rate = $[\text{NO}_2]^2[\text{F}_2]$)



} $\text{F}(\text{g})$ = intermediate



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

k_{cat}

k_{uncat}