12/12/17. Chemistry (Ruchi Miss)

Chapters

1) Concept of Qualitative Analysis.

2) Acid Base Theories.

ACIDS, BASES THEORIES.

1) Arrhenius concept:

MCQ

[Water system concept]

In 1884, Arrhenius suggested theory of electrolytic dissociation for acids and bases. Acc. to Arrhenius concept, an acid is any hydrogen containing compound which produces H^+ ions (or hydronium H_3O^+ ions); ~~In~~ in aq. sol^n and base is any compound which produces OH^- ions in aq. sol^n.

Compounds like HCl, CH_3COOH are acids as they produce H^+ ions in aq. sol^n;

$HCl \longrightarrow H^+ + Cl^-$

$H^+ + H_2O \longrightarrow H_3O^+$.

Compounds like NaOH, NH_4OH are bases as they produce OH^- ions in aq. sol^n

$NaOH \longrightarrow Na^+ + OH^-$

* Applications of Arrhenius Concept

1) Aq. sol^{n}s of oxides of non-metals (SO_3, SO_2, CO_2,) are acidic as they produces H^+ ions in water.

eg:- $H_2O + SO_3 \longrightarrow H_2SO_4$

$2H^+$ SO_4^{-}

2) Compounds like NH_3 and aq. sol's of metallic oxides like CaO, Na_2O are basic as they produce OH^- ions in water.

eg: i) $CaO + H_2O \longrightarrow Ca(OH)_2$

Ca^{2++} $2OH^-$

ii) $Na_2O + H_2O \longrightarrow 2NaOH$

$2Na$ $2OH^-$

3) Neutrilization of acids by base in aq. sol^n can be understood by this concept.

4) Quantitatively, strength of an acid ~~as~~ and base can be expressed in terms of ionization or dissociation constant in aq. sol^n.

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

$$Ka = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

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* Limitations of Arrhenius concept.

1) Acc to this concept, acidic and basic property is dependent only on its <u>aqueous solution</u>.

eg HCl is an acid only aq solution, true is not considered as acid gaseous state.

2) It does not explain acidic and basic character in non-aq. solvents

3) It could not account for acidic character shown by the salts like $AlCl_3$ in aq. sol^n.

4) Neutralization reactions are limited to aq. sol^ns only but neutralization reactions do occur in non-aq solvent and even in absence of solvents or in the gas phase.

eg: formation of NH_4Cl (solid) by ~~comp~~ combination of NH_3 (g) and HCl (g), cannot be explained.

$$\underset{(g)}{NH_3} + \underset{(g)}{HCl} \longrightarrow NH_4Cl\,(s)$$

ammonium chloride.

2.) Lowry Bronsted Concept: MCQ

[Protonic Concept]

Lowry and Bronsted in 1923 proposed a concept for acids and bases. It does not requires solvent participation. Acc. to Lowry and Bronsted, acid is an proton donar and base is a proton acceptor. eg: $HCl \longrightarrow H^+ + Cl^-$

HCl looses 1 proton to give ~~Cl~~ H^+, hence it a acid, similarly Cl^- accepts a proton, hence it a base.

$$* \; \underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \longrightarrow \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-}$$

In the above reaction CH_3COOH donates the proton, hence it is an acid. H_2O accepts some protons, so it acts as a base.

Similarly in reverse Hydronium (H_3O^+), it donates a proton and acts as acid and acetate ion (CH_3COO^-) accepts a proton and behaves as a base.

Such pair of acid and base which can be formed by mutual gain or loss of proton is known as conjugated acids base pair.

$$* \underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{conjugated acid}}{NH_4^+} + \underset{\text{conjugated base}}{Cl^-}$$

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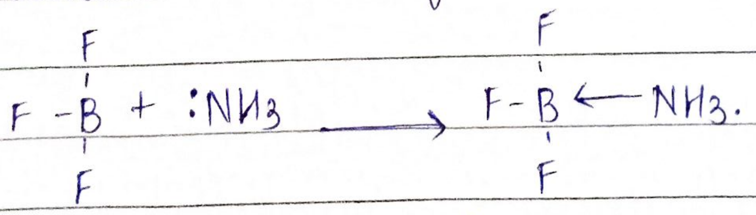
3) Lewis Concept:

MCQ

[Electron pair acceptor donar concept]

Lewis defined acid as a subtance which can accept an electron pair from other subtance and form co-ordinate covalent bond. Similarly base is defined as a subtance which can donate an electron pair and form co-ordinate covalent bond. In other words, acid is an electron pair acceptor and base is a electron pair ~~don~~ donar. An acid should have a vaccant orbital to accept the electron pair donated by the base.

eg:- when NH_3 reacts with BF_3, boron accepts electron pair from Nitrogen from NH_3 and form coordinate covalent bond. Therefore BF_3 is an acid and NH_3 is a base.



$$F-\underset{F}{\overset{F}{B}} + :NH_3 \longrightarrow F-\underset{F}{\overset{F}{B}}\leftarrow NH_3.$$

On the basis of Lewis concept, process of neutralization is the formation of coordinate covalent bond between an acid

Adduct·

and base to form neutrilization products called ~~Adduct~~

* The concept of base in Lowry Bronsted concept and the concept of base in Lewis concept is same.

* **Lewis Acids :-***

① Simple Cations:- All simple cations are potential Lewis acids. eg :- Cu_2^+, Ag^+.

② Molecules with central atom having incomplete octate :- Electron deficient molecules like BF_3, $AlCl_3$, etc readily accept electron pair from Lewis bases. Hence they are Lewis acids.

$Cl_3Al + N(C_2H_5) \longrightarrow$

③ Molecules having multiple bonds between atoms that differ in electronegativity. eg:- CO_2, SO_2, etc. In these molecules, O_2 is more electronegative than C or S. Hence 'π' electron density in the molecule is shifted towards O_2 ie away from C or S. Hence C, or S atoms readily accepts electron pair from Lewis base and form coordinate covalent bond.

④ Molecules containing a central ~~atter~~ atom with vacant d-orbital :- In molecules like $TiCl_4$, SF_4; The central atom has vacant d-orbital and they readily accept electron pair from Lewis base and form ~~adduct~~ adduct.

* Lewis Acid Strength Of Simple Cations.

The lewis acid strength depends on the foll. properties of the cations;

① Ionic radius of cation - Smaller the radius, greater is the tendency to accept electron pair and hence stronger is the lewis acid strength.

② Oxidation state of the cation - Lewis acid strength increases with the increase in its oxidation state. eg: Lewis acid strength of Fe^{2+} is less than that of Fe^{3+}.

* Lewis Bases.

① Anions / All negative ions:- Anions or all negative ions like Cl^-, F^-, OH^-, etc can donate lone pair of e^- to lewis acids.

② Molecules having central atoms with one or more unshared electron pair - eg:- NH_3, H_2O, H_2S, etc have lone pair of electrons; hence are lewis bases.

③ Molecules having double bonds like C=C:- The electron pair from π bond is donated to the lewis acid and forms π complexes.

* Lewis base strength.

① Size of the central atom - Lewis base strength decreases with the ~~size of~~ increase in the size of the central atom.

② It also depends on the lone pair of electron. Greater the no. of lone pair, lesser is the tendency to donate and lesser is the base strength.

* Advantages of Lewis concept.

① Lewis concept is more general that than Lowry Bronsted concept

② Concept includes the reaction in which protons are not involved

③ Acidic and Basic property of non-metallic and metallic oxides can be explained.

④ Many high temp.; non-solvent reactions are included.

* Limitations.

① Relative strength of lewis acids and bases cannot be explained.

② Acid-Base reactions should be fast reaction bu many lewis acid-base reactions are slow.

4) * Solvent solute system.

[Autoionisation Concept]

Acc. to this concept, the substances which ~~might~~ when dissolved in a solvent form cation characterist of that solvent i.e increases the catonic characteristics of the solvent are called acids. Similarly substance which when dissolve in solvent forms anionic characte-istics of solvent i.e increase in the ~~anor~~ ~~anionic~~

anionic characteristics of the solvent ~~are~~ are called base.

eg:- $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

Acid Base.

* Advantage of solute solvent system.

The concept helps to explain the acid and base reactions occurring in aq. and non aq. solvent which may be protonic or non protonic

* Limitations.

1) Limited to ~~at~~ solute solvent system only. Does not explains acid base reaction which occurs in absence of solvent.

2) This concept concentrates more on ionic reactions and chemical properties. It ignores physical property.

5) Lux-Flood Concept

According to this concept, acid ~~when~~ which accepts oxide ions and base is the substance which donates oxide ions.

6) HSAB Concept. (Hard Soft Acid Base)

i) Hard Base - They are having high electronegativity and low polarizability and are hard to oxidized. They include nitrogen, oxygen, fluorine.

ii) Soft Base- Electronegative is hard they include substances of low electronegativity and high polarizability and are easily ~~to~~ oxidized eg Phosphorous, Sulphur, Bromine, etc.

iii) Hard Acids - Atoms or substances are smaller in size and high positive charge are hard acids. eg Lithium, Sodium, Potassium.

iv) Sof Acids- Large in size, low positive charge

★ PEARSON PRINCIPLE.

According to pearson, hard acid prefer to bind hard base and soft acids prefer to bind with soft bases to form complexes.

Pearson's Principle ~~a~~ is an approximate qualitative prediction of relative stabilities for the complexes and is not a theory or any explanation of the observation.

★ Applications of HSAB

1) Relative stability of the complexes.

eg:- $[AgI_2]$ is more stable than $[Ag$ ~~I_2~~ $F_2]^-$

AgI_2 anion is more becoz Ag^+ is a soft acid and I^- is soft base. Hence they combine to give AgI_2^-.

F^- is hard base and Ag^+ is soft acid. So AgF_2^- is less stable.

$Ag^+ + 2I \longrightarrow [AgI_2]^-$

soft hard   soft base

$Ag^+ + 2F^- \longrightarrow [AgF_2]^-$

soft Hard   hard base.

2) ~~S)~~ Occurance of Minerals- $[Ca^{2+}, Mg^{2+}, Al^{3+}]$

$CaCO_3$, $MgCO_3$, Al_2CO_3.

$Cu^+ \longrightarrow Cu_2S$

$Ag^+ \longrightarrow Ag_2S$

$Hg^+ \longrightarrow Hg_2S$

* sulphide - S^{2-}

sulphate SO_4^{2-}

sulphite - SO_3^{2-}

3) Poisoning of metal Catalyst

4) Course of chemical Reaction.

① $H^+ + CH_3HgOH \rightleftharpoons H_2O + CH_3Hg^+$

② $H^+ + CH_3HgSH \rightleftharpoons H_2S + CH_3Hg^+$

★ Application of Acid Base Concept.

① In Acid Base titration

★ i) Acid Base Titration
ii) Redox titration.
iii) Complexometric titration.
iv) Precipitation titration.

★ Acid Base Titration - In this, neutrilization involves determination of amount of acid and base required for the ~~completion~~ complete rea^n. of acid and base. This point is known as equivalence point or theoretical end point which involves indicator. The end point of acid depends on pH. The pH of sol^n depends on analyte and titrant.

A graph of pH versus volume of titration is known as nutrillization curve or titration curve. PH during the titration can be theoritically calculated which is used in the concentration of titration curve.

★ Construction of titration curve :-

- Titration of strong Acid and strong Base.

1) At the start of titration, we have taken 10 cm^3 of 0.1 M HCl. In beginning the pH is 1.

2) We will add 5 cm^3 of 0.1 M NaOH

$$[H^+] = \frac{\overset{\text{concentration of HCl}}{5} \times \overset{\text{Molarity}}{0.1}}{\underset{\text{acid + base}}{15}}$$

$= 0.033$

$pH = \log [H^+]$

$= -\log$ of 0.033

$= 1.418$

3) 99 cm^3 of NaOH.

$[H^+] = \frac{0.1 \times 0.1}{19.9} = 0.00050$

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

$= -\log [0.005]$

$= 3.30.$

4) when 10 cm^3 of NaOH is added (at equilance pt), soln will be neutral and pH will be equal.

5.) When 10.1 cm^3 of NaOH is added. Total volume is 20.1.

$[OH^-] = \frac{0.1 \times 0.1}{20.1} = 0.0004975$

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

$= -\log [0.0004]$

$= +3.30$

$\because pH + pOH = 14.$

$\therefore pH + 3.30 = 14$

$\therefore pH = 10.7$

6.) When 11 cm^3 of NaOH has been added. Calculate pH.

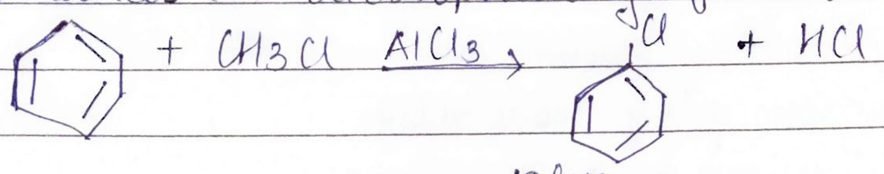
$[OH^-] = \frac{\cancel{0}1 \times 0.1}{21} = 0.000476.$

∴ $pOH = -\log[0.00^{0}476]$
$=$ ~~3.322~~ 2.32

∵ $pH + pOH = 14$
∴ $pH +$ ~~3.32~~ $= 14$
∴ $pH =$ ~~10.68~~ 11.68.

* Friedel Craft's Reaction.

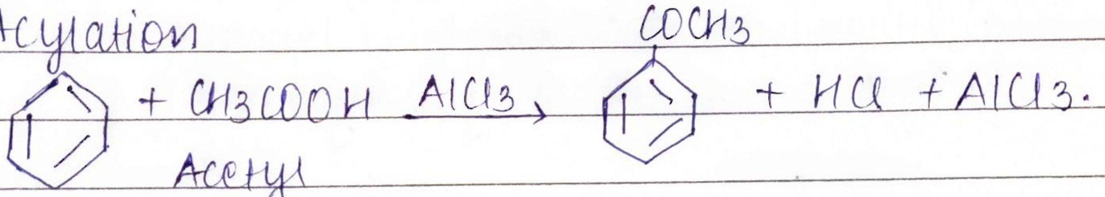
A] Alkylation : Alkyl halides with $AlCl_3$ as a Lewis acid catalyst is used in this process $AlCl_3$ enhances (↑) electrophilicity of the alkyl halides.



(Subs)

toluene

B] Acylation



Acetyl chloride

Acetophenone.

* electrophile ⟶ +ve charge ⟶ goes to e⁻ rich atom.