

Uncertainty = Margin of error in a given measurement.

Analytical Balances: Mettler Model

←	PB 302	$\pm 0.01g$	least precise
←	PE 160	$\pm 0.001g$	
←	AB 104/204	$\pm 0.0001g$	Most precise

TD = Calibrated to deliver

TC = Calibrated to contain

x = observed value x_t = true value

Absolute error: $\Delta x = x - x_t$

Relative error: $\frac{\Delta x}{x_t}$

errors

- Indeterminate (random): Cause poor precision
- Determinate (systematic): Cause poor accuracy but don't affect precision.

Acid-Base Titration

KHP = Potassium Hydrogen Phthalate.

Strong Acid/Base = strong electrolyte \Rightarrow Complete dissociation in water

Weak Acid/Base = weak electrolyte \Rightarrow Incomplete dissociation.

Ion-Product Constant of water = K_w

$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ C$$

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

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

$$pH + pOH = 14$$

Volumetric Analysis = A technique used for determining the amount or concentration of a certain substance by doing a titration.

- Primary standard: solution of accurately known concentration contained in the buret in titration.

- Secondary standard: Is titrated with a primary standard to determine its concentration. ex NaOH.

- Standardize = determine exact concentration.

* Properties of Good Primary Standards:

- High Molar Mass
- Stable
- Not hygroscopic
- Highly pure
- Cheap & available

* Prop. of a good titration:

- fast
- Complete
- Reactants should be stoichiometric

* Neutralization:



* equivalence pt. = theoretical

end pt. = change in color.

* Indicators: Weak acids/bases.

phenolphthalein



$$\text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

if $\frac{[\text{HIn}]}{[\text{In}^-]} \geq 10 \Rightarrow$ color of HIn predominates

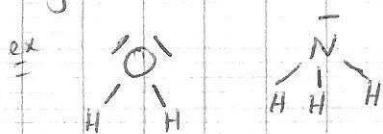
if $\frac{[\text{HIn}]}{[\text{In}^-]} \leq 0.1 \Rightarrow$ color of In⁻ predominates.

$$\text{pH} = \text{pK}_a \pm 1$$

$$C = \frac{n}{V}, n = \frac{m}{M}, \text{ at eq. pt. } n_{\text{H}^+} = n_{\text{OH}^-}$$

Determination of EDTA in Shampoo and Magnesium in an unknown.

- * Coordination Compound: Typically consists of a complex ion & a counter ion. In this compound, part of molecular bonding is coordinate covalent.
- A complex ion contains a central Metal cation bonded to one or more e^- donating groups. The molecules or ions that surround the ~~ligand~~ ~~metal~~ metal in a complex ion are ligands.
- A ligand has at least 1 unshared pair of valence e^- (s)



- donor atom: atom in a ligand that is bound directly to the metal atom.
- Coordination number = no. of donor atoms surrounding the central metal.
- Chelate: cyclic complex formed when a cation is bonded by two or more donor groups in a single ligand.
- Complexometric titration: formation of a colored complex indicates end-point.

* Common Structures of Coordination Compounds:

linear, square planar, tetrahedral, & Octahedral.

* Types of ligands:

- Based on charge

Neutral, $-$ vely charged
 NH_3, H_2O Cl^-, F^-, OH^-

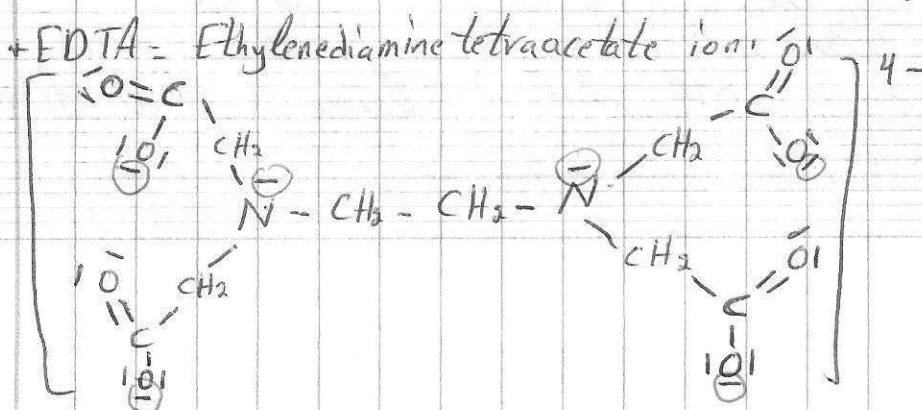
- Based on # of e^- donating groups (pairs)

one pair: Monodentate NH_3

bidentate, tetradentate...

$NH_2CH_2CH_2NH_2$

EDTA: Hexadentate



Semi-Micro Qualitative Analysis of Ag^+ , Cu^{2+} , Fe^{3+} & Al^{3+}

Ag^+ : Silver ion, Cu^{2+} : Copper ion, Fe^{3+} : ferric ion, Al^{3+} : Aluminium ion,

Group Reagent: Is the reagent that, when added to a mixture of ions, precipitate one or more ions & leave the others in solution.

Separation Methods: Precipitation, amphotericism & Complexation

Precipitation:

Group reagent

HCl (Cl^-)

H_2S (S^{2-})

$NH_3 + NH_4Cl$ (OH^-)

Ion precipitated

Ag^+

Cu^{2+}

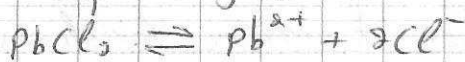
Al^{3+}, Fe^{3+}

Precipitation: $Q > K_{sp}$

Solubility product of a compound is the product of the Molar concentration of constituent ions each raised to the power of its stoichiometric coefficient.



$$K_{sp} = [Ag^+][Cl^-]$$



$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

Smaller $K_{sp} \Rightarrow$ less soluble compound.

Molar solubility (mol/l): no. of mols of solute dissolved in 1 l of a saturated solution.

Solubility (g/l): no. of grams of solute " " " " 1 l. . .



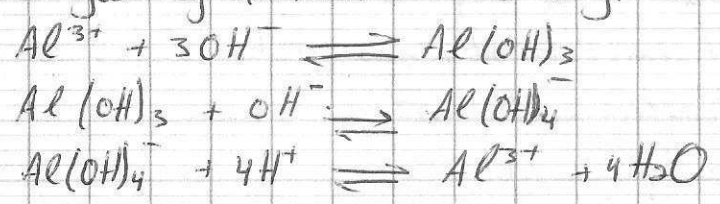
$$K_{sp} = [Ag^+][Cl^-] = s^2 \Rightarrow s = \sqrt{K_{sp}}$$

Solubility (g/l) = Solubility (M/l) \times M
molar mass

- * **Common Ion Effects:** Is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.
The presence of a common ion decreases the solubility of the salt.

* **Amphoterism**

- Some metal hydroxides will redissolve in an excess of hydroxide ion to yield hydroxy-complex ions.
- In such a case the slightly soluble metal hydroxide acts as a weak acid toward the base OH^- .
- It is therefore possible to separate amphoteric metal hydroxides from other insoluble hydroxides.
- After filtration, the complex ion in the filtrate may be destroyed by addition of acid to yield the simple metal ion.

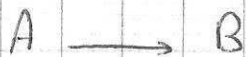


* **Separation based on formation of ammine complexes.**

- Certain metal ions complex with ammonia to give ammine complex ions.
- Addition of concentrated ammonia to a mixture of metal ions results in the formation of slightly soluble metal hydroxides (NH_3 reacts as base) followed by complexing of some metal ions (NH_3 reacts as a complexing agent)



Factors Affecting Rxn Rates.



$$\text{Rxn rate} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

Factors affecting rxn rates:

- Nature of the rxn
- Concentration of reactants.
- Surface Area
- Temperature.
- Presence of a catalyst.



$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

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

overall order is $m+n$

Order

Rate law

Integrated Rate law

0

$$\text{rate} = k \text{ (M/s)}$$

$$[A] = [A]_0 - kt$$

1

$$\text{rate} = k[A] \text{ (s}^{-1}\text{)}$$

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

2

$$\text{rate} = k[A]^2 \text{ (M}^{-1}\text{s}^{-1}\text{)}$$

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

as temp. \uparrow , rate \uparrow

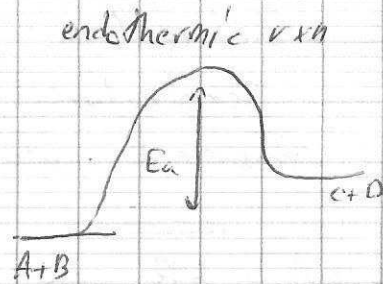
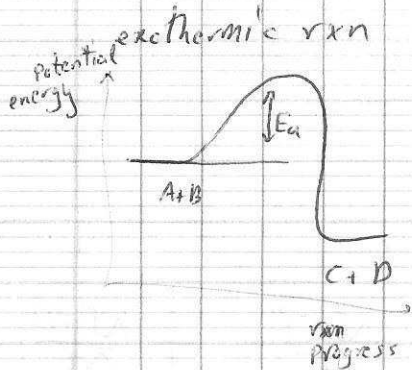
Half life $t_{1/2}$ is the time required for the concentration of a reactant to decrease to half of its initial concentration

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

$$0\text{-order} \Rightarrow t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

$$1^{\text{st}}\text{-order} \Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

$$2^{\text{nd}}\text{-order} \Rightarrow t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$



Activation Energy E_a = minimum amount of Energy required to initiate a chemical rxn.

$$k = A e^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

Arrhenius eqn.

E_a = activation energy (J/mol)

R = gas const = 8.314 J/K.mol

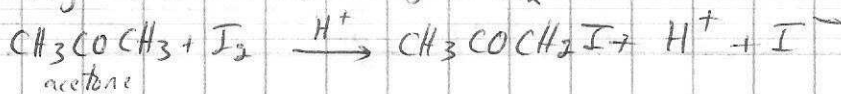
T = absolute temp. in Kelvin

A = frequency factor

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

A catalyst is a substance that increases the rate of a rxn through decreasing activation energy.

* larger surface area \Rightarrow higher rate.



* Absorption Spectrum: Plot of absorbance A vs. wavelength λ .

* Spectrophotometer: A lab instrument that measures the amount of light transmitted through a sample.

Components: Source of light, Monochromator (wavelength selector), Sample container, Radiation detector, Recorder.

$I_t < I_o$
transmitted light \leftarrow incident light

Transmittance: $T = \frac{I_t}{I_o}$ $T < 1$ $\%T = \frac{I_t}{I_o} \times 100$

Absorbance: $A = -\log T$

* Beer-Lambert's Law:

factors that control the amount of light energy absorbed:

- Concentration
- thickness of sample
- Probability of light absorption (Molar absorptivity coefficient or extinction coefficient).

$$A = \epsilon b c$$

A : absorbance at λ_{max}

ϵ : extinction coeff, ($M^{-1} cm^{-1}$), $f(\lambda, temp, solvent)$

b : width of cuvet (cm)

c : Molar concentration.

Calibration curve: ~~Plot~~ Plot of A vs. C .

Equilibrium $\rightarrow aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \dots \text{equilibrium cst expression}$$

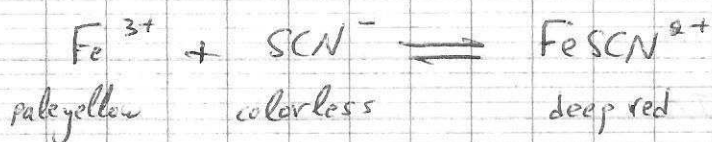
* Le Chatelier's Principle:

When a stress is applied to a system at equilibrium the system will shift in such a direction to relieve the stress & establish a new state of equilibrium.

* factors affecting ~~change in~~ chemical equilibrium:

- Change in concentration,
- Change in temperature
- Change in volume or pressure.

* Formation of FeSCN^{2+} complex ion:



$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$$

$$\lambda_{\text{max}} = 447 \text{ nm}$$

Spectrophotometric determination of pK_a of BTB

* K_b = base ionization cst

$$K_a \times K_b = K_w$$

* A buffer solution is a solution of a weak acid or a weak base, and the salt of the weak acid or weak base. It has the ability to resist changes in pH upon addition of small amounts of either acid or base, or upon dilution.

* Henderson - Hasselbalch Eqn. (for buffer solutions)

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

acetate: CH_3COOH .

* Buffer Capacity represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH. It is determined by the magnitudes of $[HA]$ & $[A^-]$.
optimal buffers equimolar mixture of acid & its salt.
 $\Delta pH = pK_a$

* Acid-Base Indicators: Are weak acids or weak bases.

acidic form: HIn

basic form: In^-



$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

when $[In^-] = [HIn] \Rightarrow pH = pK_a$

* BTB: 3,3'-dibromothymol sulfon-phthalein (pH range: 6 → 7.6)
Yellow in acidic & Blue in basic.

$pK_a = pH$ where $A = \frac{A_{max}}{2}$

$$\frac{[In^-]}{[HIn]} = \frac{A_{\lambda_2} - A_{\lambda_1} \text{ (lowest pH)}}{A_{\lambda_1} - A_{\lambda_2} \text{ (highest pH)}}$$

Plot pH vs. $\log \frac{[In^-]}{[HIn]}$ \Rightarrow y-intercept = pK_a

Thermodynamics of the dissolution of Borax.

* 1st law of thermodynamics: law of conservation of energy ($E_{univ} = \text{cst}$).

* 2nd law: Predict whether a rxn is spontaneous.

In any spontaneous process: $\Delta S_{universe} > 0$ (entropy increase)

* Entropy S : Is a measure of randomness or disorder.

* Enthalpy H : Used to quantify heat flow into or out of a system in a process @ cst pressure.

$$\Delta H = H(\text{products}) - H(\text{reactants}) = \text{heat given off/absorbed in a rxn}$$

$\Delta H > 0 \Rightarrow$ endothermic, $\Delta H < 0 \Rightarrow$ exothermic.

* Standard free-energy of a rxn (ΔG°_{rxn})



$$\Delta G^\circ_{rxn} = [c\Delta G^\circ_f(C) + d\Delta G^\circ_f(D)] - [a\Delta G^\circ_f(A) + b\Delta G^\circ_f(B)]$$

$$\Delta G^\circ_{rxn} = \sum_n \Delta G^\circ_f(\text{products}) - \sum_m \Delta G^\circ_f(\text{reactants})$$

↑
stich. coeff.

* ΔG°_f : standard free energy of formation, which is the free energy change that occurs when 1 mole of the compound is formed from its elements in their standard states.

$\Delta G^\circ_f = 0$ for element in its stable form.

$$\boxed{\Delta G = \Delta H - T\Delta S}, \text{ spontaneous process} \Rightarrow \text{free energy} \downarrow$$

G = Gibbs free energy

$\Delta G < 0 \Rightarrow$ spontaneous ($\Delta S_{univ} > 0$)

$\Delta G > 0 \Rightarrow$ non-spontaneous

$\Delta G = 0 \Rightarrow$ equilibrium ($\Delta S_{univ} = 0$)

$$\Delta G = \Delta G^\circ + RT \ln Q \quad Q = \text{rxn quotient}$$

at equilibrium: $\Delta G = 0$ & $Q = K \Rightarrow \Delta G^\circ = -RT \ln K$

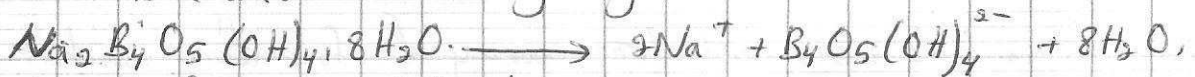
$$\Delta G^\circ = -RT \ln K \quad \& \quad \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Rightarrow \ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

plot $\ln K$ vs. $\frac{1}{T} \Rightarrow$ str. line & slope = $-\frac{\Delta H^\circ}{R}$ & y-intercept = $\frac{\Delta S^\circ}{R}$

+ Borax = Sodium tetraborate octahydrate

- slightly soluble salts acts as weak base in water,
- Naturally occurring compound,
- Important source of Boron,
- It is a water softening agent.

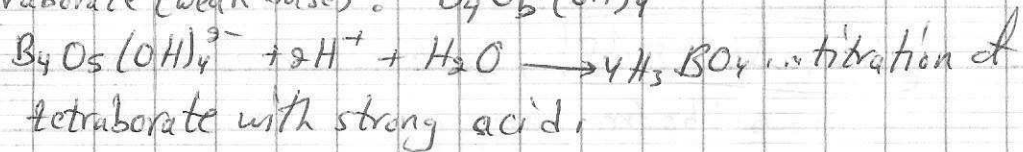


$$K = [\text{Na}^+]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] = K_{sp}$$

> borax solvation rxn.

$$\text{Stoich.} \Rightarrow K_{sp} = 4 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]^3$$

tetraborate (weak base): $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$



$$\ln \frac{K_{sp1}}{K_{sp2}} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

theoretical values: $\Delta H^\circ = 110 \text{ kJ/mol}$ & $\Delta S^\circ = 380 \text{ J/Kmol}$

Impurities in natural water,

* MCLs = Maximum Contaminant Levels established by the Environmental Protection Agency (EPA) for some of the most common and/or potentially dangerous identified water pollutants,

* Water Contaminants:

- Materials dissolved in water:

o Inorganic Compounds

> dissolved gases O_2 , N_2 , NH_3 , H_2S , (NO_x) ,

> Metal & Metalloid +ve ions: aluminum, arsenic, lead, mercury, calcium, magnesium, sodium, potassium, zinc, copper...

> -ve ions: chloride, fluoride, nitrate, nitrite, phosphate, sulfate...

o Organic Compounds:

> Synthetic organic chemicals, carbon tetrachloride,

> Benzene & Vinyl chloride.

- Materials Suspended in water: Sand, clay...

- Microorganisms: Viruses, Bacteria, Protozoans, Cryptosporidia & giardia.

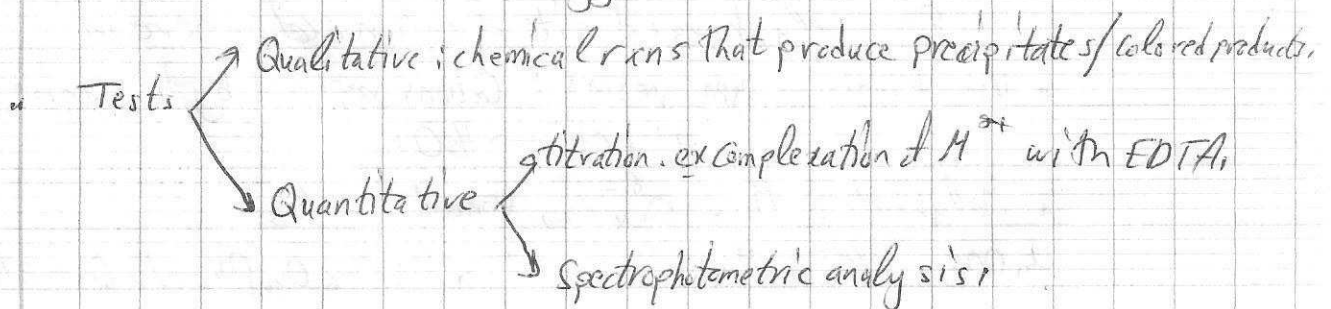
* Phosphate is a major contaminant of water,

It is an ingredient in detergents & fertilizers,

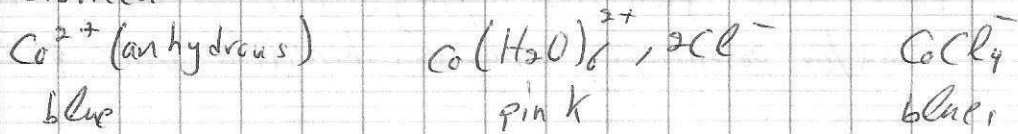
Phosphate causes eutrophication (excessive growth of algae),

PO_4^{3-}

→ depletion of dissolved oxygen in water,

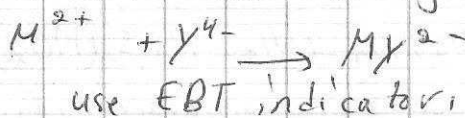


* Distillation: dissolve few crystals of cobalt chloride in water & distillate.



* Cations in tap water:

hardness in Ca^{2+} & Mg^{2+} ; complex with EDTA:

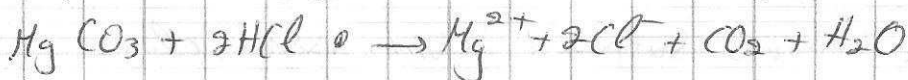
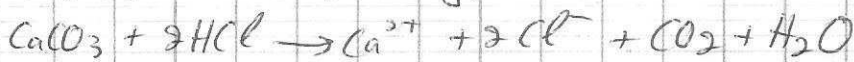


* Anions:

chloride Cl^- : use silver ion test: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$

sulfate SO_4^{2-} : Barium ion test: $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$

Carbonate: Add HCl (fizzing):



used for water softening.

* Resins: Are polymers with cross-linking (connections between long chains in a polymer). A resin has active groups in the form of electrically charged sites that attract ions.

Key factors: affinity for a specific ion & no. of active sites.

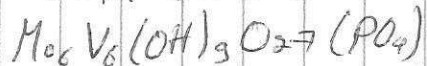


R: -vely charged site of cation exchange resin

* Use deionizing type resins: cations replaced by H^+ , anions by OH^-



* Molybdate: $\text{Mo}_7\text{O}_{24}^{6-}$, vanadate: VO_3^-



vanadomolybdo phosphoric acids