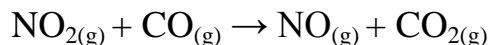


#80 Notes **Unit 10: Kinetics, Equilibrium, Energy and Electrochemistry**
Ch. Rates, Equilibriums, Energies

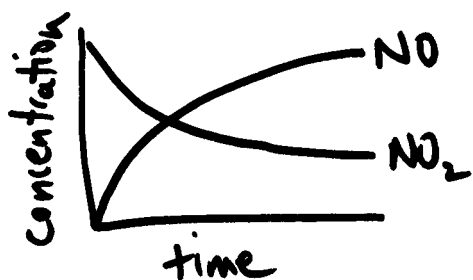
Ch.

I. Reaction Rates



Rate is defined in terms of the rate of disappearance of one of the reactants, but it can also be defined by the rate of appearance of one of the products.

$$\text{Rate} = \frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-\Delta[\text{CO}]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t}$$



- rate can be measured for a specific time (instantaneous rate = slope) or over a time interval (average rate)

II. Integrated Rate Laws

$$\text{Rate} = k [\text{reactant 1}]^x [\text{reactant 2}]^y$$

\uparrow \uparrow
 \uparrow concentrations (molarity)
 rate constant, (k), depends on size, speed, kind of molecule, temperature, etc.

-x,y are usually integers

Ex. 1) $\text{A} + \text{B} \rightarrow \text{C}$

	initial [A]	initial [B]	initial rate	rate = $\frac{-\Delta[\text{B}]}{\Delta t}$
row 1	0.100 M	0.100 M	4.0×10^{-5}	
row 2	0.100 M	0.200 M	4.0×10^{-5}	
row 3	0.200 M	0.100 M	$1.6 \times 10^{-4} = 16 \times 10^{-5}$	

Compare two rows where only one concentration is changing (only "A" or only "B").

comparing row 1 & 2: A remains the same, B is doubling and the rate is the same.

(going down the rows) $\text{rate} = k [\text{A}]^1 [\text{B}]^2$

$1X$ $2X$ 2^0 equals 1, so $[\text{B}]^0$

comparing row 1 & 3: A is doubling, B is the same and the rate is four times bigger.

(going down the rows) rate = k [A] [B]

$$4X \quad 2X$$

$$2^2 \text{ equals } 4, \text{ so } [A]^2$$

$$\text{Rate} = k[A]^2[B]^0 \text{ or Rate} = k[A]^2$$

(2nd order, since powers add up to "2")

Find rate constant:

(A is 2nd order, B is zero order)

$$\text{Rate} = k[A]^2$$

$$4.0 \times 10^{-5} = k (0.100 \text{ M})^2 \quad \text{plugging in values from row \#1.}$$

$$\mathbf{4.0 \times 10^{-3} = k} \leftarrow \text{Book does all 3 rows and averages (just do one row).}$$

Ex. 2) $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$

	$[(\text{CH}_3)_3\text{CBr}]_0$	$[\text{OH}^-]_0$	$\text{rate} = \frac{+\Delta[\text{Br}^-]}{\Delta t}$
row 1	0.10 M	0.18 M	1.0×10^{-3}
row 2	0.20 M	0.10 M	2.0×10^{-3}
row 3	0.10 M	0.10 M	1.0×10^{-3}

comparing row 1 & 3: $(\text{CH}_3)_3\text{CBr}$ is the same,

(going up the row)

OH^- is basically doubling and the rate is the same.

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]$$

$$1X$$

$$2X$$

2^0 equals 1, so $[\text{OH}^-]^0$

comparing row 2 & 3: $(\text{CH}_3)_3\text{CBr}$ is doubling,

(going up the row)

OH^- is the same and the rate is doubling.

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]$$

$$2X$$

$$2X$$

2^1 equals 2, so $[(\text{CH}_3)_3\text{CBr}]^1$

$$\mathbf{\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1 [\text{OH}^-]^0 = k [(\text{CH}_3)_3\text{CBr}]^1} \quad (1^{\text{st}} \text{ order overall})$$

Find the rate constant:

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1$$

$$(1.0 \times 10^{-3}) = k (0.10 \text{ M}) \quad \text{using row \#1}$$

$$\mathbf{1.0 \times 10^{-2} = k}$$

What would the rate be, if $[(\text{CH}_3)_3\text{CBr}] = 0.26 \text{ M}$ & $[\text{OH}^-] = 0.45 \text{ M}$?

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1$$

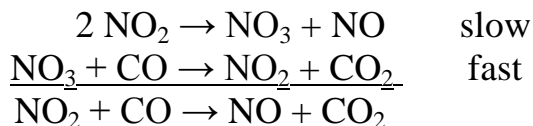
$$\text{rate} = (1.0 \times 10^{-2}) (0.26 \text{ M})$$

$$\mathbf{\text{rate} = 2.6 \times 10^{-3}}$$

III. Reaction Mechanisms

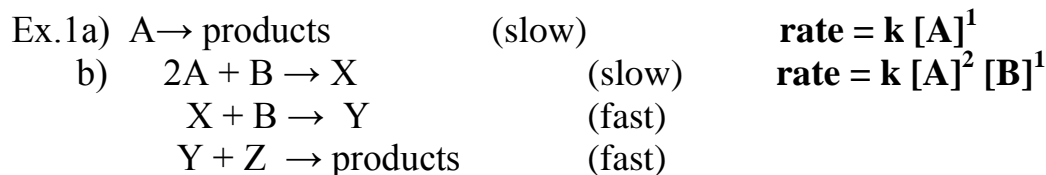
-are the series of steps or reactions necessary to achieve an overall process.

*The slowest step always determines the rate law.



*NO₃ is an intermediate. (It's first a product, then a reactant, which cancel.)

Rate = $k [\text{NO}_2]^2$ rate law from the slowest step!



*Find the slow reaction or if only one reaction, assume it is slow! Use the slow reaction.

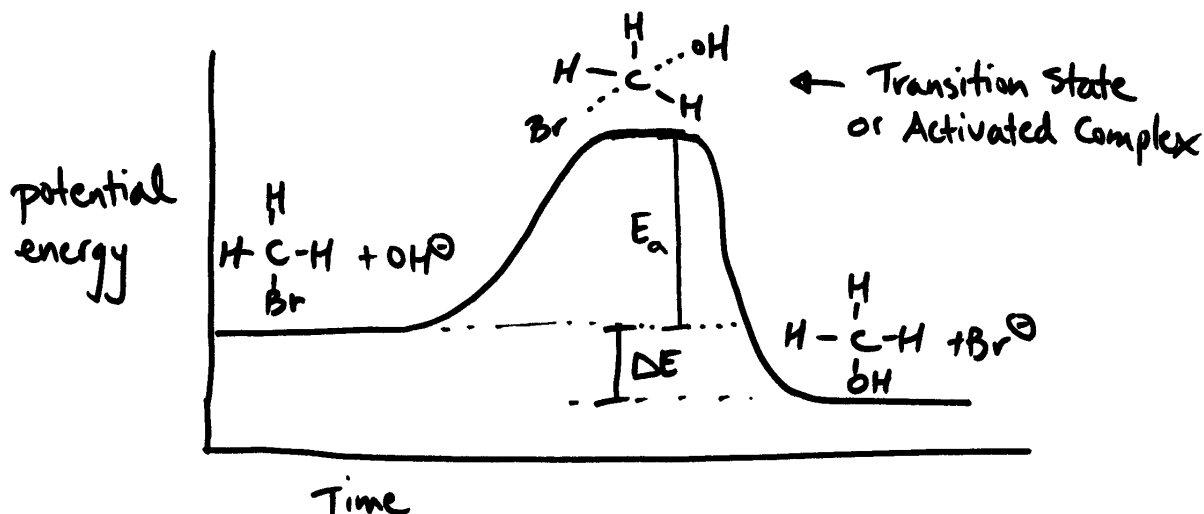
IV. Chemical Kinetics/ Collision Model

Ionic compounds in reactions do not need to rearrange their electrons, since the ions just change partners. These reactions occur quickly.

Covalent compounds in reactions must change their electron clouds. The energy to do this comes from collisions! *The rate can be increased by increasing the temperature, since this increases the velocity of the particles ($\text{KE} = \frac{1}{2} m v^2$). The number and power of collisions increase.

But the rate does not go up by as much as it should.

Arrhenius proposed the existence of a threshold or activation energy that must be overcome in order to produce a reaction.



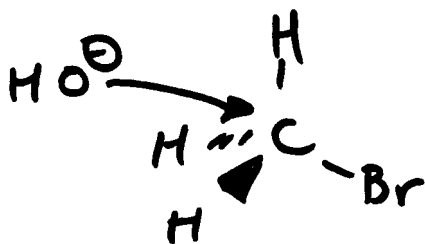
E_a = activation energy needed for reaction to occur.

ΔE = overall energy change for the reaction, above it is (-) so exothermic.

The kinetic energy of the moving molecules is changed into potential energy as the bonds are broken and formed.

**Only collisions with enough energy (activation energy) will be able to form the activated complex and then the products.

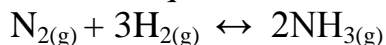
The reaction rate is still smaller, than the rate of collisions with enough energy to form the activated complex, because of molecular orientations.



The OH^- must hit from the opposite side to eject the Br^- .

*Catalysts: lower the E_a , allowing reactions to go faster.

*Inhibitors: slow the reaction.

I. Equilibrium Equations

at equilibrium:

Forward Rate = Reverse Rate

$$k_f[\text{N}_2]^1[\text{H}_2]^3 = k_r[\text{NH}_3]^2$$

$$\frac{k_f}{k_r} = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1[\text{H}_2]^3}$$

$$\mathbf{K} = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1[\text{H}_2]^3} \quad \leftarrow \text{Molarity} \quad \begin{array}{l} \leftarrow \text{products} \\ \leftarrow \text{reactants} \end{array}$$

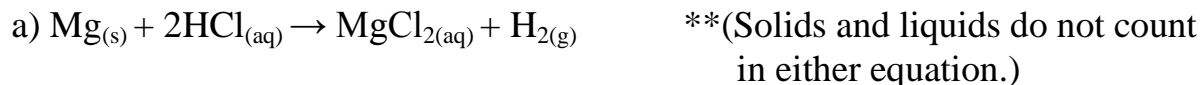
*Exception: Pure solids and pure liquids are not included (“aq” and “g” are included).
{H₂O_(l) not included, H₂O_(g) included}

K_p is for gases only!

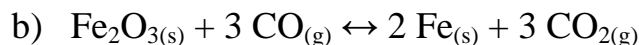
$$\mathbf{K}_p = \frac{\mathbf{P}_{\text{NH}_3}^2}{\mathbf{P}_{\text{N}_2} \mathbf{P}_{\text{H}_2}^3} \quad \text{**P in atmospheres}$$

$$\mathbf{K}_p = \mathbf{K}(\mathbf{RT})^{\Delta n} \quad \mathbf{R} = \mathbf{0.08206} \frac{\mathbf{L} \cdot \mathbf{atm}}{\mathbf{mol} \cdot \mathbf{K}}$$

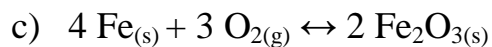
$\Delta n = \text{mols products} - \text{mols reactants}$

Ex. 1) Write the K equation and is K = K_p?

$$\mathbf{K} = \frac{[\text{MgCl}_2]^1 [\text{H}_2]^1}{[\text{HCl}]^2} \quad \begin{array}{l} \mathbf{K}_p = \mathbf{K} (\mathbf{RT})^{\Delta n=2 \text{ mols product} - 2 \text{ mols reactant}} \\ \mathbf{K}_p = \mathbf{K} (\mathbf{RT})^0 \\ \mathbf{K}_p = \mathbf{K} \end{array}$$



$$\mathbf{K} = \frac{[\text{CO}_2]^3}{[\text{CO}]^3} \quad \begin{array}{l} \mathbf{K}_p = \mathbf{K} (\mathbf{RT})^{3 \text{ mols product} - 3 \text{ mols reactant}} \\ \mathbf{K}_p = \mathbf{K} (\mathbf{RT})^0 \quad \text{so } \mathbf{K}_p = \mathbf{K} \end{array}$$



$$\mathbf{K} = \frac{\mathbf{1}}{[\text{O}_2]^3} \quad \begin{array}{l} K_p = K (RT)^{0 \text{ mols product} - 3 \text{ mols reactant}} \\ K_p = K (RT)^{-3} \quad \text{so } \mathbf{K_p} \neq \mathbf{K} \end{array}$$

Ex.2) For $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \leftrightarrow 2 \text{NH}_{3(g)}$: What is the concentration of NH_3 at equilibrium, if at equilibrium there is 0.0402 mol N_2 and 0.1207 mol H_2 in 2.00 L? $K = 0.105$

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} \quad M_{\text{N}_2} = \frac{0.0402 \text{ mol}}{2.00 \text{ L}} = 0.0201 \text{ M} \quad M_{\text{H}_2} = \frac{0.1207 \text{ mol}}{2.00 \text{ L}} = 0.06035 \text{ M}$$

$$0.105 = \frac{[\text{NH}_3]^2}{(0.0201\text{M})^1 (0.06035 \text{ M})^3}$$

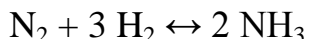
$$4.64 \times 10^{-7} = [\text{NH}_3]^2$$

$$\mathbf{6.81 \times 10^{-4} \text{ M} = [\text{NH}_3]}$$

#83 Notes II. Le Chatelier's Principle

If a system is in equilibrium and a condition is changed, then the system will shift toward restoring the equilibrium.

A) Concentration



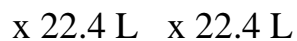
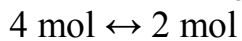
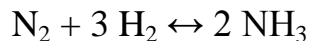
Ex. 1) increase N_2 : increases collisions, so it speeds the reaction going to the right
(products)
shifts right (*too much N_2 , so it will shift to the other side (products)*)

Ex. 2) increase NH_3 : **shifts left** (*too much NH_3 , shifts to the other side (reactants)*)

Ex. 3) decrease H_2 : **shifts left** (*too little H_2 , so it must shift toward H_2 to increase it (reactants)*)

B) Pressure (only affects gases)

Ex. 1) increase P, by decreasing volume (*if decreasing volume, the reaction will shift toward the side that is the most compact (smallest volume)*)



the right side is more compact **shifts right**

(if increase volume, shifts to the left, larger volume side)

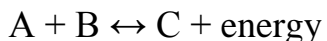
Ex. 2) increase P, by adding Ne, **no change** (Ne is not in the reaction, other gases will not change the volume, since gases are "point masses" (ideal))

C) Temperature

Ex. 1) $\text{Girls} + \text{Boys} \leftrightarrow \text{Dancing} + \text{heat}$ (exothermic, heat produced, $\Delta H = (-)$
energy on product side)

Increase Temperature, Add heat, less dancing, **shifts left**

Ex. 2) Decrease T, for exothermic reaction ($\Delta H = (-)$, energy on product side)

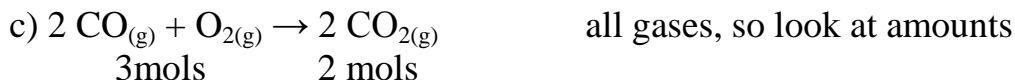
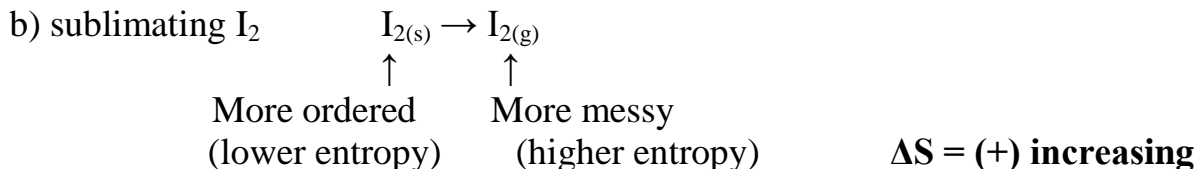
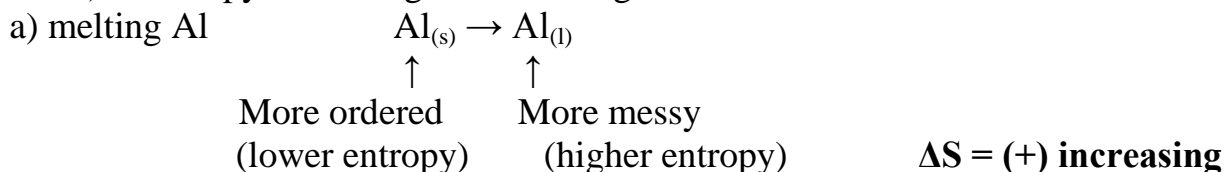


decrease T, too little energy, **shifts right**

#84 Notes II. Entropy (S)
-is the disorder in a system.

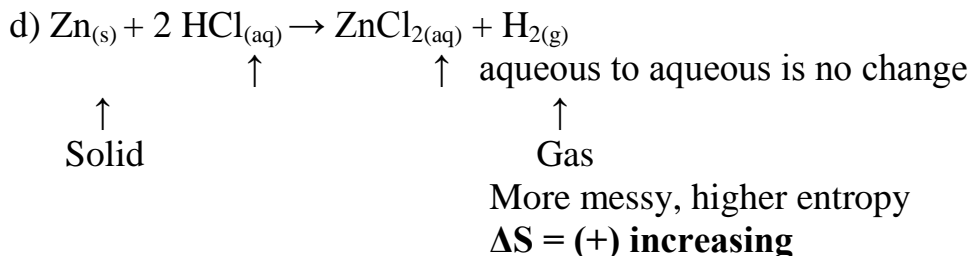
In nature systems get more messed up (gain entropy).

Ex. 1) Is entropy increasing or decreasing?

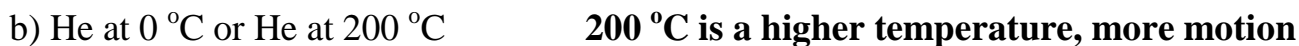


Three objects can get more disorganized than 2 objects.

High entropy Low entropy $\Delta S = (-)$ decreasing



Ex. 2) Which has more entropy?



**** The higher the temperature and the lower the pressure, the higher the entropy!**

STP = 273 K & 1 atm

III. Relationship between ΔH , ΔG , & ΔS

$$\Delta G = \Delta H - T\Delta S \quad \begin{array}{l} \Delta G \text{ in kJ/mol, } \Delta H \text{ in kJ/mol, } T \text{ in Kelvin,} \\ \Delta S \text{ in J/(mol}\cdot\text{K) **so change to kJ/(mol}\cdot\text{K)} \end{array}$$

Ex.1) Will a reaction be spontaneous at 25 °C, if $\Delta H = 542 \text{ kJ/mol}$ and $\Delta S = -14 \text{ J/(mol}\cdot\text{K)}$?

$$\frac{-14 \text{ J}}{\text{mol}\cdot\text{K}} \left| \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \right. = -0.014 \text{ kJ/(mol}\cdot\text{K)}$$

$$\Delta G = \Delta H - T\Delta S = (542 \text{ kJ/mol}) - [(298 \text{ K}) (-0.014 \text{ kJ/(mol}\cdot\text{K)})]$$

$$\Delta G = 542 \text{ kJ/mol} + 4.172 \text{ kJ/mol} = \mathbf{546 \text{ kJ/mol}} \text{ (+) so } \mathbf{\textit{nonspontaneous}}$$

#85 Notes IV. Free Energy and Equilibrium

$$\Delta G = \Delta G^\circ + RT \ln Q_p$$

ΔG is at **non-equilibrium** conditions

ΔG° is at equilibrium, calculated by

$$\Delta G_{\text{reaction}} = \sum n\Delta G_{\text{products}} - \sum n\Delta G_{\text{reactants}}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

Q_p is K_p at non-equilibrium conditions

$$\text{Remember: } K_p = K (RT)^{\Delta n}$$

At equilibrium $\Delta G = 0$, so $0 = \Delta G^\circ + RT \ln K_p$

$$\Delta G^\circ = -RT \ln K_p$$

Ex. 1) Find ΔG for $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \leftrightarrow 2 \text{NH}_{3(g)}$ at 25°C , if $P_{\text{N}_2} = 0.050 \text{ atm}$,
 $P_{\text{H}_2} = 0.0010 \text{ atm}$, and $P_{\text{NH}_3} = 0.012 \text{ atm}$.

$$\Delta G^\circ_{\text{reaction}} = \sum n\Delta G_{\text{products}} - \sum n\Delta G_{\text{reactants}} \quad (\text{old } \Delta G \text{ energy table})$$

$$\Delta G^\circ = [(2 \text{ mol NH}_3) (-16.45 \text{ kJ/mol})] - [(1 \text{ mol N}_2) (0 \text{ kJ/mol}) + (3 \text{ mol H}_2) (0 \text{ kJ/mol})]$$

$$\Delta G^\circ = -32.9 \text{ kJ}$$

$$Q_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2}^1 P_{\text{H}_2}^3} = \frac{(0.012 \text{ atm})^2}{(0.050 \text{ atm})^1 (0.0010 \text{ atm})^3} = 2.88 \times 10^6$$

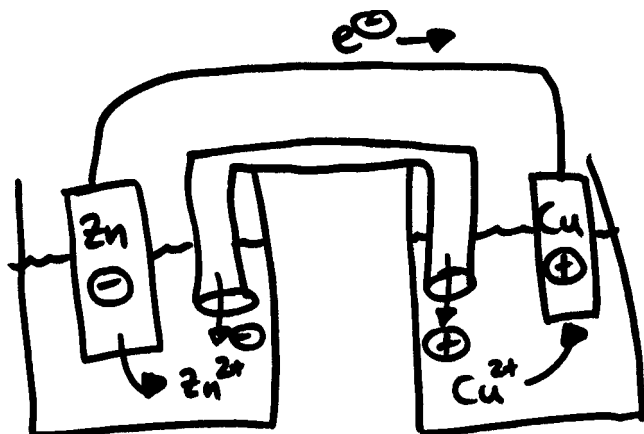
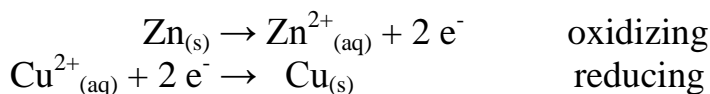
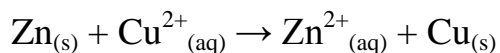
$$\Delta G = \Delta G^\circ + RT \ln Q_p$$

$$\Delta G = \frac{(-32.9 \text{ kJ} \quad | \quad 1 \times 10^3 \text{ J})}{1 \text{ kJ}} + (8.31 \text{ J/mol}\cdot\text{K}) (298 \text{ K}) \ln (2.88 \times 10^6)$$

(14.87)

$$\Delta G = -32900 \text{ J} + 36832 \text{ J} = 3932 = \mathbf{3.9 \times 10^3 \text{ J or } 3.9 \text{ kJ}}$$

I. Galvanic Cells



Oxidized
Anode (-)

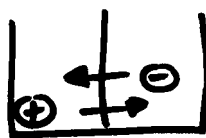
Reduced
Cathode (+)

The salt bridge adds ions to keep the solutions balanced:

(-) ions are added to
balance the arriving
Zn²⁺ (+) ions.

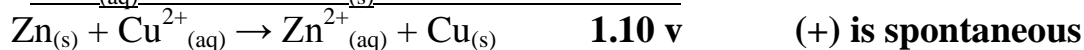
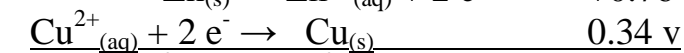
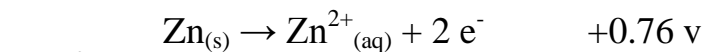
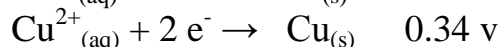
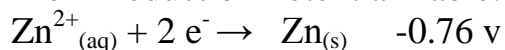
(+) ions are added to
replace the departing
Cu²⁺ (+) ions.

** or cells separated by porous disk



Cell potential = electromotive force (emf) = ϵ_{cell}

From Reduction Potential Table:

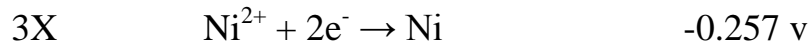


** If given 2 reduction potentials, make the reaction spontaneous. (flip one of them)

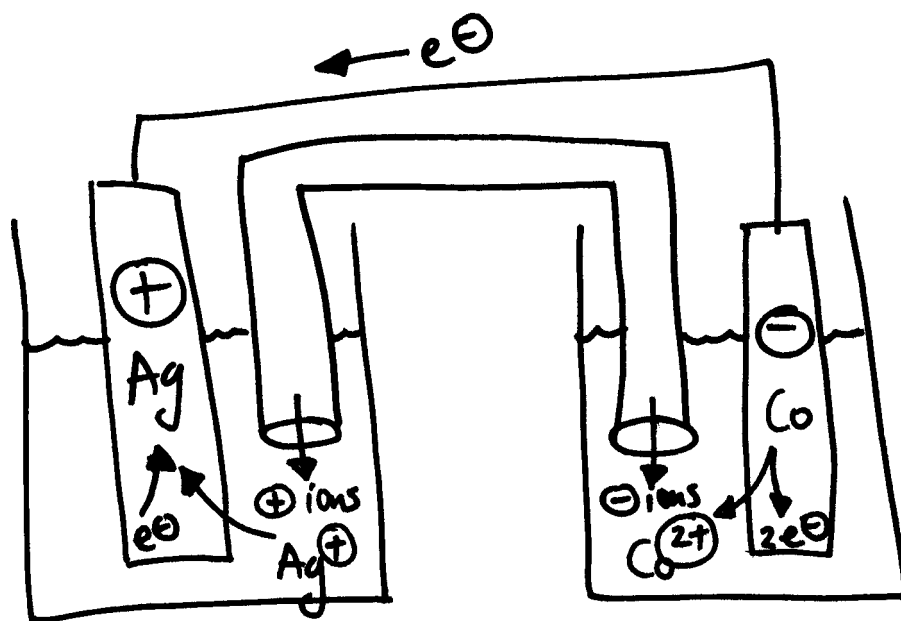
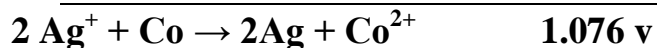
Ex.1a) Find the cell potential for:



Reaction must be spontaneous! Which should we flip?



b) Find cell potential **and sketch the galvanic cell.**



Reducing

Cathode (+)

Oxidizing

Anode (-)

The salt bridge adds ions to keep the solutions balanced:

(+) **ions** are added to
replace the **departing**
Ag⁺ (+) ions.

(-) **ions** are added to
balance the **arriving**
Co²⁺ (+) ions.

End of Notes (Assignments #87-88 are Review Assignments. There are no notes for these assignments.)