

Atomic Structure

- Atomic number # P
 Mass number p + n
 Isotopes => atomic mass weighted average of isotope masses

- Rutherford, Bohr, quantum theory

- Electron Configurations $8O \quad 1s^2 2s^2 2p^4$
 Orbital Notation $\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow$

- Electron configuration of ions
 * transition metal ions $Zn^{+2} [Ar] 3d^{10}$

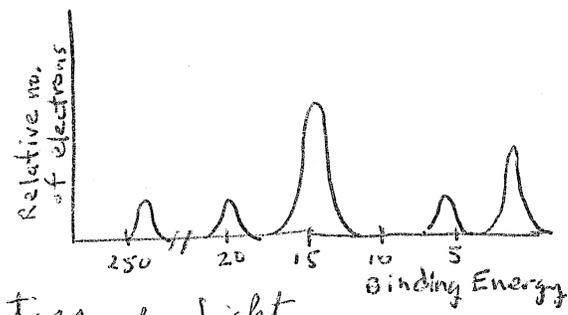
- Electron Dot symbol $8O \quad \cdot\ddot{O}\cdot$

- Ionization energy : Trends
 A. Coulombic attraction
 magnitude of nuclear charge
 distance from nucleus

Successive ionization energies

- Atomic Radius : Trends distance and coulombic attraction.
 Ionic Radius :

- PES

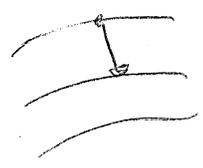


- Properties of Light

$$c = \lambda \cdot \nu \quad c = 3.0 \times 10^8 \text{ m/s}$$

$$\lambda = \frac{c}{\nu} \quad \nu = \frac{c}{\lambda}$$

$$E = h\nu \quad h = \text{Planck's Constant } 6.63 \times 10^{-34} \frac{\text{J}\cdot\text{s}}{\text{photon}}$$



$$\Delta E = E_{Hi} - E_{Lo}$$

$\Delta E = \lambda$ of light emitted from atom
 Bright Line spectra.

Periodic Table

Periods 1-7 = # energy levels are equal in a period

- atomic radius dec. (inc. nuclear charge)
- I.E. inc. (inc. nuclear charge)
- metals → non metals
- Electronegativity inc.

Groups

1-18
 Same number of valence electrons
 atomic radius inc. (added E. level)
 I.E. dec. (e further from nuclear attraction)



- Group 1 alkali metals
- Group 2 alkaline earths
- Group 17 Halogens
- Group 18 Noble Gases
- Groups 3-12 Transition Metals (colorful ions)

Metals, non metals, metalloids

Sublevel Blocks s, p, d, f

Radioactive elements: atomic number > 84

+ ions smaller than Atoms (usually lose valence shell of electrons)

- ions larger than Atoms (valence shell increases to stable octet and repulsive forces between electrons expand size)

Molecular Geometry

different shapes (3)

I. Draw Lewis Structure



#electron pairs around central atom

- A. Bonding Pairs
- B. Lone Pairs

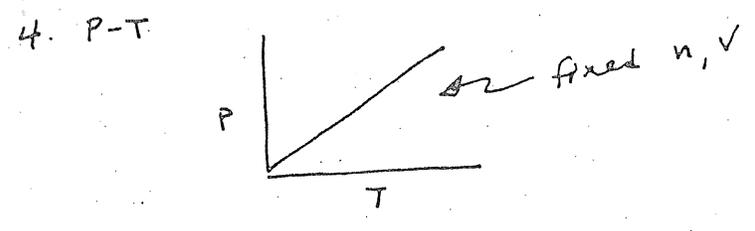
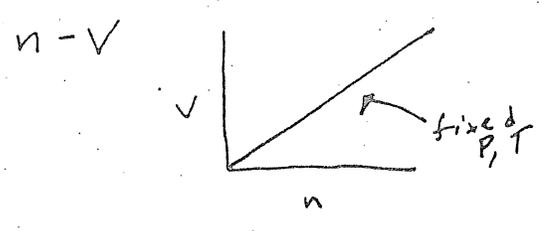
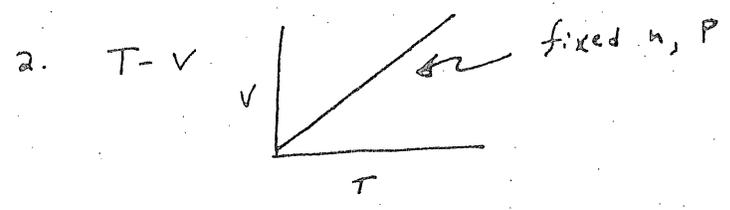
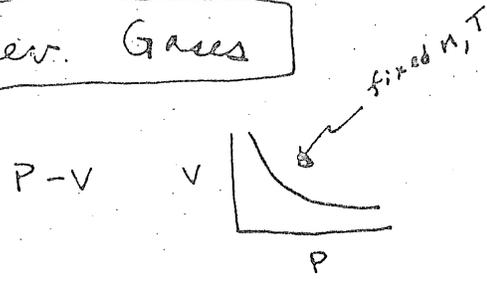
Note: double bond counts only as 1 pair.

#e pairs	bonding pairs	Lone pairs	Hybridization	Bond angle	Shape
2	2	0	sp	180	Linear
3	3	0	sp ²	120	Trigonal planar
3	2	1	sp ²	120	Bent
4	4	0	sp ³	⊗ 109.5	Tetrahedral
4	3	1	sp ³	⊗ 107.5	Pyramidal
4	2	2	sp ³	⊗ 105.5	Bent
5	5	0	sp ³ d	90°, 120	Trigonal Bipyramidal
5	4	1	sp ³ d	90°, 120	See Saw
5	3	2	sp ³ d	90	T-shaped
5	2	3	sp ³ d	180	Linear
6	6	0	sp ³ d ²	90	Octahedral
6	5	1	sp ³ d ²	90	Square Pyramid
6	4	2	sp ³ d ²	90	Square planar

Lone Pairs push angle in

Bond Polarity - Electronegativity differences
 Molecular Polarity "Dipole Moment" : Bond Polarity + geometry (asymmetrical - symmetrical)

Rev. Gases



$PV = nRT$
 $PV = \frac{gRT}{MM} \rightarrow P = \frac{gRT}{MM \cdot V} = P = \frac{dRT}{MM}$
 $MM = \frac{dRT}{P}$

note: $n = \frac{g}{MM}$ To find MM of gas experimentally

Partial Pressures $P_{total} = P_1 + P_2 + P_3$ (collection of gas over water = subtract V.P. of the water.)

Partial Pressure ratio same as mole ratio
 $P_1 = X_1 P_T$
 $X_1 =$ mole fraction of gas 1
 $P_T =$ Total Pressure

Ideal Gas :
 No attractive forces between molecules
 AT High Temp and Low Pressure real gases more ideal
 Large container Volume also.

speed of gas molecule $u = \sqrt{\frac{3RT}{MM}}$
 RMS Root mean Speed $R = 8.31$

Diffusion $\frac{u_2}{u_1} = \sqrt{\frac{MM_1}{MM_2}}$
 MM in kg/mol
 $u = m/s$

Types of Substances and IMF's

Metallic :

metallic bonds " + ions in sea of mobile electrons"
good conductors of heat & electricity
insoluble in water, alkali and alkaline earths react with water
malleable
high m.p.

Ionic :

ionic bonds "crystal lattice"
No individual molecules.
generally water soluble
solutions conduct electricity
high m.p.
no conductivity in solid phase

molecular :

covalent bonds hold the molecules together
Van der Waals forces (London dispersion forces)
or dipole forces, or Hydrogen bonds exist
between molecules
(London Dispersion)
van der Waals : non polar molecules : weak
low m.p. insoluble in water, non-conducting
Dipole : polar molecules : weak but stronger than Van der Waals, soluble in water, generally non conducting
Hydrogen Bonds : between molecules containing
Molecular \rightarrow O-H (water, alcohols) N-H (ammonia)
H-F (Hydrogen Fluoride)
very soluble in water

Network Solids :

covalent bonds in network array - very strongly held together : Diamond, SiO₂, SiC.
Hard, high m.p., insoluble, nonconducting.

Liquids

(6)

1. Intermediate strength IMF's

2. Evaporation (l) + energy \rightarrow (g) endothermic

(a) Occurs at surface of liquid

(b) Increase Temp. inc rate of evaporation

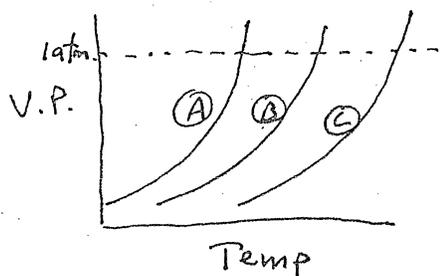
(c) Increase surface area, inc rate of evaporation

3. Variations in strength of IMF's between liquids govern which liquids evaporate faster than which.

[small non polars (van der Waals) evaporate faster]

4. Vapor Pressure = pressure exerted by the vapor above a liquid in closed container: equilibrium (l \rightleftharpoons g)

5. Vapor pressure graphs



V.P. increases exponentially with temp.
Ⓐ weakest IMF's Ⓒ Strongest IMF's

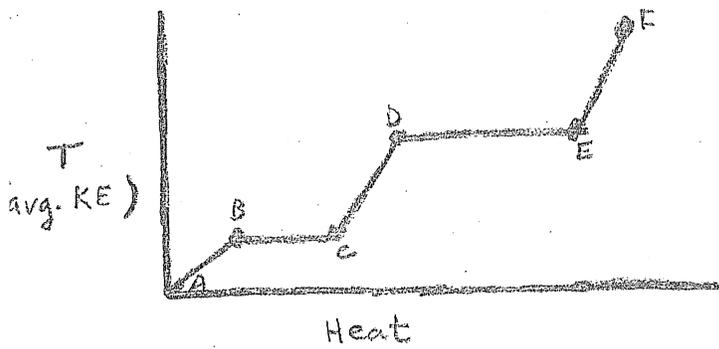
6. A liquid boils when V.P. = prevailing atmospheric pressure.
Normal Boiling Point Temp. at which vapor pressure = 1 atm.

increase surface area
increases how much evaporates
higher temp evaporates faster

8. High Heats of Vaporization
Low V.P.
High B.P.
Strong IMF's.

Phase changes, Temp, Heat

(7)



"warming curve"

\overrightarrow{AB} Solid phase warming KE inc

\overrightarrow{BC} Melting. KE remains same, PE of molecules inc.
Heat of Fusion ΔH_f Heat in kJ required to melt 1 mole of substance at the melting temp.

\overrightarrow{CD} Liquid phase warming KE inc

\overrightarrow{DE} Liquid boils KE constant

\overrightarrow{EF} Gas phase warming KE inc.

"cooling curve" follows reverse path

\overrightarrow{ED} condensation

\overrightarrow{CB} freezing

Stoichiometry

1. % composition $\frac{\text{mass part}}{\text{mass whole}} \times 100$
2. Empirical formulas
3. Molecular formulas \rightarrow Molar Mass
4. Balanced Equation : mole proportions

ICE Diagrams

Limiting Reagent

Theoretical Yield

% yield $\left. \begin{array}{l} \text{ICE says} \\ \text{question says} \end{array} \right\} \text{over } \%$

5. Quantity given of substance in balanced equation

(A) $\text{mols} = \frac{\text{given mass}}{MM}$

(B) $\text{mols} = \frac{PV}{RT}$ (gases)

(C) $\text{mols} = M \times L$ solution

6. Solution Concentration

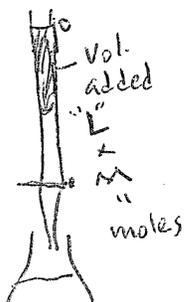
$$\text{Molarity} = \frac{\text{mols solute}}{L \text{ sol'n}}$$

7. In titrations the volume of Titrant that

is added to reach endpoint is converted to moles of titrant.

$\text{The molarity of the titrant} \times \underline{\text{Liters added}} = \text{mols.}$

$MA(L) = \text{mol}$



Kinetics

9



rate of disappearance of A : 2x's that of B

rate of appearance of C : $\frac{1}{2}$ x that of A disappearance

II Rate Law expression

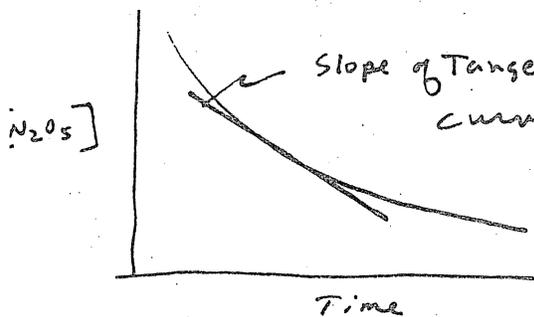
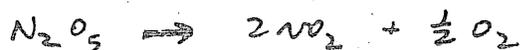
$$\text{rate} = k[A]^m[B]^n$$

	[A]	[B]	Rate of appearance of C	Order
1.	—	—	—	1:1 \rightarrow 1st order
2.	—	—	—	3:1 \rightarrow 2nd order
3.	—	—	—	2:1 \rightarrow 2nd order
4.	—	—	—	2:1 \rightarrow 2nd order

From the data determine m and n

Once m & n determined, use data from 1 set of data and solve for k (units included)

Graphs:



Slope of Tangent to point on curve is instantaneous rate at that time (slope = -) \therefore rate = -(slope)

[] slow rate over time

Equilibrium

reciprocal
value

$Q > K_{sp}$
FORM

1. Rate of forward = Rate of reverse
2. K_c or $K_p = \frac{\text{Products}}{\text{Reactants}}$

$2A_{(g)} + B_{(g)} \rightarrow C_{(g)}$

Start			
Δ			
Eg			

$$K = \frac{[C]}{[A]^2 [B]}$$

K_c if [] Molarity units
 K_p if Partial Pressures used

A large K indicates that products are favored

K_c K_p K_{sp} K_a K_b all equilibrium constants

\rightarrow K for forward = $\frac{1}{K}$ for reverse \leftarrow

$\Delta G = -RT \ln K$ (Note: if $K > 1$ $\Delta G = (-)$ spontaneous.)

Le Chatelier's Principle : Equilibrium shifts with changes

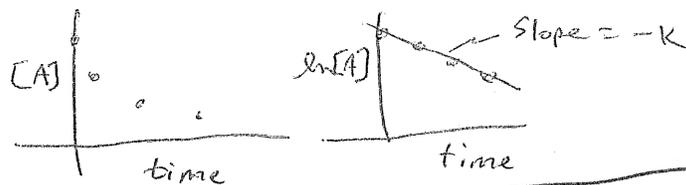
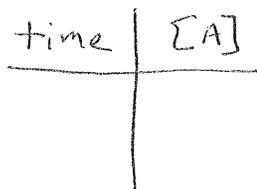
in T, ~~P~~ and [] : (Note: only T effect the numerical value of K)

effects
shifts to small

\uparrow or \downarrow []
shift to other side

Integrated Rate Laws (A) 1st order $A \rightarrow \text{products}$

(11)

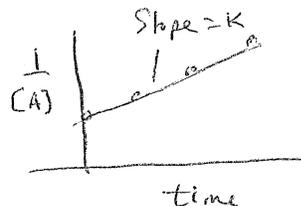
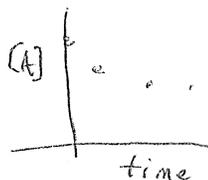
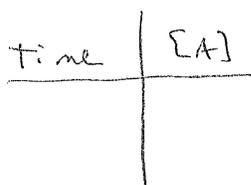


$\ln[A]$ straight
1st order

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

$$t_{1/2} = \frac{0.693}{k}$$

B. Second Order
 $A \rightarrow \text{products}$



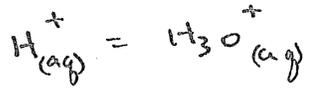
$\frac{1}{[A]}$ straight
2nd order

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

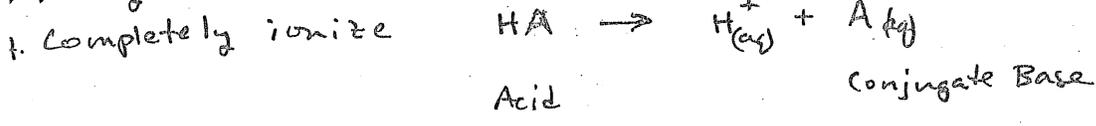
$$T_{1/2} = \frac{1}{k[A]_0}$$

Notes: Half Life of 1st order reaction is independent of $[A]_0$.
Half Life of 2nd order reaction is dependent on $[A]_0$.

Acids & Bases



Strong acids: HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄



$$[HA] = [H^+]$$

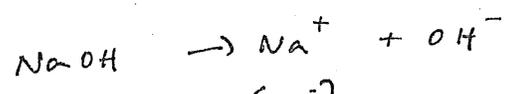
B. $pH = -\log [H^+]$

$$[H^+] = 10^{-pH}$$

Strong Bases

NaOH, KOH, LiOH, RBOH, Ca(OH)₂

A. Completely ionize



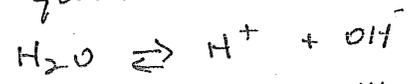
$$[NaOH] = [OH^-]$$

B. $pOH = -\log [OH^-]$

$$[OH^-] = 10^{-pOH}$$

C. $pH + pOH = 14$

I. Water equilibrium

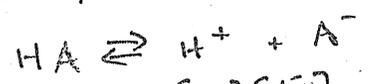


$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$

In pure water $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$
 $pH = 7$

II. Weak acids K_a values Higher $K_a =$ Stronger acid

A. Incomplete ionization



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \sqrt{K_a \cdot [HA]}$$

Note: at equilibrium $[H^+] = [A^-]$
 and $[HA] \approx$ The original value of $[HA]$

V. Weak Bases



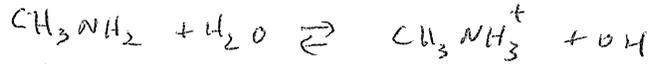
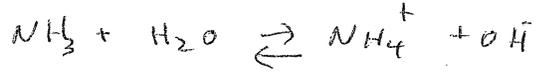
$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$[OH^-] = \sqrt{K_b \times [A^-]}$$

$$K_b = \frac{1.0 \times 10^{-14}}{K_a}$$

$$pOH = -\log [OH^-]$$

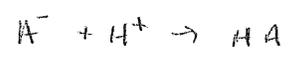
$$pH = 14 - pOH$$



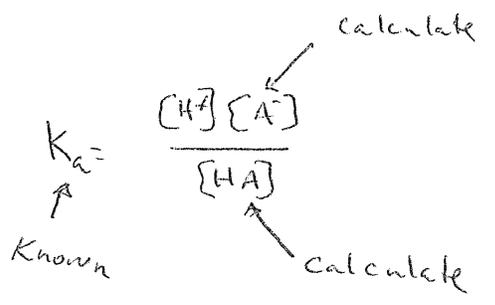
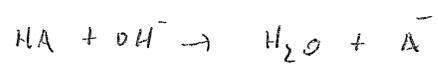
VI. Buffer solutions : Resist changes in pH
weak acid + conjugate base



Add acid to buffer

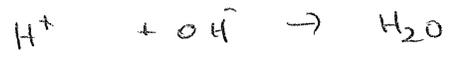


Add base to buffer

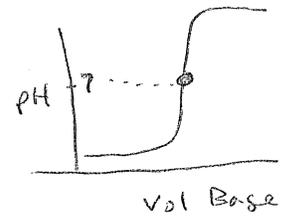


VII Acid + Base Reaction

A. Strong acid + strong base



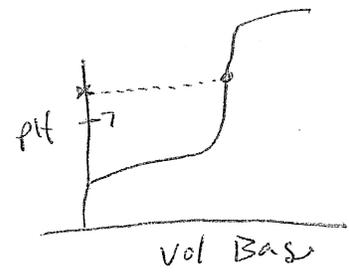
@ equiv. point $pH = 7$
 $M_a V_a = M_b V_b$



B. Weak acid + strong base



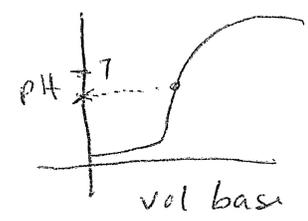
@ equiv. point $pH > 7$
 $M_a V_a = M_b V_b$



C. Strong Acid + weak base



@ equiv. point $pH < 7$
 $M_a V_a = M_b V_b$



Strong + Strong

	H^+	OH^-	\rightarrow	H_2O
I	moles	moles		
C	-moles	-moles		
E	moles	0		

$\frac{\text{moles}}{\text{Total vol}} = [H^+]$
 $pH = -\log [H^+]$

Weak A + Strong B

	HA	OH^-	\rightarrow	H_2O	A^-
I	moles	moles			
C	-moles	-moles			moles
E	moles	0			moles

$\frac{\text{moles}}{\text{total vol}} = [HA]$ $\frac{\text{moles}}{\text{total vol}} = [A^-]$

$K_a = \frac{[H^+][A^-]}{[HA]}$

Known

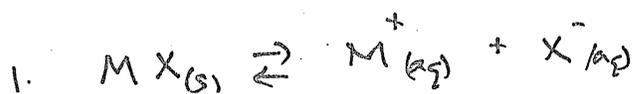
Calc. $[H^+]$
 $pH = -\log [H^+]$

Solution Equilibrium

K_{sp}

15

Saturated Solutions / precipitation



$$K_{sp} = [M^+][X^-]$$

note: $[M^+] = [X^-]$

2. Given Molar solubility: moles/L

$$[M^+] = [X^-] = [MX]$$

A. Calculate K_{sp}



Note: $[X^-] = 2[M^{+2}]$ and $2[MX_2]$

B. Calculate K_{sp}

Given Molar Solubility of MX_2

$$[M^{+2}] = [MX_2]$$

$$[X^-] = 2[MX_2]$$

$$K_{sp} = [M^{+2}][X^-]^2$$

3. Common Ion effect: Calculation of Molar Solubility in solution containing a common ion.

$$K_{sp} = [M^+][X^-]$$

use the value given for the concentration of that ion already in solution.

4. Predicting if a ppt. will form

$$Q = [M^+][X^-]$$

Need to know of each ion

the after mixing Molarity of the ppt.

if: $Q > K_{sp}$ a ppt. will form
 $Q < K_{sp}$ a ppt. will not form.

Thermodynamics

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1 Calorimetry

$$Q = m c \Delta T$$

$$c = \frac{4.18 \text{ J}}{1^\circ \text{C}}$$



The heat released or absorbed during reaction

The Heat of Reaction : ΔH : (-) for exothermic
(+) for endothermic

Heat is stoichiometrically related to equation

$$\Delta H = \sum \Delta H_f \text{ prod.} - \sum \Delta H_f \text{ react.}$$

$$\Delta H_f : \text{elements} = 0$$

$$\Delta H = \sum \text{BE}_{\text{react.}} - \sum \text{BE}_{\text{prod.}}$$

3 Entropy : Disorder : S

$$\Delta S = \sum S^\circ_{\text{prod.}} - \sum S^\circ_{\text{react.}}$$

(usually entropy values are given in Joule units not Kilojoule)

$$\Delta G = \Delta H - T \Delta S^*$$

$$\Delta G = -RT \ln K$$

$$R = 8.31 \times 10^{-3} \frac{\text{KJ}}{\text{mol K}}$$

T = Kelvin Temp.

ΔG - spontaneous

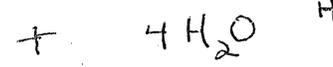
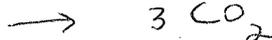
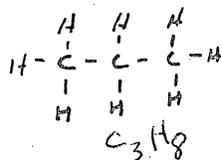
ΔG + not spontaneous

ΔG 0 Equilibrium

Note: $\Delta H = T \Delta S$ at equilib.

K = Equilibrium Constant

5 ΔH can be estimated from table of Bond Energies.



Sum the B.E.

Sum the B.E.

$$\Delta H = \sum \text{B.E.}_R - \sum \text{B.E.}_P$$

Oxidation Reduction Electrochemistry

1. Oxidation Loss of e^- Change in charge \rightarrow

Half Reaction $Li \rightarrow Li^+ + 1e^-$

$Cl^- \rightarrow Cl^{+5} + 6e^-$

2. Reduction gain of e^- Change in charge \leftarrow

Half Reaction $S + 2e^- \rightarrow S^{-2}$

$Fe^{+3} + 1e^- \rightarrow Fe^{+2}$

3. oxidizing and reducing agents

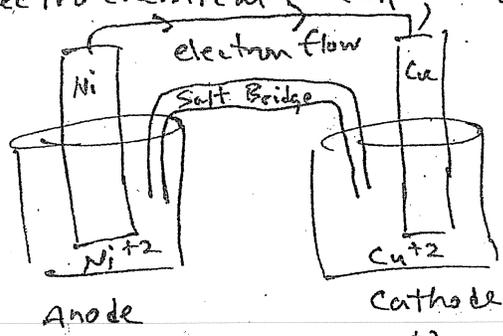
4. Rules for assigning charges "oxidation numbers"

- A. Free elements 0
- B. Alkali metals +1 in comp'ds
- C. Alkaline earths +2 " "
- D. Hydrogen +1 in comp'ds
- E. Oxygen -2 in comp'ds
- F. Sum of charges in comp'd = 0
- G. Sum of charges in polyatomic = charge on polyatomic

$Fe^{+2} + MnO_4^- + H^+ \rightarrow Fe^{+3} + Mn^{+2} + H_2O$

Identify oxidizing and reducing agent
write half reactions
balance equation!

5. Electrochemical Cell, Galvanic Cell, Voltaic Cell, Battery

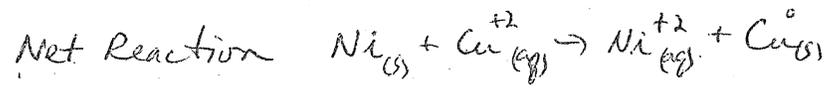
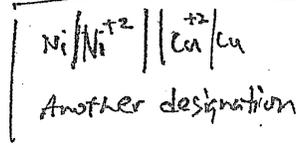


- 2 Half Cells
- A. Oxidation = Anode
Ni
 - B. Reduction = Cathode
Cu

$Ni \rightarrow Ni^{+2} + 2e^-$ $v = .25$

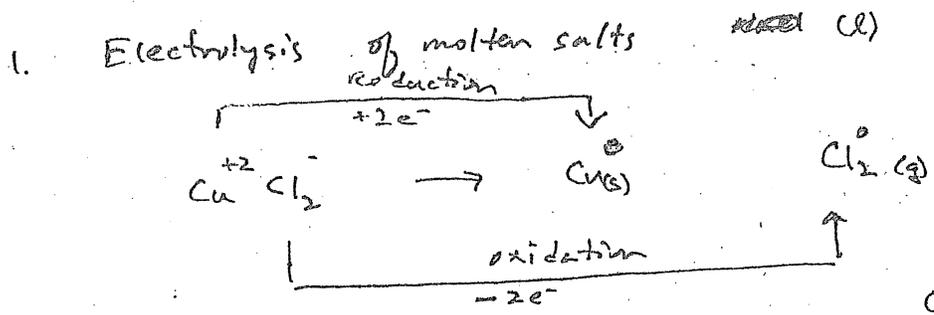
$Cu^{+2} + 2e^- \rightarrow Cu$ $v = .34$

$E_{cell}^{\circ} = E_{ox}^{\circ} + E_{red}^{\circ} = .59 \text{ volts}$



Electrolytic Cell : Electrolysis Electroplating

Non Spontaneous redox reactions $\Delta G \oplus$
Forced redox with help of power supply



Cation reduced to metal
Anion oxidized to element

Calculations
 $C = \text{amps} \times \text{seconds}$
 $q = I \times t$
 1 mole $e^- = 96,500 \text{ coulombs}$

2. Electrolysis of Salt Solutions (aq)

- If metal is transition element, it will be reduced at (-) electrode
- If metal is alkali or alkaline earth then the Hydrogen in water will be reduced at - electrode
 $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$
- If anion is F^- , NO_3^- , or SO_4^{2-} then the O in the water will be oxidized at + electrode
 $2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4e^-$
- All other anions will be oxidized at the \oplus electrode
 $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ etc.

3. Electroplating :

object to be plated is the - electrode
The object attracts metal cations to itself and the cations are reduced to metal atoms which "stick" to the objects surface.