

Chemical Kinetics

Kinetics vs Thermodynamics

- Thermodynamic tells us which direction rxn will go (ex: carbon stable as graphite)
 - State fcn = final and initial state (independent of path)
- Kinetics tells us how quickly rxn will go (ex: diamond \rightarrow graphite is very slow)
 - Path fcn = depends on path.

At macroscopic level: define rate of rxn, order of rxn and rate laws (3).

At microscopic (molecular) level: predict plausible rxn mechanism from experimental rate laws
 \rightarrow process of going through steps from R \rightarrow P

Reaction Rate = increase in molar concentration of product of a reaction per unit of time or decrease in molar concentration of reactant per unit time. $\left[\frac{\text{mol}}{\text{L}\cdot\text{s}} \text{ or } \frac{\text{M}}{\text{s}} \right]$

rate is a positive quantity.

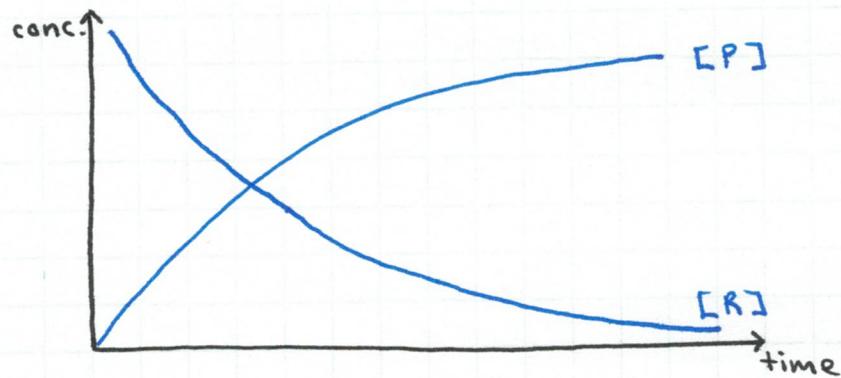
reactant \rightarrow product

$$\text{rate} = \frac{\Delta [\text{product}]}{\Delta t} = \frac{[\text{P}]_{t_2} - [\text{P}]_{t_1}}{t_2 - t_1}$$

$$\text{rate} = - \frac{\Delta [\text{reactant}]}{\Delta t}$$



The rate of this rxn can be found by measuring the conc. of O_2 or NO_2 at various times and see how they increase with time. Or, the rate can be found by measuring the conc. of N_2O_5 and see how it decreases with time.



$$\text{Rate of formation of } \text{O}_2 = \frac{\Delta [\text{O}_2]}{\Delta t}$$

$$\text{Rate of formation of } \text{NO}_2 = \frac{\Delta [\text{NO}_2]}{\Delta t}$$

$$\text{Rate of decomposition of } \text{N}_2\text{O}_5 = - \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t}$$

We can relate these equations by taking into account the stoichiometric coefficients:

$$\frac{\Delta [\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta [\text{NO}_2]}{\Delta t} = - \frac{1}{2} \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t}$$

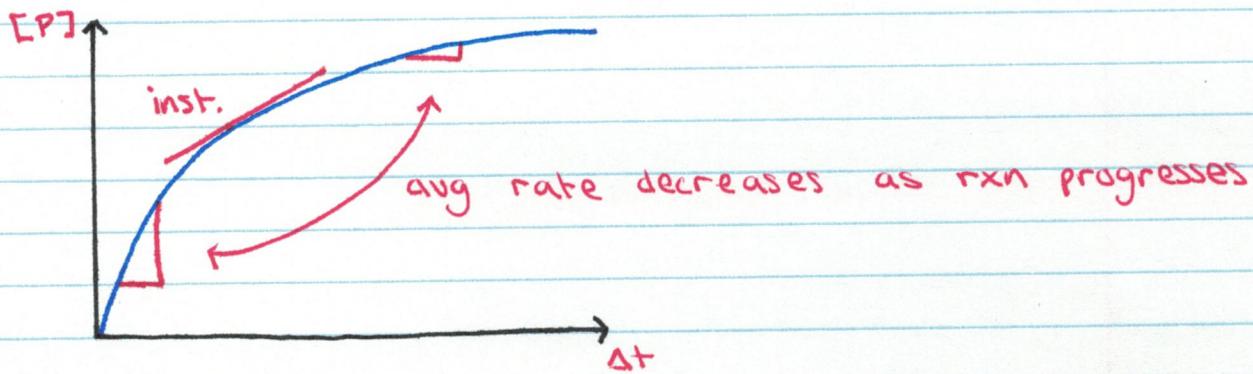
Calculating Average Rate

- * The average rate of rxn decreases as the rxn proceeds
 - less reactants available
 - less collisions (reactions)
 - slower rate.

rate = slope of secant

Calculating Instantaneous Rate

rate = slope of tangent



Conditions that affect the rate of rxn:

1. concentration of reactants

- rate increases when concentration of reactants increases (more collisions).
- sometimes rate is unaffected by conc. of a particular reactant as long as it is present.

2. Temperature at which rxn occurs

- rxn speed up when temp. increase

3. Catalyst

- substance that increases rate
→ lowers activation energy.

Rate Laws:

- Differential Rate Law = the "Rate Law"
 - how rxn rate changes with conc.
- Integral Rate Law
 - how conc. of reactants varies with time

The Rate Law

- Rate of rxn depends on conc. of one or more reactants.
- Reaction order: w.r.t a specific reactant, is the exponent of that species in the rate law.
- Overall order: the sum of the orders of all reactants in rate law.



Describe only [reactants]

$$\text{rate} = K \cdot [A]^m \cdot [B]^n$$

$$\frac{\text{overall}}{\text{order}} = m+n$$

- K: rate constant
- m and n: order of the reactants (can be integer, zero, or fraction)



$$\text{rate} = K[A]^n$$

zero order ($n=0$): rate independent of conc.
(always equal to K)

$$\text{rate} = K[A]^0 = K \quad \therefore K \text{ in } \frac{\text{M}}{\text{s}}$$

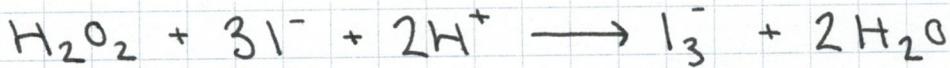
1st order ($n=1$): rate directly proportional to [A]

$$\text{rate} = K[A] \quad \therefore K \text{ in } \frac{1}{\text{s}}$$

2nd order ($n=2$): rate proportional to $[A]^2$

$$\text{rate} = K[A]^2 \quad \therefore K \text{ in } \frac{1}{\text{M.s}}$$

ex: Determine order of rxn w.r.t every reactant and determine overall order for:

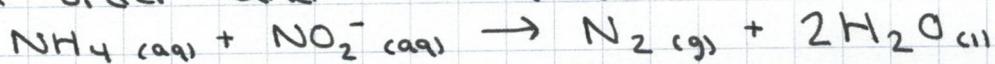


$$\text{rate} = K[\text{H}_2\text{O}_2] \cdot [\text{I}^-]$$

rxn order: $\text{H}_2\text{O}_2 \Rightarrow 1$, $\text{I}^- \Rightarrow 1$, $\text{H}^+ \Rightarrow 0$ * H^+ also a species

$$\text{overall order} = 1 + 1 + 0 = 2$$

ex: Determine the orders for both reactants, the overall order and K value.



experiment	$[\text{NH}_4]_i$	$[\text{NO}_2^-]_i$	initial rate (M/s)
1	0.1	0.005	1.35×10^{-7}
2	0.1	0.010	2.7×10^{-7}
3	0.2	0.010	5.4×10^{-7}

$$\text{rate} = K[\text{NH}_4]^m \cdot [\text{NO}_2^-]^n$$

m

$$\frac{\text{exp 3}}{\text{exp 2}} = \frac{5.4 \times 10^{-7}}{2.7 \times 10^{-7}} = \frac{K(0.2)^m (0.01)^n}{K(0.1)^m (0.01)^n}$$

$$2 = \left(\frac{2}{1}\right)^m \Rightarrow m = 1$$

n

$$\frac{\text{exp 2}}{\text{exp 1}} = \frac{2.7 \times 10^{-7}}{1.35 \times 10^{-7}} = \frac{K(0.1)^m \cdot (0.01)^n}{K(0.1)^m \cdot (0.005)^n}$$

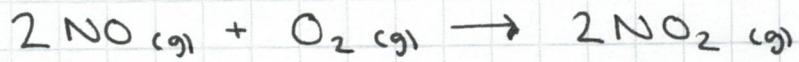
$$2 = (2)^n \Rightarrow n = 1$$

Find K (sub exp 1):

$$1.35 \times 10^{-7} \frac{\text{M}}{\text{s}} = K (0.1 \text{ M})^1 (0.005 \text{ M})^1$$

$$K = 2.7 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$$

ex: Determine rate law



	$[\text{NO}]_i$	$[\text{O}_2]_i$	initial rate
1	0.02	0.01	0.028
2	0.02	0.02	0.057
3	0.04	0.02	0.228

$$\therefore \text{rate} = K [\text{O}_2]^1 \cdot [\text{NO}]^2$$

Integrated Rate Law

- How reactant concentration changes over time (Note: depends on order)

Zero order

$A \rightarrow \text{products}$

$$\text{rate} = -\frac{\Delta [A]}{\Delta t} = K[A]^0 = K$$

$$[A]_0 \int_{[A]_0}^{[A]_t} d[A] = -K \int_0^t dt$$

$$[A]_t - [A]_0 = -Kt$$

$$[A]_t = -Kt + [A]_0$$

$$\text{slope} = -K : y = mx + b$$

First order

$A \rightarrow \text{products}$

$$\text{rate} = -\frac{\Delta [A]}{\Delta t} = K[A]$$

$$[A]_0 \int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = -K \int_0^t dt$$

$$\ln [A]_t - \ln [A]_0 = -Kt$$

$$\ln [A]_t = -Kt + \ln [A]_0$$

$$y = mx + b$$

Second order

$A \rightarrow \text{products}$

$$\text{rate} = -\frac{\Delta [A]}{\Delta t} = K[A]^2$$

$$[A]_0 \int_{[A]_0}^{[A]_t} [A]^{-2} d[A] = -K \int_0^t dt$$

$$(-[A]_t^{-1}) - (-[A]_0^{-1}) = -Kt$$

$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

$$\text{slope} = K : y = mx + b$$

How to determine the order experimentally

- { · zero order : $[A]$ vs t is linear
- 1st order : $\ln[A]$ vs t is linear
- 2nd order : $\frac{1}{[A]}$ vs t is linear

plot each with experimental data
→ verify which yields a straight line.

Integrated Rate Laws for rxns with more than one reactant



$$\text{rate} = K [A]^m \cdot [B]^n \cdot [C]^p$$

set experimental conditions:

$[B]_0 \gg [A]_0$ } follow $[A]$: only $[A]$ will
 $[C]_0 \gg [A]_0$ } change significantly.
 $[B]$ and $[C]$ will remain relatively constant.

$$\therefore \boxed{\text{rate} = K' [A]^m} \quad \text{follow only one reactant}$$

$$\text{with } K' = K [B]_0 \cdot [C]_0$$

Half-Life ($t_{1/2}$)

- time required for $\frac{1}{2}$ of reactants to be consumed. $[A]_{t_{1/2}} = \frac{[A]_0}{2}$

* the longer the half life,
the slower the rxn.

$$t = t_{1/2} \quad \text{and} \quad [A]_t = \frac{1}{2} [A]_0$$

Zero order $[A]_t = \cancel{\text{initial value}} - Kt + [A]_0$
 $\frac{1}{2} [A]_0 = - Kt + [A]_0$

$$t_{1/2} = \frac{[A]_0}{2K}$$

- half life gets shorter as rxn progresses
- each $t_{1/2}$ is half of previous one

First order $\ln [A]_t = - Kt + \ln [A]_0$
 $\ln \left(\frac{[A]_0}{2[A]_0} \right) = - Kt$

$$t = \frac{-\ln(1/2)}{K} \Rightarrow t_{1/2} = \frac{\ln(2)}{K}$$

- half life doesn't depend on conc.
- each $t_{1/2}$ is equal

Second order $\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$
 $\frac{2}{[A]_0} - \frac{1}{[A]_0} = Kt$

$$t_{1/2} = \frac{1}{K[A]_0}$$

- half life gets longer as rxn progresses
- each $t_{1/2}$ is double the previous one

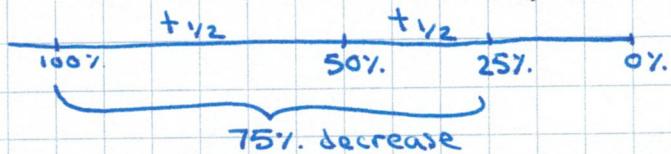
ex: SO_2Cl_2 vapor decomposes in a first-order rxn. At 320°C , the rate constant is $2.2 \times 10^{-5} \frac{1}{\text{s}}$

$$\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$$

(a) what is the half-life of SO_2Cl_2 at 320°C ?

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{\ln(2)}{2.2 \times 10^{-5}} = 3.15 \times 10^4 \text{ s}$$

(b) How long would it take for 75% of SO_2Cl_2 to decompose? (25% left)



$$t = 2(t_{1/2}) = 2(3.15 \times 10^4) = 6.3 \times 10^4 \text{ s}$$

ex: An isotope ① has rate constant $k = 0.0016 \text{ y}^{-1}$ for radioactive decay. (note: radioactive decay = First order)
An isotope ② has rate constant $k = 0.011 \text{ d}^{-1}$ for decay.

(a) What are the half-lives for each isotope?

$$\textcircled{1}: t_{1/2} = \frac{\ln(2)}{k} = \frac{\ln(2)}{0.0016 \text{ y}^{-1}} = 430 \text{ years}$$

$$\textcircled{2}: t_{1/2} = \frac{\ln(2)}{k} = \frac{\ln(2)}{0.011 \text{ d}^{-1}} = 63 \text{ days} \Rightarrow \text{faster}$$

(b) Which isotope decays faster? $\textcircled{2}$

(c) If you are given a dose of ② containing 1.6×10^{15} atoms. How many atoms remain after 2 days?

$$\begin{aligned} \ln[A]_t &= -kt + \ln[A]_0 \\ &= -(0.011 \cancel{\text{d}^{-1}})(2 \cancel{\text{d}}) + \ln(1.6 \times 10^{15}) \end{aligned}$$

$$\ln[A]_t = 34.99$$

$$[A]_t = e^{34.99} = 1.57 \times 10^{15} \text{ atoms}$$

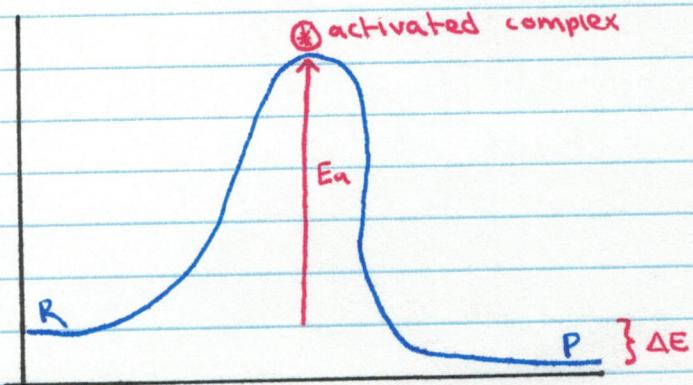
Collision Model

- molecules collide to react
 - molecular orientation
 - activation energy, E_a
 - temperature

A) For reactants to form products \Rightarrow relative orientation of reactants must allow formation of any new bond necessary to form product.

B) Activation energy

- collisions must involve enough energy to produce reaction, must equal or exceed E_a (activation energy)
- to get from reactant to product, molecule must go through a high energy state called activated complex (transition state).
- Activation energy is the energy that must be overcome to produce rxn.



Effect of temp. on Reaction Rate

→ K varies with temperature

* increase in temp \Rightarrow increase in K
 \therefore faster rate

Arrhenius Equation:

$$\ln(K) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

$$y = mx + b$$

A : constant representing effective collision frequency (same unit as K)

E_a : (J/mol)

R : (8.314 $\frac{\text{J}}{\text{K}\cdot\text{mol}}$)

T : (Kelvin)

Determining the activation energy (E_a)

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Recall: $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

Derive: $\ln(K_1) = -\frac{E_a}{R} \left(\frac{1}{T_1} \right) + \ln(A)$

$\ln(K_2) = -\frac{E_a}{R} \left(\frac{1}{T_2} \right) + \ln(A)$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{E_a}{R} \left(\frac{1}{T_1} \right) + \frac{E_a}{R} \left(\frac{1}{T_2} \right)$$

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

ex: A first order rxn has rate constant $4.6 \times 10^{-2} \text{ s}^{-1}$ at 0°C and $8.1 \times 10^{-2} \text{ s}^{-1}$ at 20°C . What is the value of the activation energy?

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

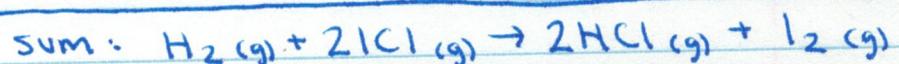
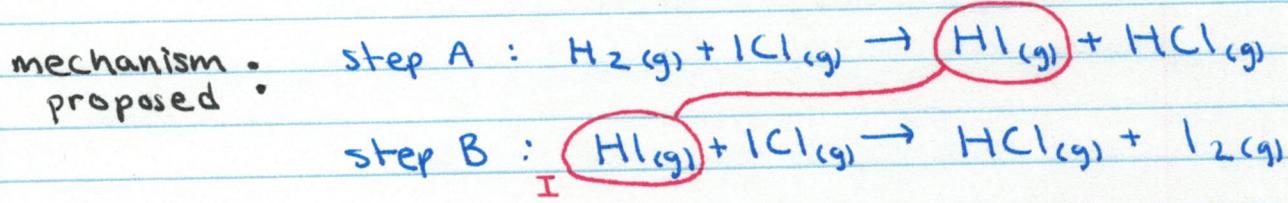
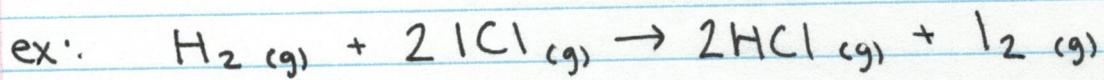
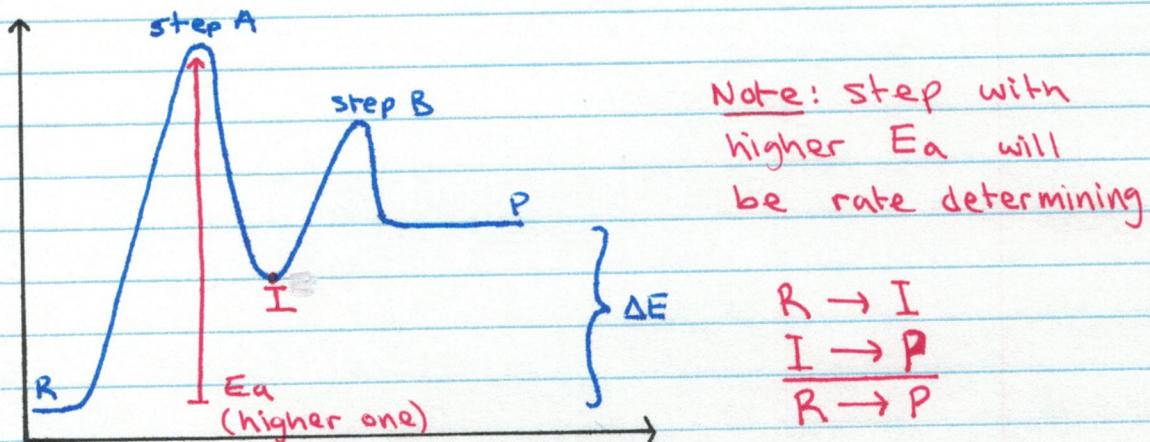
$$\ln\left(\frac{8.1 \times 10^{-2}}{4.6 \times 10^{-2}}\right) = \frac{E_a}{8.314} \left(\frac{1}{273\text{K}} - \frac{1}{293\text{K}}\right)$$

$$E_a = 1.88 \times 10^4 \frac{\text{J}}{\text{mol}} = 18.8 \frac{\text{kJ}}{\text{mol}}$$

Reaction Mechanism

rxn mechanism = sequence of bond-making and bond-breaking steps that occur during the conversion of R to P.

- each step in a rxn mechanism is an elementary step
- an intermediate = a species produced during a rxn that does not appear in the net equation bc it reacts in the subsequent step in the mechanism



* For a proposed mechanism to be valid, the sum must equal the initial formula.

Rate Laws from Elementary Steps

* use coefficients for order
(JUST for elementary steps)

- elementary steps characterized by their molecularity (number of reactant molecules)
 - Unimolecular - rxn involving 1 molecule
 - Bimolecular - collision of 2 molecules
 - Termolecular - collision of 3 molecules

Rate Determining Step

- For valid rxn mechanism:
 - 1) sum of elementary steps = overall rxn
 - 2) mechanism must agree with experimentally determined rate law
- * One step will be much slower \Rightarrow rate determining
- the rate determining step in a rxn mechanism limits the overall rate
 \therefore determines the overall rate law



The rate law was determined experimentally:

$$\text{rate} = K \cdot [\text{O}_3]^2$$

⇒ order of NO_2 zero
∴ NO_2 shouldn't be present in proposed mechanism slow elementary step.

Proposed mechanism:



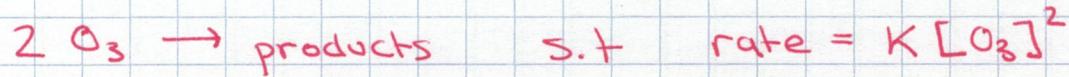
∴ sum of elementary steps works

rate law of rate determining step:

$$\text{rate} = K [\text{O}_3] \cdot [\text{NO}_2] * \text{does not agree with experimentally determined rate law}$$

∴ NOT valid

Note: to be valid, the slow step would have to be:



Electrochemistry

Redox Reactions

→ transfer of electrons from reducing agent to the oxidizing agent

Lose e^- : "oxidation"

OIL ($\text{oxy} \Rightarrow \text{loss}$)

Gain e^- : "reduction"

RIG ($\text{red.} \Rightarrow \text{gain}$)

species oxidized = loses e^- = reducing agent
species reduced = gains e^- = oxidizing agent.

Electrochemical Cells

→ redox rxn can generate electrical current

→ electrochemical cell = device that

generates electricity through redox rxns

→ electrochemical cells that use chemical rxns to produce an electric current are also called galvanic cell / voltaic cell

Half-Cells

- in electrochemical cells, a strip of metal M is called an electrode
- an electrode in a sol'n containing ions of the same metal is called a half-cell. (M^{n+})



- ion M^{n+} may collide with electrode, gain $n e^-$ from it and convert to $M_{(s)}$. ion is reduced.
- metal M on surface may lose $n e^-$ to the electrode and enter sol'n as M^{n+} . metal is oxidized.

Galvanic (Voltaic) Cells

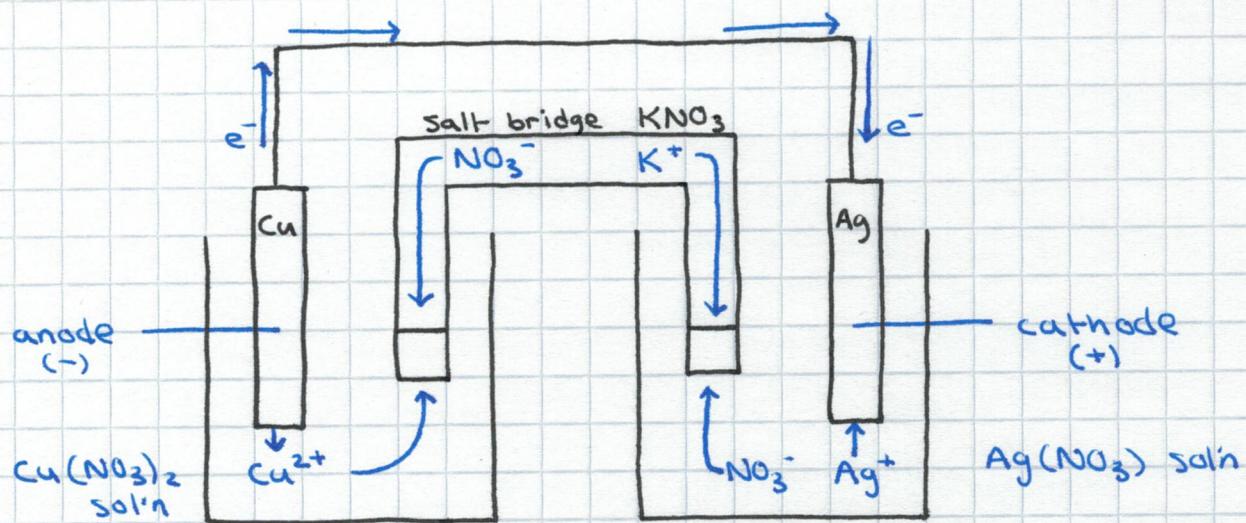
- 2 half cells connected with a salt bridge that allows cations and anions to move between the two half cells (the electrolyte chosen for salt bridge should contain ions that will not react with chemical reactants in both half-cells)

(-) → Anode : electrode where oxidation occurs
 (+) → Cathode : electrode where reduction occurs

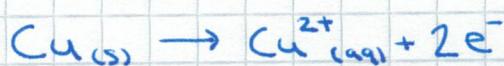
AO
CR

Anode ⇒ oxidation that occurs produces e^- which gives the anode a negative sign.

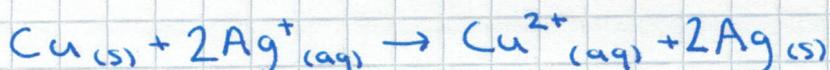
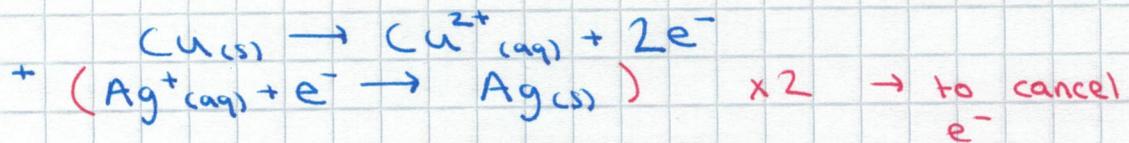
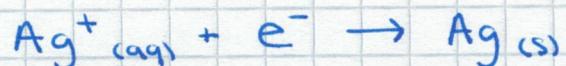
Electrons flow in external circuit from anode (-) to cathode (+).



Anode (' $\frac{1}{2}$ oxidation)



Cathode (' $\frac{1}{2}$ reduction)

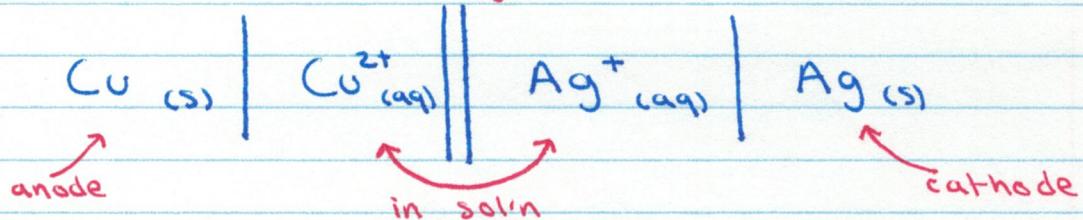


Cell Diagram or Line Notation

- Anode placed at left
 - Cathode placed at right CR
 - || : indicates salt bridge separating substances in different phases are separated by single vertical line (|)
 - species in sol'n are placed on either side of the double vertical line.
 - different species within same sol'n are separated from each other by comma.
 - Electrodes shown at each extremity.

ex'.

half-cell (anode) salt bridge half-cell (cathode) CR



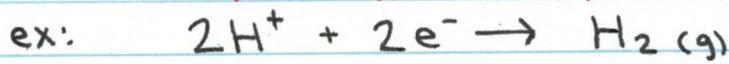
Galvanic Cells with Inert Electrodes

- Not all half rxns involve a metal $M(s)$ as a reactant or product.



both are ions, not metals

cannot use Cu(s) as electrode (interfere)



no metals \Rightarrow H₂ is a gas

- If no reactant or product can serve as electrode, an inert electrode (chemically unreactive - will not interfere) must be used.

* Pt (s) or Au (s)

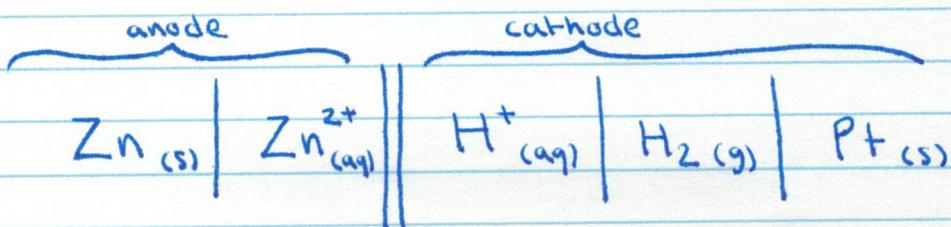
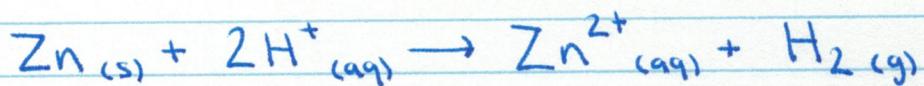
ex: Anode (oxidizing):



Cathode (reduction):



no metals
in rxn



Cell Potentials

- Force that moves e^- from anode to cathode comes from difference in potential energy of e^- at 2 electrodes.
- * Potential energy of e^- is higher at anode.

Cell potential (E_{cell}) = electromotive
= potential difference between 2 electrodes
that pushes e^- through external circuit.

E_{cell}° in units of volt (V)

$\rightarrow 1 \text{ V} = 1 \text{ joule per coulomb of charge transferred}$

- Measure E_{cell}° with voltmeter
- Work is required to move electrons in a wire or to move ions through a sol'n to an electrode.

Standard Cell Potentials (E_{cell}°)

\rightarrow cell potential measured at standard cond.:

- reactants / products present in their standard states
- Solutes in aqueous sol'n have concentration of 1.0 M
- gaseous reactants / products have pressure of 1.0 atm
- E_{cell}° measured at 298 K (usually)

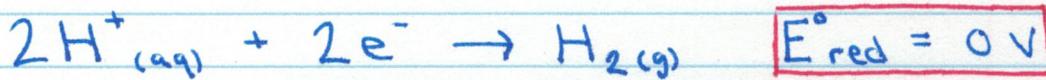
Calculating Standard Cell Potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{oxi}}$$

- When E°_{cell} is pos., rxn is spontaneous in forward direction
- A galvanic cell will always run spontaneously in the direction that produces a positive cell potential

Tabulated Standard Reduction Potential

- Absolute potentials cannot be measured for any half-reactions
→ Scientists have defined the hydrogen electrode as having standard reduction potential of exactly 0 V.
(used as reference point)



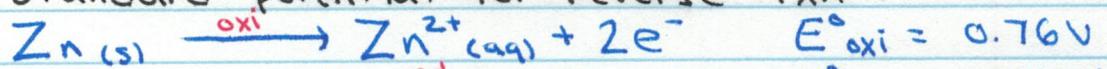
- When hydrogen standard electrode is coupled with any other half-rxn in galvanic cell, the cell potential is measured and electrode potential of other half-rxn can be determined.

ex: E°_{cell} measured with voltmeter : 0.76V

$$E^\circ_{\text{red}} = 0\text{ V}$$

$$\therefore E^\circ_{\text{cell}} = 0.76\text{ V} = 0\text{ V} + E^\circ_{\text{oxi}} \Rightarrow E^\circ_{\text{oxi}} = 0.76\text{ V}$$

Standard potential for reverse rxn :



Relative Strength of Oxidizing Agents and Reducing Agents.

Red $\frac{1}{2}$ rxn	E°_{red} (V)
$\boxed{\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)}$	+ 1.36
$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$	0
$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$	- 0.76

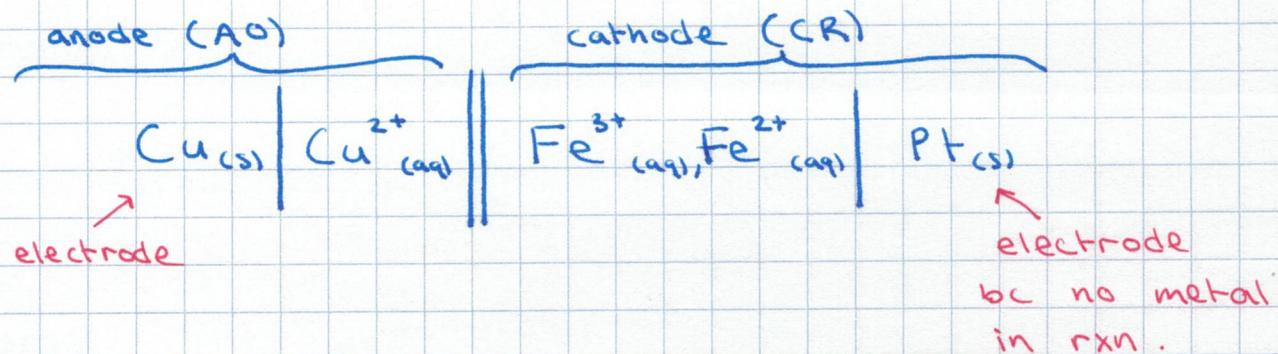
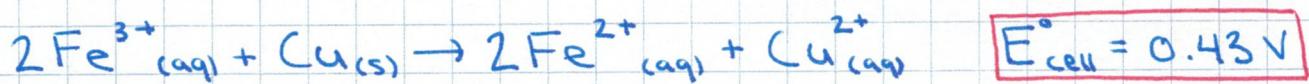
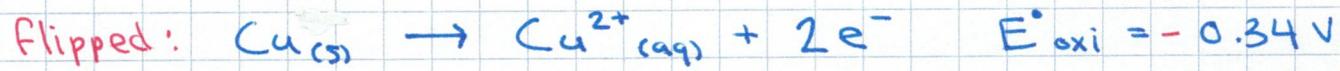
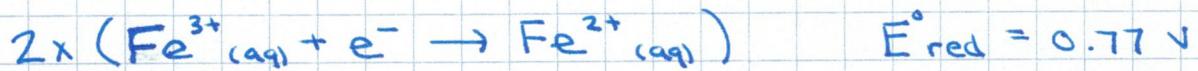
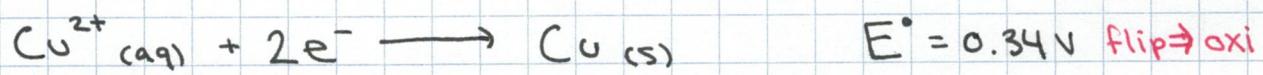
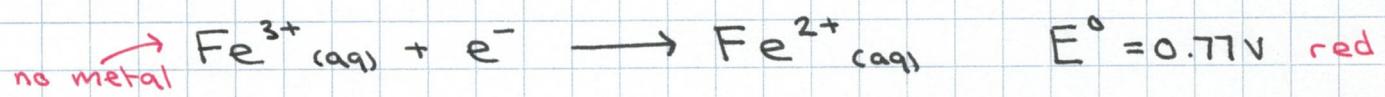
↑ species reduced = oxidizing agent.

- Cl_2 is a stronger oxidizing agent bc it has higher red. potential
- Zn^{2+} is a stronger reducing agent bc (if reverse) it has higher oxi. potential

Calculating Standard Cell Potentials

- When combining 2 half-rxns to obtain balanced redox rxn: one of the reduction half-rxns must be reversed to obtain oxidation half-rxn.
 E°_{cell} needs to be pos. ∵ half-rxn with higher red. potential stays forward, other rxn runs reversed (oxi) → flip sign.
- Half-rxns are multiplied by integer to cancel e^- .
- Do not multiply E° by integer (value remains regardless of amount of substance) = intensive property.

ex: consider half-rexns (both are reductions)



Cell Potential, Free Energy, Equilibrium Constant

For a spontaneous rxn that proceeds in forward direction at standard conditions:

- $E^\circ_{\text{cell}} > 0$ (pos)
- $\Delta G^\circ < 0$ (neg.)
- $K \gg 1$ (reach eq very far right)

Relationship between ΔG° and E°_{cell}

$$\boxed{\Delta G^\circ = -nFE^\circ_{\text{cell}}}$$

n: number of e^- transferred in redox eqn

F: faraday's constant = 96485 C/mol e^-

Derive:

$$\Delta G^\circ = W_{\text{useful}}$$

$$E^\circ_{\text{cell}} = \frac{W}{q}$$

$$q = nF$$

$$\therefore E^\circ_{\text{cell}} = -\frac{\Delta G^\circ}{nF}$$

$$-nFE^\circ_{\text{cell}} = \Delta G^\circ$$

Relationship between E°_{cell} and eq constant

$$\boxed{E^\circ_{\text{cell}} = \frac{RT}{nF} \ln(K)}$$

Derive:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

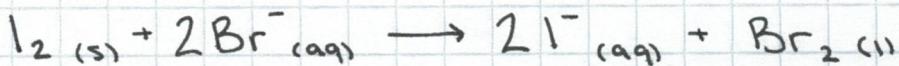
$$\Delta G^\circ = -RT \ln(K)$$

$$\therefore -nFE^\circ_{\text{cell}} = -RT \ln K$$

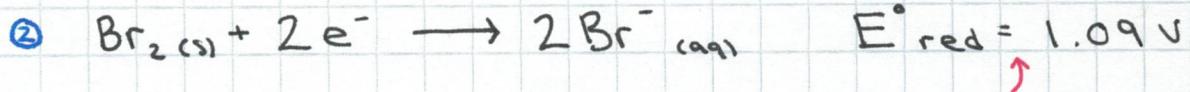
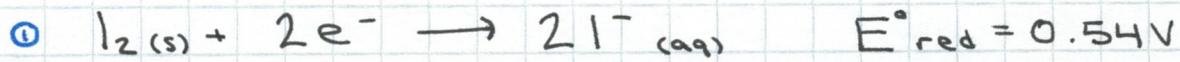
$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln(K)$$

$$\text{units: } V = \frac{J}{C}$$

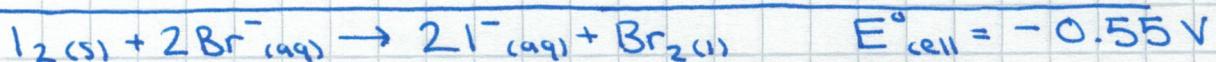
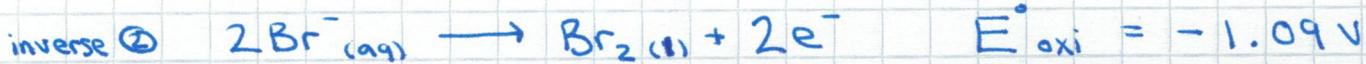
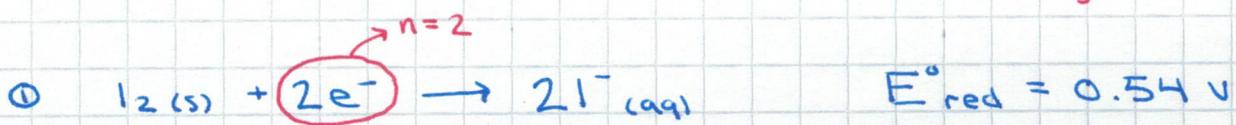
ex: Find ΔG° for the following rxn at 298 K :



use standard electrode potentials :



even though this value is greater, here we are not building a cell. We are looking for rxn above.



$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{cell} \\ &= -(2).F.(-0.55) \\ &= 1.1 \times 10^5 J\end{aligned}$$

is the reaction spontaneous?

- E°_{cell} neg. } \therefore rxn not spontaneous under
- ΔG° pos. } standard conditions

Find K :

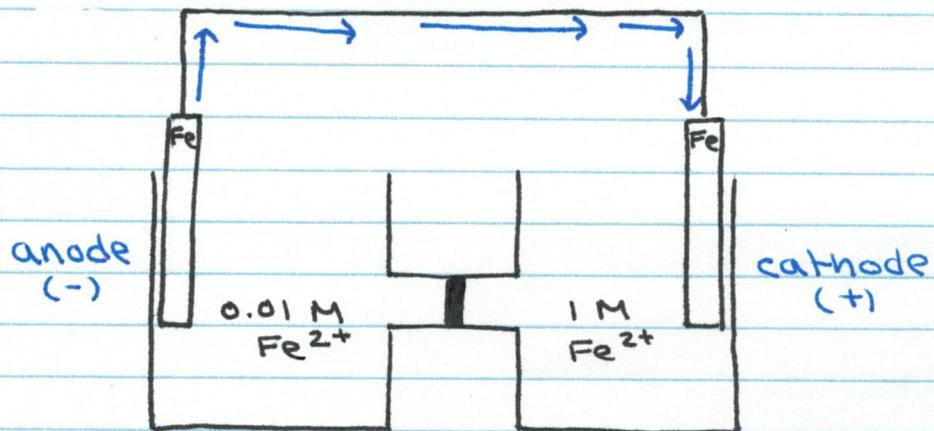
$$E^\circ_{cell} = \frac{RT}{nF} \ln(K) \quad \text{or} \quad \Delta G^\circ = -RT \ln K$$

$$K = e^{\frac{nFE^\circ_{cell}}{RT}}$$

$$K = 2.49 \times 10^{-19} \quad \therefore \text{eq reached early}$$

Concentration Cells

- same components in each half-cell but different concentrations (non-standard)
- cell potential generated bc difference in ion concentration.



Left side: increase $[\text{Fe}^{2+}]$



oxidation
(anode)

Right side: decrease $[\text{Fe}^{2+}]$



reduction
(cathode)

$$E^\circ_{\text{cell}} = 0$$

Cell Potential at Non-Standard Cond.

- E_{cell}° (standard) for all solutes at 1 M
- If concentrations are not 1 M:
 - predict using Le Châtelier
 - derive relationship between E_{cell}° and E_{cell} .

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln(Q)$$

Derive: $\Delta G_f = \Delta G^{\circ} + RT \ln(Q)$

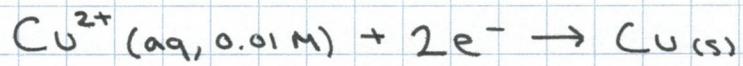
$$\frac{-nFE_{\text{cell}}}{-nF} = \frac{-nFE_{\text{cell}}^{\circ}}{-nF} + \frac{RT \ln(Q)}{-nF}$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln(Q)$$

Note: $Q = \frac{[\text{products}]^m}{[\text{reactants}]^n}$

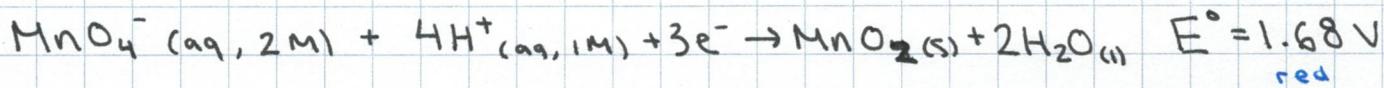
- $Q < 1$: greater conc. of reactants drives rxn in forward direction
 $\Rightarrow E_{\text{cell}} > E_{\text{cell}}^{\circ}$
 - $Q > 1$: greater conc. of products drives rxn in reverse direction
 $\Rightarrow E_{\text{cell}} < E_{\text{cell}}^{\circ}$
- When redox rxn reaches eq: $Q = K$, redox rxn has no tendency to occur: $E_{\text{cell}} = 0$, since the cell has no more ability to do work ($\Delta G = 0$) \Rightarrow battery doesn't work anymore.

ex: An electrochemical cell is based on the following half-reactions:



$$E^\circ = 0.34\text{ V}$$

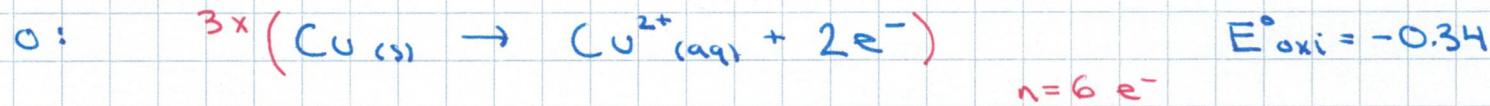
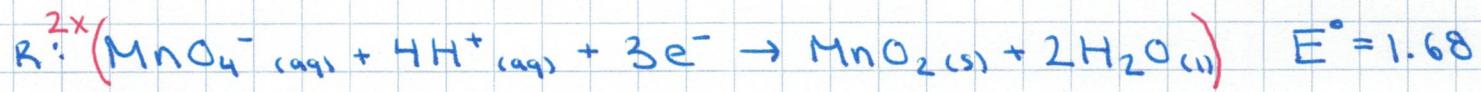
flip
oxi



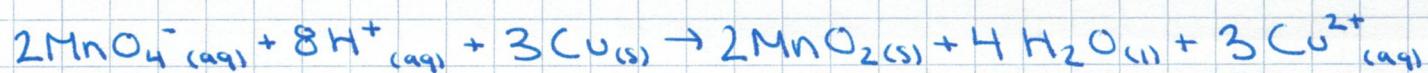
$$E^\circ = 1.68\text{ V}$$

red

Write the overall rxn and calculate the cell potential E_{cell} at 25°C



$$n = 6 \text{ e}^-$$



$$E^\circ_{\text{cell}} = 1.34\text{ V}$$

$$Q = \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^-]^2 \cdot [\text{H}^+]^8} = 2.5 \times 10^{-7} < 1$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln(Q) = 1.41\text{ V}$$

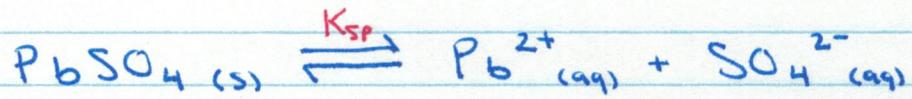
Note: more spontaneous than at standard conditions.

Solubility and Complex Ion

Solubility Product

- When a slightly soluble ionic compound is added to water, it usually goes into sol'n as the ions.
 - As dissolution occurs, the conc. of cations and anions increases, making it more likely to collide and reform the solid phase
- Saturated: (equilibrium is reached) between solid compound and ions in sol'n.
At this point, no more solid dissolves (saturated).
 - Can write equilibrium expression based on solubility product K_{sp}

ex'.



slightly soluble
ionic compound

$$K_{sp} = [Pb^{2+}]_{eq} \cdot [SO_4^{2-}]_{eq} = 1.3 \times 10^{-8}$$

Solubility = quantity (g) that dissolves to form a saturated sol'n

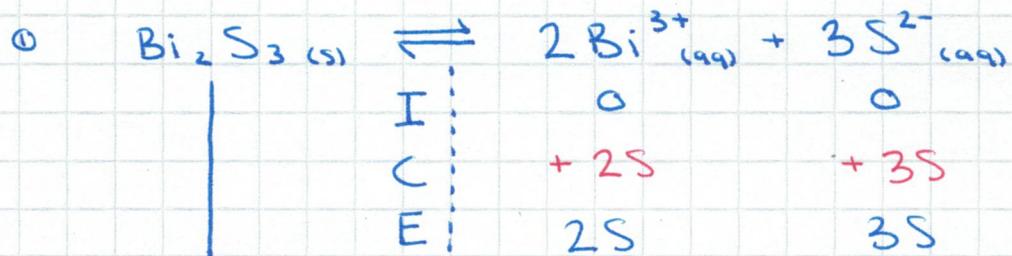
$$\left[\frac{g}{L} \right]_{\text{solute}}^{\text{sol'n}}$$

Molar Solubility = max. number of moles of solute that dissolves in forming a litre of saturated sol'n

$$[\text{mol/L}]$$

Solubility Product = K_{sp} = eq constant for eq between solute (ion) and saturated sol'n

ex: Calculate solubility product for Bi_2S_3 which has molar solubility of 1.0×10^{-15} mol/L at 25°C



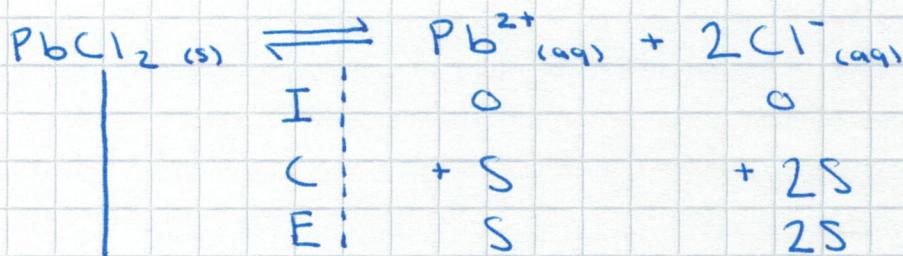
$$S = \text{molar solubility of } \text{Bi}_2\text{S}_3 \\ = 1.0 \times 10^{-15}$$

$$\textcircled{2} \quad K_{sp} = [\text{Bi}^{3+}]^2 \cdot [\text{S}^{2-}]^3 \\ = [2S]^2 \cdot [3S]^3$$

$$\boxed{K_{sp} = 1.08 \times 10^{-73}}$$

ex: Calculate solubility (g/L) and molar solubility of PbCl_2 in water ($K_{sp} = 1.17 \times 10^{-5}$)

S = molar solubility of PbCl_2



$$K_{sp} = [\text{Pb}^{2+}] \cdot [\text{Cl}^{-}]^2 = 1.17 \times 10^{-5}$$

$$(S) \cdot (2S)^2 = 1.17 \times 10^{-5} \\ 4S^3 = 1.17 \times 10^{-5}$$

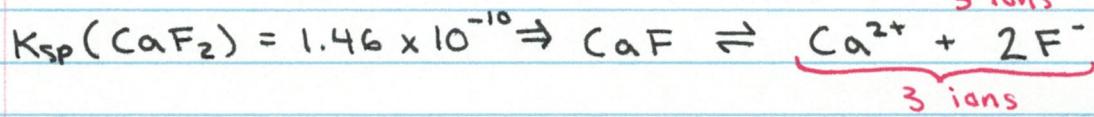
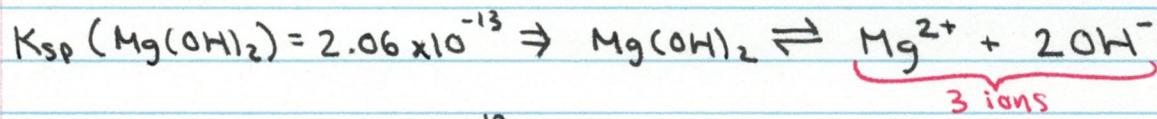
$$\boxed{S = 1.43 \times 10^{-2} \text{ M}}$$

Express solubility in g/L

$$1.43 \times 10^{-2} \frac{\text{mol}}{\text{L}} \cdot \frac{278.1 \text{ g}}{\text{mol PbCl}_2} = \boxed{3.98 \text{ g/L}}$$

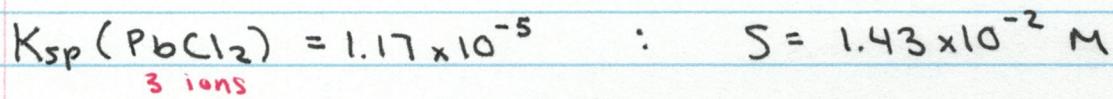
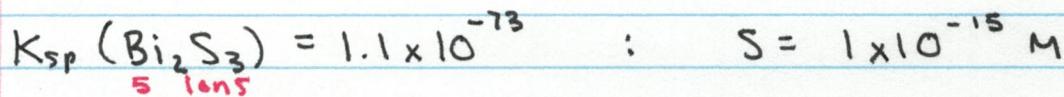
Comparing Solubilities of Salts

- If salts being compared produce the same number of ions, we can compare solubility by comparing K_{sp} values.
→ larger K_{sp} value is more soluble



∴ CaF_2 more soluble bc larger K_{sp}

- If salts compared produce different number of ions, we cannot compare K_{sp} values directly.
⇒ calculate molar solubilities and compare



∴ $PbCl_2$ is more soluble bc larger S

Factors that affect Solubility

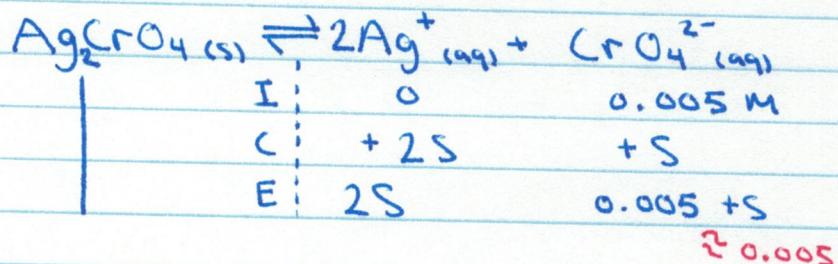
→ Affected by temp ($T \uparrow \therefore$ solubility \uparrow)
as well as by presence of other solutes

- Presence of common ions
- pH of solution
- Presence of complexing agents.

A) Solubility and Common Ion

→ solubility of slightly soluble salt usually decreases in presence of common ion.

ex: calculate molar solubility of Ag_2CrO_4 in presence of 0.005 M K_2CrO_4 ($K_{\text{sp}} = 9.0 \times 10^{-12}$). compare to molar solubility in pure water 1.3×10^{-4} mol/L.



S = molar
solubility
of Ag_2CrO_4

$$K_{\text{sp}} = (2S)^2 (0.005)$$

$$9 \times 10^{-12} = 4S^2 (0.005)$$

$$S = 2.1 \times 10^{-5} \text{ M}$$

validate

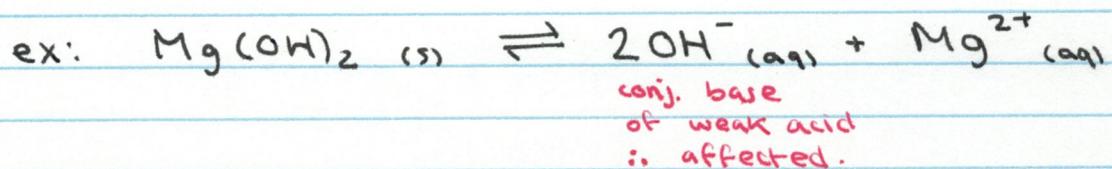
$$\frac{2.1 \times 10^{-5}}{0.005} \times 100 < 5\%$$

$\therefore S_{\text{pure}} > S_{\text{common ion}}$

\therefore Solubility decreases in presence of common ion.

B) Solubility and pH

- Compound that contains a basic anion, the conjugate base of a weak acid
→ solubility increases as sol'n becomes more acidic (ie. add H_3O^+)
- The more basic the anion, the more the solubility is influenced by pH
- * Salts with anions of negligible basicity (conj. base of strong acids) are unaffected by pH change.



when H_3O^+ added:



$[\text{OH}^-]$ in sol'n decreases

∴ rxn shifts right ∴ solubility increases

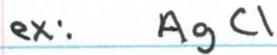
when OH^- added:

common ion ∴ rxn shift left ∴ solubility decrease



↳ F^- : conj. base of weak acid (HF)

∴ Solubility increase when add H_3O^+

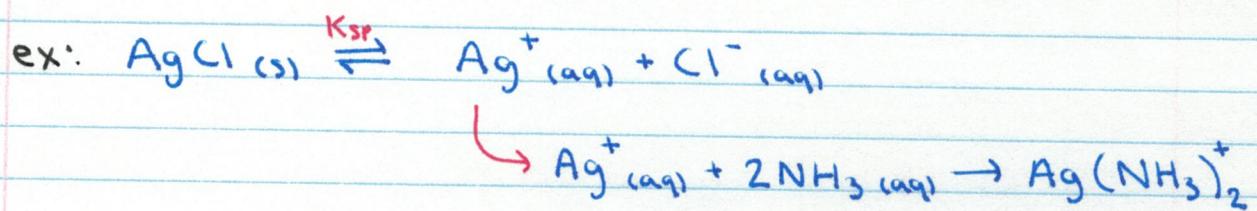
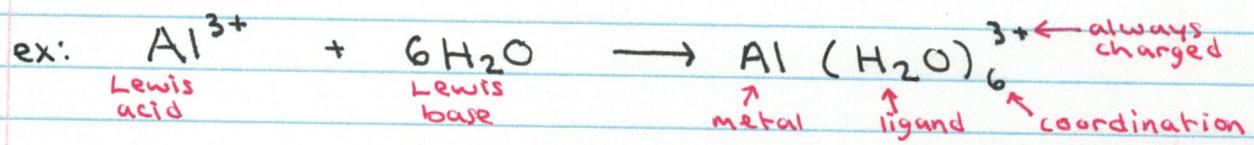


↳ Cl^- : conj. base of strong acid (HCl)

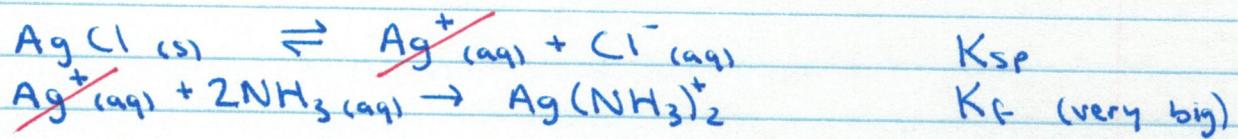
∴ unaffected.

c) Solubility and Complex Ion

- complex ion = charged species formed of a metal ion surrounded by ligands
 - ligand = lewis base, molecule or ion having a lone pair to donate (ex: H_2O , NH_3 , CN^-)
 - the metal ion acts as lewis acid
 - coordination number = number of ligands attached
 - in (aq) sol'n metal ions and ligands exist in equilibrium $\Rightarrow K_f$: formation/stability constant
 - * General rule: solubility of metal salts increase in presence of suitable Lewis base, if the metal forms a complex.



bc Ag^+ is being consumed to form complex ion
rxn shifts right $\therefore \text{AgCl}$ more soluble



$$\kappa = \kappa_{sp} \cdot \kappa_f$$

Precipitation Rxn

→ reverse process of dissolution:

formation of solid from sol'n

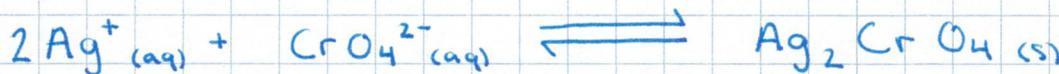
→ use Q vs K_{sp} to predict precipitation

- $Q < K_{sp}$: no precipitation occurs; solution is not saturated (unsaturated)
- $Q = K_{sp}$: solution is saturated (at equil.)
sol'n contains undissolved solute and dissolved solute in equil.
* ion concentration have reached maximum value.
- $Q > K_{sp}$: oversaturated: precipitation will occur until $Q = K_{sp}$
since the sol'n is supersaturated.

Note: if a precipitate forms, an amount of ions remain in sol'n. We can calculate eq. concentration of ions remaining in sol'n after precipitation occurs.

ex: A sol'n of 0.15L $1 \times 10^{-2}\text{M}$ Na_2CrO_4 is added to 0.25L of 0.1M AgNO_3 sol'n. Will $\text{Ag}_2\text{CrO}_4(s)$ ($K_{sp} = 9.0 \times 10^{-12}$) precipitate? Find equil. ion concentrations.

① Determine if precipitate will form
consider K_{sp}



For K_{sp} , consider reverse



calculate Q and K

$$K_{sp} = [\text{Ag}^+]_{eq}^2 \cdot [\text{CrO}_4^{2-}]_{eq} = 9 \times 10^{-12}$$

$$Q = [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}]$$

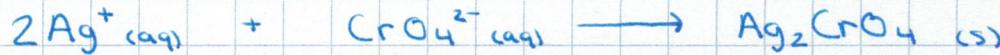
$$Q = \left(\frac{(0.1\text{M} \cdot 0.25\text{L})}{0.4\text{L}} \right)^2 \cdot \left(\frac{(0.0\text{M} \cdot 0.15\text{L})}{0.4\text{L}} \right) = 1.46 \times 10^{-5}$$

total volume

$Q > K_{sp} \therefore \text{precipitation}$

② Determine $[\text{Ag}^+]_{eq}$ and $[\text{CrO}_4^{2-}]_{eq}$

* Assume complete precipitation rxn



B:	0.025 mol	0.0015 mol	
		2:1 ratio there is less than half $-2(0.0015)$	(LR)

A: 0.022 mol 0

Set equilibrium (reverse rxn)

$\text{Ag}_2\text{CrO}_4(s)$	\rightleftharpoons	$2\text{Ag}^+(\text{aq})$	$+ \text{CrO}_4^{2-}(\text{aq})$
		$\frac{0.022}{0.4} = 0.055\text{M}$	0
C:		$+2S$	$+S$
E:		$0.055 + 2S$	S

≈ 0.055

$$K_{sp} = [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}]$$

$$9 \times 10^{-12} = (0.055)^2 \cdot (S)$$

$$S = 3 \times 10^{-9}\text{ M}$$

$$\therefore [\text{CrO}_4^{2-}] = 3 \times 10^{-9}\text{ M}$$

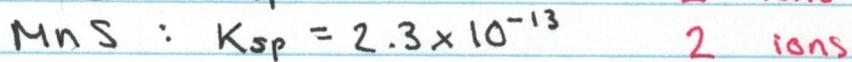
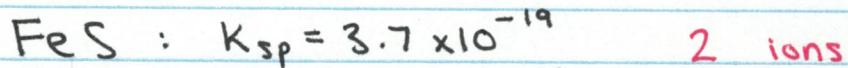
$$\begin{aligned} \therefore [\text{Ag}^+] &= 0.055 + 2(S) \\ &= 0.055\text{ M} \end{aligned}$$

$$\text{Validate } \frac{3 \times 10^{-9}}{0.055} \times 100 < 5\%$$

Selective Precipitation of Ions

- Metal ions can be separated from each other based on the solubilities of the salts they form
- Selective precipitation = separation of ions in an aqueous sol'n by using a reagent that forms a precipitate with 1 or more ions.

ex: To a mixture of 1×10^{-3} M Fe^{2+} and 1×10^{-3} M Mn^{2+} , a sol'n of S^{2-} is added. Which salt will precipitate first?

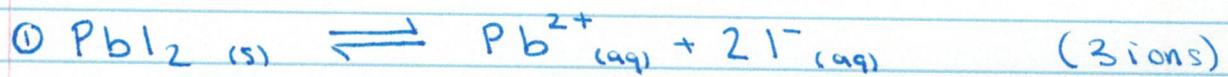


Smaller K_{sp} values precipitate first
∴ FeS salt will precipitate first

Note: We can only compare K_{sp} values to find relative solubilities bc both salts produce the same number of ions.

... if unequal number of ions produced

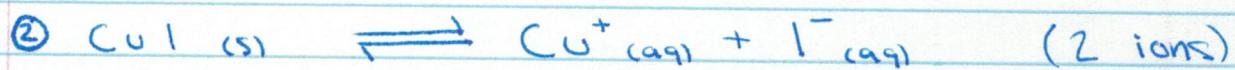
ex: A sol'n contains 1×10^{-4} M Cu^+ and 2×10^{-3} M Pb^{2+} . When I^- is added to sol'n PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) and CuI ($K_{\text{sp}} = 5.3 \times 10^{-12}$) precipitate. What conc. of I^- is required to precipitate each salt? Which salt will precipitate first?



$$K_{\text{sp}} = [\text{Pb}^{2+}] \cdot [\text{I}^-]^2$$

unknown ⇒ how much $[\text{I}^-]$ to reach equil (saturated sol'n)

$$[\text{I}^-] = 2.6 \times 10^{-3} \text{ M}$$



$$K_{\text{sp}} = [\text{Cu}^+] \cdot [\text{I}^-]$$

unknown

$$[\text{I}^-] = 5.3 \times 10^{-8} \text{ M}$$

∴ CuI requires less $[\text{I}^-]$ to saturate

∴ CuI will precipitate first.