

KINETICS
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Chapter 17 (Pauling 16)

Rate Influencing Factors

- Nature of Reactants (reactivity/redox potential does not equal rate!)
Lithium for example does not equal rate. You can't predict it.
- Surface Area
more area exposed means faster rate and less time
- Temperature
10K doubling (rule of thumb) $R=2^n$ where $n=\Delta T/10$
typically rate increases with temperature
- Concentration (most important)
How molarity [x]. $R=\Delta[x]/\Delta t$
- Catalysts and Inhibitors (energy threshold)
catalyst - less energy required to create activated complex
inhibitor - more energy required to create activated complex

Differential Rate Law

- rate depends on concentration
- "Rate Law" ... ("write the rate law")

Integrated Rate Law

- concentration depends on time
(graphs from lecture)
- equimolar when the rate of consumption equals the rate of production, $A \rightarrow B$
- nonequimolar when rate of consumption is not equal to rate of production, $A \rightarrow 2B$
- single step rxn if $R=k[x]^n$ with n = molar coefficient

Rates of Consumption vs. Production

- consumption rate: $R_c = -\Delta[x]/\Delta t = k[x]^n$
- production rate is the same as the consumption rate only non negative (rate is always +)

RDS and Rates

- the RDS (rate determining step) is the slowest rate (small k) or the step in a chemical rxn

Method of Initial Rates

-comparison of concentration with rates (looking at exponents)

$$-\Delta[x]^n = \Delta R$$

Order of the Reactions

-exponent

-when the order matches the coefficient, it's single step

Method of Linearizing Plots

	<u>ORDER</u>		
Diff. Rate Law	0 R = k	1 R = k[x]	2 R = k[x] ²
Int. Rate Law	$[x] = -kt + [x]_0$	$\ln([x]) = -kt + \ln([x]_0)$	$1/[x] = kt + 1/[x]_0$
Linear	[x] vs. time	ln([x]) vs. time	1/[x] vs. time
Relationship betw/ rate constant to gradient of plot	gradient = -k	gradient = -k	gradient = k
Half life	$t_{1/2} = [x]_0 / 2k$	$t_{1/2} = \ln 2 / k$	$t_{1/2} = 1 / k [x]_0$

-use when you can't use "method of initial rates"

- $t_{1/2} = [x] / 2^n$ with n = number of half lives

- all radioactive decay is first order!!!

$$R \propto k \quad R \propto 1/t_{1/2}$$

-overall order of a reaction: add exponents in the rate law

Chemical Equilibrium

-change is minimized within any system (stability, balanced, opposed)

-chemical equilibrium occurs when **Rates are equal, opposite and unchanging!**

Equilibrium Condition

Law of Mass Action

- Concentration of pure liquids and solids do not change!!! (don't include them in the equilibrium expression. Only include gasses and aqueous phases)
- dependent on temperature and reaction

Le Chatalier's Principle

-any system in equilibrium will react in a manner that reduces the effects of any stress placed on that system

-action and reaction are equal, but not opposite!!!

Pressure

- only for gas - number of mols count
- shift equilibrium, not equilibrium constant
- only reacting products/gases count

Concentration (amount)

- increases rate
- shifts equilibrium, not equilibrium constant
- pure substances don't count

Temp

- depends on endo/exo direction
- shifts equilibrium and equilibrium constant
- K values change depending on direction

Catalysts/Inhibitors

- have equal influences
- shift nothing
- accelerates/decelerates the time in which equilibrium is reached

Common Ion Effect

-if you have a solution, and you added something, if a common ion is present, something will probably precipitate because of LeChetalier's Principle

Solubility Product Equilibrium (K_{sp})

treat each thing like x, or multiply by the coefficient to find the concentration. Just go in reverse if K_{sp} is given.