

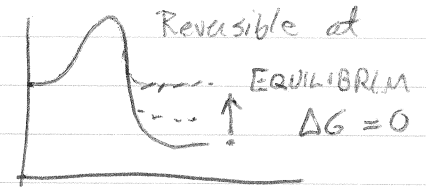
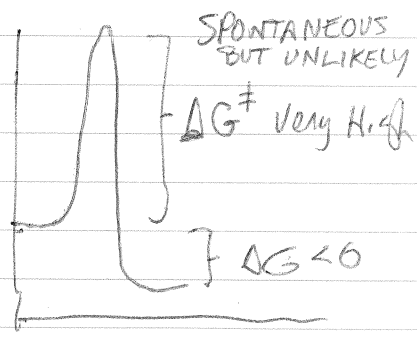
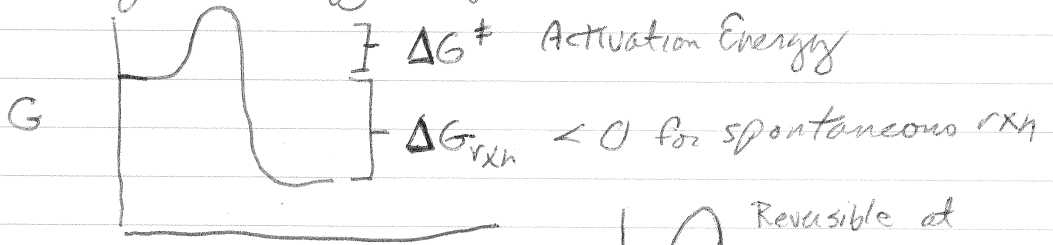
① Kinetics: Quantitative expressions that describe the rate of chemical rxn

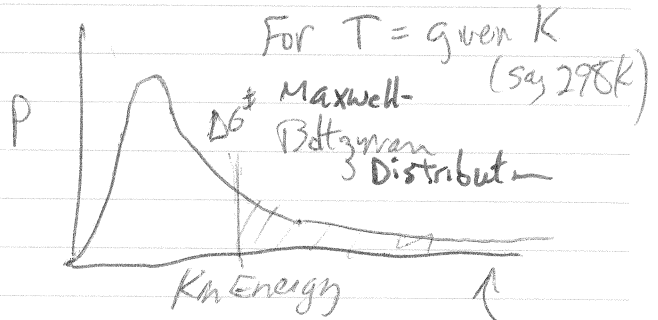
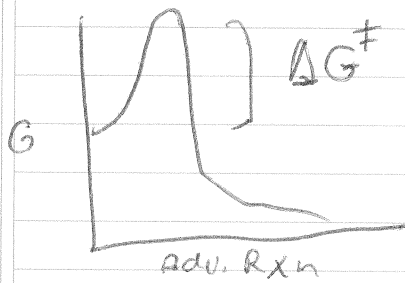
REACTION: Most general definition - Change from one chemical state to another.

- Examples:
- 1) $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$ Acid/base
 - 2) $\text{CdS}_{(s)} \rightarrow \text{Cd}^{2+} + \text{S}^{2-}$ Dissolution (min.)
 - 3) $\text{TCE}_{(l)} \rightarrow \text{TCE}_{(aq)}$ " (org. liq.)
 - 4) $\text{O}_2(g) \rightarrow \text{O}_2(aq)$ Dissoln of gas \rightarrow soluble
 - 5) $^{13}\text{C} \rightarrow ^{12}\text{C} + \alpha$ Radioactive Decay
 - 6) $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ Redox Rxn
 - 7) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}' + \text{H}_2\text{O} \rightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{R}'\text{OH}$ Ester hydrolysis
 - 8) $\text{R} + "h\nu" \rightarrow \text{R}'$ Photolytic Decay
PHOTON ENERGY

② Rxns either reversible or irreversible
 (1,2,3,4,5,6) (5,7,8)

General free energy diagram





E.g. For $\text{HCl}_3^- \rightarrow \text{H}^+ + \text{Cl}_3^{2-}$
 ΔG^\ddagger small, most molecules possess enough KE.

"Boltzmann Tail"

For $\frac{1}{2}\text{N}_2 + \text{O}_2 \rightarrow \text{NO}_2$ ΔG^\ddagger huge only minuscule fraction of molecules possess $\text{KE} \geq \Delta G^\ddagger$
 Hence "cannot" occur at room temp

Raise temp to say 1500K. Now many molecules possess ΔG^\ddagger and NO_2 forms

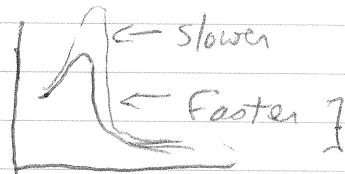
ASIDE:
 Another possibility:
 Add ΔG^\ddagger
 via light energy
 photochemistry

(Question: spark IC engine ~2400 K which produces more NO_x pollution?
 Diesel engine ~2700 K)

Rate Laws / Rate Coefficients

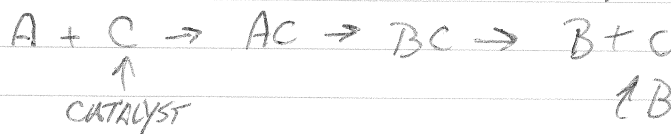
E.g. $A \rightarrow B$ $\frac{d[A]}{dt} = \frac{dC_A}{dt} = -k_f[A]$

k_f depends on ΔG^\ddagger Large ΔG^\ddagger , small k_f & vice versa



What if ΔG^\ddagger can be reduced?
 k_f speeds up

⇒ CATALYSIS



↑ By def'n C unchanged by the rxn

So, some rxns slow, some medium, some fast
CONTINUUM OF RATES

For 1st Order, linear so all k values can be directly compare

E.g. $k_1 = 2 \times 10^{-3} \text{ s}^{-1}$
 $k_2 = 0.5 \times 10^{-3} \text{ s}^{-1}$ Rxn 1 proceeds 4x faster than Rxn 2

$$T_{1/2}^1 = \frac{0.69}{2 \times 10^{-3} \text{ s}^{-1}} = 347 \text{ s} \approx 6 \text{ min}$$

$$T_{1/2}^2 = \frac{0.69}{0.5 \times 10^{-3}} = 1390 \text{ s} \approx 23 \text{ min}$$

BIG PICTURE NOTION: synthetic chemicals in Env.

ALL organic compounds can break down (decay)
It's just a question of "k", how fast
(or $T_{1/2}$)

E.g. Glyphosate	} $T_{1/2} \approx \dots \sim 10 \text{ d}$	
Atrazine		$T_{1/2} \approx 125 \text{ d}$
PCBs		$T_{1/2} \sim \text{decades (20-30y)}$

We will return to this in coming lectures on specific processes of decay

REACTION PATHWAYS:

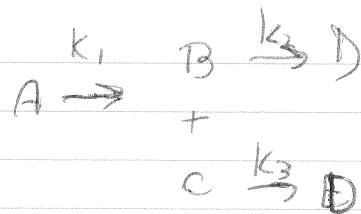
Not just $A \rightarrow B$. Often $A \rightarrow B \rightarrow C \rightarrow D$ ①

LOOK AT EACH something OR $A \rightarrow \begin{matrix} B \rightarrow D \\ + \\ C \rightarrow D \end{matrix}$ ②



k s^{-1}	7×10^{-3}	7×10^{-4}	7×10^{-6}
$T_{1/2}$ s	100 s	1000 s	100,000 s

What is the overall rate of formation of D? $\frac{d[D]}{dt}$



Again let $k_1 = 7 \times 10^{-3}$
 $k_2 = 7 \times 10^{-4}$
 $k_3 = 7 \times 10^{-6}$

What's overall rate of conversion to D $\left(\frac{d[D]}{dt}\right)$

A: $k \approx k_2 = 7 \times 10^{-4}$ $\tau_{1/2} = 1000 \text{ s}$

(Really 7.07×10^{-4} but big deal)

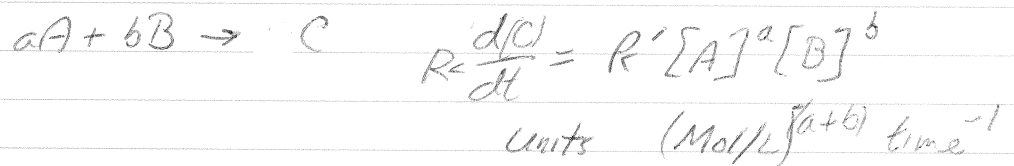
PARALLEL RXN: (1) Additive if similar in magnitude
 (2) FASTEST rate is governing if rates are orders of magnitude apart.

NON-LINEAR RATE EXPRESSIONS (NOT 1st ORDER)



$R = 2^{\text{nd}}$ order w/ units $\frac{(\text{mol/L})^2 \text{ M}}{\text{time}}$

More generally w/ stoichiometry



Note also ~~o~~ stoich. relationship AMONG rates

$$R = -\frac{d[C]}{dt} = \frac{1}{a} \frac{d[A]}{dt} + \frac{1}{b} \frac{d[B]}{dt}$$

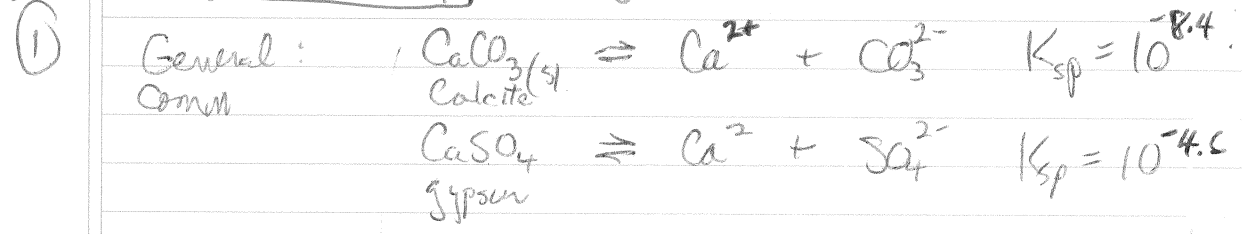
OR more generally $aA + bB \rightarrow cC$

$$R = -\frac{1}{c} \frac{d[C]}{dt} = \frac{1}{a} \frac{d[A]}{dt} + \frac{1}{b} \frac{d[B]}{dt}$$

OR $\frac{1}{a} \frac{d[A]}{dt} + \frac{1}{b} \frac{d[B]}{dt} - \frac{1}{c} \frac{d[C]}{dt} = 0$

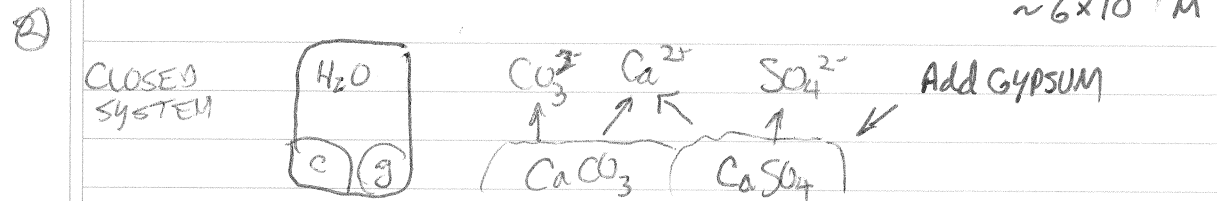
OR $\sum_{i=1}^n \frac{1}{a_i} \frac{d[A_i]}{dt} = 0$

RECAP of SOLUBILITY AND Ex of Metal Sulfide



$[Ca^{2+}][CO_3^{2-}] = 10^{-8.4}$
 Sol^y product $[Ca^{2+}] = [CO_3^{2-}] = \sqrt{10^{-8.4}} = 10^{-4.2}$

COMMON ION EFFECT



CONGRUENT DISSOLUTION

$(Ca^{2+})^2 = 10^{-4.6}$
 $[Ca^{2+}] = 10^{-2.3}$

$[Ca^{2+}][CO_3^{2-}] = 10^{-8.4}$

$[CO_3^{2-}] = \frac{10^{-8.4}}{10^{-2.3}} = 10^{-6.1}$ $\sim 100\times$ (lower than the $[Ca^{2+}] = [CO_3] = 10^{-4.2}$)
 $\sim 8 \times 10^{-7} M$

③ OPEN the jar, allow CO₂ to enter, add unlimited supply of CO₃²⁻

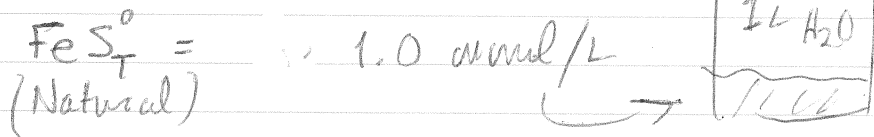
Now [CO₃²⁻] rises causing CaCO₃(s) to ppt out
 But then the lower [Ca²⁺] causes gypsum to dissolve
 But the "new" Ca²⁺ reacts w/ CO₃²⁻ to ppt as calcite

Eventually all of the gypsum ^{may} dissolves & only remaining solids is calcite

Can see generally why $\Delta G_{calc}^{sp} = 2.3RT \log K_{sp}^{calc} = -44 kJ/m$
 $\Delta G_{gyp}^{sp} = 2.3RT \log K_{sp}^{gyp} = 26 kJ/m$

The lowest energy state achievable is the calcite system. So, if possible, gypsum will disappear in favor of less soluble calcite.

AN IMPORTANT POLLUTANT APPLICATION OF COMMON ION EFFECT Revisit Sulfide system



Add 0.1 mmol Cd^{2+} (like $CdCl_2$)

Initial $[Cd^{2+}] = 10^{-4.0} \text{ M} = 1 \times 10^{-4} \text{ M}$

$[Cd^{2+}][S^{2-}] = 10^{-27.0}$

$[Fe][S^{2-}] = 10^{-18.1}$

$[S^{2-}] = \sqrt{10^{-14.1}} = 10^{-9.0}$

← More soluble, so it will dissolve. $CdS_{(s)}$ ppt's at the expense of $FeS_{(s)}$

At end $[Cd^{2+}] = \frac{10^{-27.0}}{10^{-9.0}} \approx "0" (= 10^{-18} \mu\text{M})$ 1 attomol/L

$FeS_T \approx 1.0 \text{ mM} - 0.1 \text{ mM} = 0.9 \text{ mM}$
 $FeS_T^0 - Cd_T$

We will revisit soon. EPA protocol, treats metal sulfides as just a simple, arithmetic mass balance based on the supply of natural FeS

One other point ACTIVITY

Readily $\{Cd^{2+}\}\{S^{2-}\} = K_{sp}$ When $\{Cd^{2+}\} = \gamma[Cd^{2+}]$

$\gamma^2[Cd^{2+}][S^{2-}] = K_{sp}$ For ions $0 < \gamma < 1$
 $= \frac{K_{sp}}{\gamma^2} < < 1$ ∴ γ 's make $CdS_{(s)}$ MORE soluble

High I → Smaller γ → Greater sol

For NONIONS $\gamma > 1$ (E.g. O_2 or CO_2) High I → Bigger γ → LESS SOLY

E.g. DO_{SAT}
 20°
 $9.2 \text{ mg/L FRESH WATER}$
 \downarrow
 $7.5 \text{ mg/L SEAWATER}$