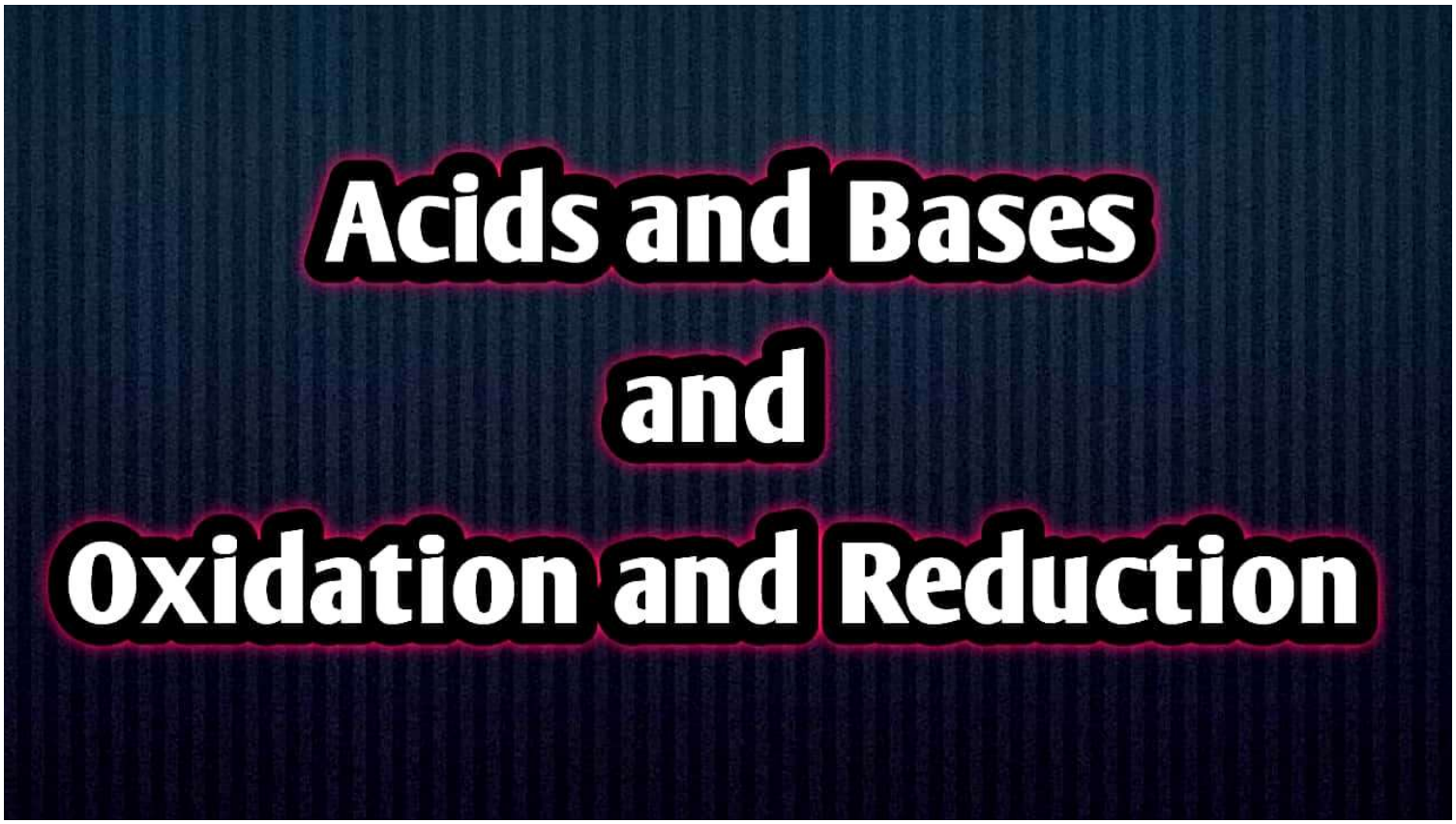

Unit-5 Acid and Base

1. Arrhenius concept :-

20%

Acc. to this concept an acid is hydrogen containing compⁿd which gives $H^{\oplus}$ (proton) ion in aq. solⁿ and base is substance which gives $OH^{\ominus}$ (hydroxyl ion) in aq. solⁿ.

Acid →

$HA \xrightleftharpoons{H_2O} H^+ + A^-$

$HCl \xrightarrow{H_2O} H^+ + Cl^-$

HNO_3 " $H^+ + NO_3^-$

H_2SO_4 " $H^+ + HSO_4^-$

HSO_4^- " $H^+ + SO_4^{-2}$

Base →

$BOH \xrightleftharpoons{H_2O} B^+ + OH^-$

$NaOH$ " $Na^+ + OH^-$

KOH " $K^+ + OH^-$

NH_4OH " $NH_4^+ + OH^-$

$Ca(OH)_2$ " $Ca^{+2} + 2OH^-$

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Strength of Acid and Base acc to arrhenius theory :—

Acid ~~Base~~ which are almost completely ionised in aq. sol^{n} are termed as ~~strong~~ acids whereas acid which are weakly ionised in aq. sol^{n} are term as weak acids.

⇒ The base which are completely ionised → Strong Base
The base which are weakly ionised → weak base.

Acidic strength $\propto K_a$
$\propto \frac{1}{pK_a}$

K_a = acid dissociation constant

$pK_a = -\log K_a = \log \frac{1}{K_a}$

Basic strength $\propto K_b$
$\propto \frac{1}{pK_b}$

K_b = Base dissoci^{n} constant

S.A	S.B	W.A	W.B
HCl, HNO_3	NaOH	CH_3COOH	NH_4OH,
H_2SO_4	KOH		$Ca(OH)_2$

Acid and Base react to give salt and water, this rxn is called neutralisation rxn.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Limitation of Arhenius theory →

1. Acc to this concept HCl is regarded as an acid only when dissolved in H_2O and not in some other solvent as when it exist in gaseous form.

2. It does not explain acidic nature of CO_2 & SO_3 gases.

★ 3. It can't explain the acidic & basic character of certain salt which does not provide H^+ & OH^- in aq. soln.

2. Bronsted Lowry concept :-

Acc^r to this concept acid are proton donor while bases are proton acceptor.

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Acid

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

Cationic sps ⇒ $H_3O^+ \longrightarrow H^+ + H_2O$

Anionic sps ⇒ $HCO_3^- \longrightarrow H^+ + CO_3^{-2}$

Bases

neutral ⇒ $H_2O + H^+ \longrightarrow H_3O^+$

Cationic ⇒ $[Al(H_2O)_5(OH)]^{+2} + H^+ \longrightarrow [Al(H_2O)_6]^{+3}$

Anionic ⇒ $HCO_3^- + H^+ \rightarrow H_2CO_3$

Conjugate Acid - Base Pair

Conjugate acid-Base pair have only diff of 1 proton. And acid have 1 proton extra from conjugate base.

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

Acid — conjugate base

$NH_3 + H^{\oplus} \longrightarrow NH_4^{\oplus}$

Base — conjugate acid

CABP-2

- Acid-1 + Base-2 ⟶ C.B-1 + C.A-2

CABP-1

CABP-2

- $HCl + NH_3 \longrightarrow Cl^{\ominus} + NH_4^{\oplus}$

Acid-1 Base-2 Base-1 Acid-2

CABP-1

Strong Acid ⇒ Weak conjugate Base
Weak Acid ⇒ Strong conjugate Base

- The acidic or basic nature of comp'd depend upon the nature of solvent used.
for eg → H_2O is proton acceptor (Base) in HNO_3 but it is proton donor in liq. NH_3.

$$\underset{\text{Base-1}}{H_2O} + \underset{\text{Acid-2}}{HNO_3} \longrightarrow \underset{\text{Acid-1}}{H_3O^{\oplus}} + \underset{\text{Base-2}}{NO_3^{-}}$$

$$\underset{\text{Acid-1}}{H_2O} + \underset{\text{Base-2}}{NH_3} \longrightarrow \underset{\text{Base-1}}{OH^{\ominus}} + \underset{\text{Acid-2}}{NH_4^{\oplus}}$$

On the basis of ability to accept or donate proton solvent are classified in 4 category.

① Protogenic or proton donor solvent

Solvent that donate proton are known as ".

Eg → HF, H_2SO_4

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④ Protophilic or proton acceptor Solvent

Solvent that accept proton are K/as "

eg → liq NH_3, Pyridine

⑤ Amphiprotic Solvent

Solvent which are proton acceptor as well as proton donor are K/as "

eg → H_2O, Acetic acid

⑥ Aprotic Solvent

Solvent that are neither proton donor ones proton acceptor are K/as "

eg → liq SO_2, N_2O_4

Relative Strength of Acid & Bases :-

Acc to this concept a strong acid has greater tendency to donate a proton and a strong base has a greater tendency to accept a proton.

⑤ Antiprotic solvent

These solvent have nothing to do with proton. Due to self ionization they also furnish cations and anions similar to protonic solvent.

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Periodic variation of Acid and Base properties :-

① Hydracid of the element of same period

$CH_4 < NH_3 < H_2O < HF$

E.N ↑ , Acidic strength ↑ →

C.B $^{\ominus}CH_3 > ^{\ominus}NH_2 > OH^{\ominus} > F^{\ominus}$ Basicity Order

★ { Acidity strength ∝ E.N (in period) } ★

② Acidic strength of Hydracid of grp 16th and 17th elements

gp 17	gp 16
HF	H_2O
∧	∧
HCl	H_2S
∧	∧
HBr	H_2Se
∧	∧
HI	H_2Te

Size ↑, A.S ↑ ↓

★ { Acidic strength ∝ Size (in gp) } ★

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F^- Cl^- Br^- I^-

→

Size ↑, charge dispersion ↑, stability ↑
e^- donating capacity ↓, Basicity ↓

* poor base are good l.g

③ Basic strength of gp 15 elements

NH_3	Size ↑
PH_3	e^- density ↓
AsH_3	e^- donating capacity ↓
SbH_3	Basic strength ↓
BiH_3 ↓	

Labelling solvent and diff Rentiating solvent :-

2015 The strength of a protonic acid is dependent upon the nature of solvent in which acid is dissolved. The solvent in which complete proton transfer occurs are called labelling solvent.

In other words, the solvent in which acid or base is 100% ionised are called labelling solvent and this effect is k/as labelling effect.

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The solvent in which complete proton transfer does not occur is called differentiating solvent.

OR The solvent in which acid or Base is partially ionised is called differentiating solvent.

This effect is klas differentiating effect.

Eg→ Hf and HCl both are 100% ionised in liq NH_3 to give 100% $NH_4^{\oplus}$

Hence these acids appear to be of equal strength and liq. NH_3 acts as labelling solvent.

But in H_2O HF is partial ionised and whereas HCl, HBr, HI is 100% ionised Hence H_2O act as differentiating solvent for these ~~Solvent~~ acid.

Acid/Base	Levelling solvent	Differentiating solvent
① Strong acid HCl, HBr, HI, HNO_3 $HClO_4$, H_2SO_4	H_2O	CH_3COOH
② Strong A → HCl W.A → CH_3COOH	liq NH_3	H_2O

③ Strong base $NaOH$, $NaNH_2$, $NaOC_2H_5$	H_2O	liq NH_3
④ Strong base – $NaOH$ W.B – NH_4OH	CH_3COOH	H_2O

3. Lewis Concept :-

The species which can accepts atleast 1 l.p are K/as lewis acids they are e^- pair acceptor.

The spes which can donate its l.p to e^- deficient species to form cordiate bond are K/as lewis base. They are e^- donor.

$A: \quad + \quad B \longrightarrow A \longrightarrow B$

e^- pair donor — lewis base (e^- rich spes)

e^- pair — Lewis Acid (e^- defficient spes)

Adduct

- **Types of lewis base**

① All –ve ions

X^-, H^-, CN^-, NO_2^-, OH^-, OR^-, CO_3^{-2}, SO_4^{-2}

② Neutral molecule which have l.p

H_2O, $R-OH$, $R-OR$, $R-SH$, $R-S-R$, NH_3, $R-NH_2$, R_2NH, R_3N,

③ Organic molecule with π e⁻

R-C=C , R-C≡CH

H_2S, PH_3, PR_3, $\ddot{C}O$

- **Types of lewis acid**

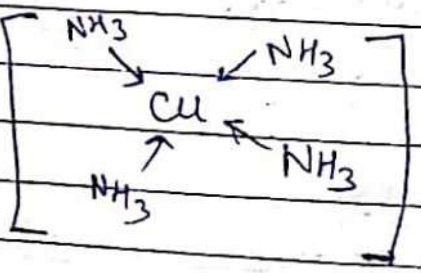
① Molecule containg a central atom with an incomplete octet.

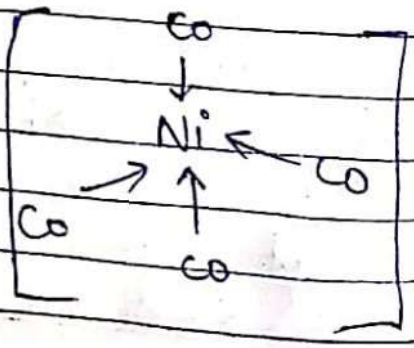
$BX_3 \rightarrow BF_3, BCl_3, BBr_3, BI_3$

$AlCl_3 \rightarrow X \neq F$

L·A	L·B	
$AlCl_3$	$+ Cl^{\ominus}$	$\longrightarrow AlCl_4^{\ominus}$
BF_3	$+ F^{\ominus}$	$\longrightarrow BF_4^{\ominus}$
BF_3	$+ :NH_3$	$\longrightarrow [F_3B \leftarrow NH_3]$

② ∴ Transⁿ metal atom as their ions

L·A	L·B	
Ag^+	$2 NH_3$	$\longrightarrow [NH_3 \rightarrow Ag \leftarrow NH_3]^+$
Cu^{+2}	$4 \ddot{N}H_3$	$\longrightarrow$ 

Ni $\quad 4 : CO \longrightarrow$ 

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③ Molecules with central atom which can expand its octet

The molecules in which central atom have vacant d - orbital. Can expand its octet by accepting e^- pair.

Eg → SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3
PF_5, SF_4, SeF_4, $TeCl_4$

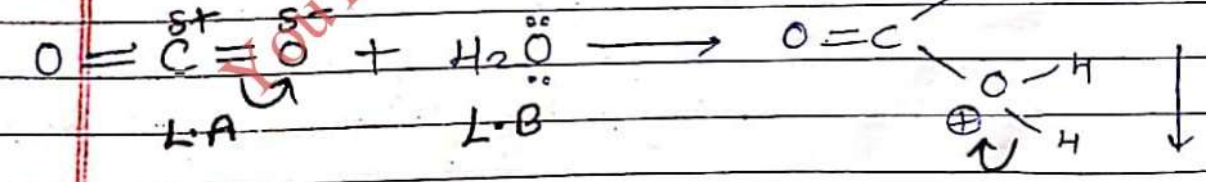
L.A L.B

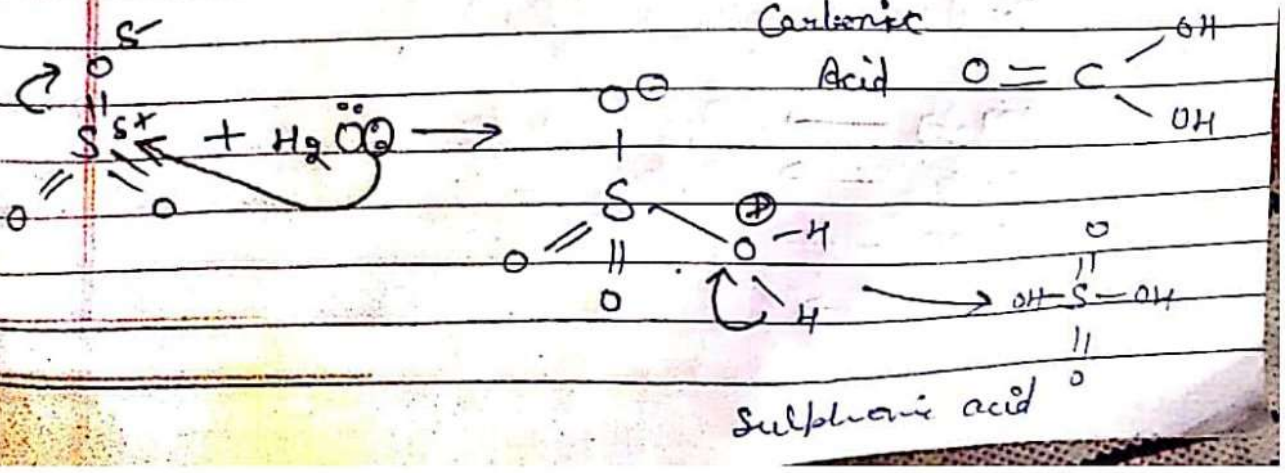
$SbF_5 + F^- \longrightarrow [SbF_6]^-$

$TiCl_4 + 2Cl^- \longrightarrow [TiCl_6]^{-2}$

④ Molecules having a multiple bond b/w atom of different ēvity

Eg → CO_2, SO_2, SO_3





⑤ Member of oxygen family

Element of Oxygen family have 6 e⁻ in their valence shell. So they can accept a lone pair and behave as lewis Acid.

L·A L·B

$\ddot{O}: + SO_3^{-2} \longrightarrow SO_4^{-2}$
Sulphate ion

$\ddot{\underset{\cdot\cdot}{S}}: + SO_3^{-2} \longrightarrow S_2O_3^{-2}$
thiosulphate ion

4. Lux Flood Concept :-

2019

Acc to this concept oxide ion acceptor are klas acids while oxide ion donor are klas base.

This is also klas oxide ion concept.

Oxide ion donor (Base) :-

$Na_2O \longrightarrow 2Na^+ + O^{-2}$
$CaO \longrightarrow Ca^{+2} + O^{-2}$
$MgO \longrightarrow Mg^{+2} + O^{-2}$
$PbO \longrightarrow Pb^{+2} + O^{-2}$

Oxide ion acceptor (Acid) :-

$SO_3 + O^{-2} \longrightarrow SO_4^{-2}$

$SiO_2 + O^{-2} \longrightarrow SiO_3^{-2}$

$CO_2 + O^{-2} \longrightarrow CO_3^{-2}$

$P_2O_5 + 3O^{-2} \longrightarrow 2PO_4^{-3}$

Hence Eg of acid Base rxn are following acc to lux flood concept :-

Base Acid

$3Na_2O + P_2O_5 \longrightarrow 2Na_3PO_4$

$PbO + SO_3 \longrightarrow PbSO_4$

$CaO + CO_2 \longrightarrow CaCO_3$

$FeO + SiO_2 \longrightarrow FeSiO_3$

Some oxide can donate as accept oxide ion hence behave as Amphoteric oxide.

(1) $ZnO \longrightarrow Zn^{+2} + O^{-2}$

Base

$ZnO + O^{-2} \longrightarrow ZnO_2^{-2}$

Acid (Zincate ion)

(2) $Al_2O_3 \longrightarrow 2Al^{+3} + 3O^{-2}$

Base

$Al_2O_3 + O^{-2} \longrightarrow 2AlO_2^-$

Acid (Aluminate ion)

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5. The Solvent system concept :-

No. of solvents undergoes auto ionisⁿ and formed cationic and anionic spⁿ

$2H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$

liq. $2NH_3 \rightleftharpoons NH_4^{+} + NH_2^{-}$

liq. $2SO_2 \rightleftharpoons SO^{+2} + SO_3^{-2}$

$2H_2SO_4 \rightleftharpoons H_3SO_4^{\oplus} + HSO_4^{-}$

$N_2O_4 \rightleftharpoons NO^{+} + NO_3^{-}$

In Solvent system concept an acid is a solute that ↑ the conc^{n} of cationic spⁿ of the solvent.

While Base is a solute which ↑ the conc^{n} of anionic spⁿ of the solvent.

$HNO_3 + H_2O \longrightarrow H_3O^{\oplus} + NO_3^{-}$
(Acid)

$HNO_3 + H_2SO_4 \longrightarrow H_2O + NO_2^{\oplus} + HSO_4^{-}$
(Base)

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Solvent	Acid	Base
H_2O	HCl, HNO_3, H_2SO_4 HCN	$NaOH$, KOH
liq NH_3	NH_4Cl, NH_4NO_3	$NaNH_2$, KNH_2
liq SO_2	$SOCl_2$	Na_2SO_3, $CaSO_3$
liq N_2O_4	$NOCl$	$NaNO_3$, KNO_3

This concept emphasize on the importance of solvent.

for eg → HNO_3 behave as Acid in H_2O becoz it increase conc of H_3O^+ ion.
While HNO_3 behave as base in H_2SO_4 becoz it increase conc of HSO_4^- ion.

eg → Acetic Acid behave as acid in aq. medium but behave as base in H_2SO_4

$$CH_3COOH + H_2O \longrightarrow H_3O^+ + CH_3COO^-$$
(Acid)

$$CH_3COOH + H_2SO_4 \longrightarrow CH_3COOH_2^{\oplus} + HSO_4^-$$
(Base)

NON AQOUS SOLVENT

Classific^{n} of solvent :-

Classific^{n} based on the behaviour toward proton :-

On the basis of this type solvent are classified into 2 catagories

① Protic Solvent →

They have H- atom in their molecular formula. These are of 2 types :-

(a) Protogenic Solvent
(Acidic Solvent)

They have strong tendency to donate proton.

eg → HF, H_2SO_4, HNO_3, HCN, CH_3COOH

(b) Protophillic Solvent
(Basic Solvent)

They have strong tendency to accept proton

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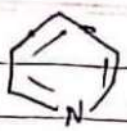
eg → NH_3,  , CH_2-NH_2 / CH_2-NH_2, NH_2-NH_2

(c) Amphiprotic Solvent (Amphoteric Solvent)

They can donate as accept proton.

eg → H_2O, CH_3COOH, etc.

(2) Aprotic Solvent →

These solvent neither donate nor accept proton.

eg →  , SO_2, CCl_4, $CHCl_3$, CS_2 etc.

Classificⁿ based on ionic property :-

This classificⁿ is based on concept of like dissolve like. Polar compⁿd are soluble in polar solvent while non polar compⁿd are soluble in non polar solvent.

(a) Ionising Solvent

They are polar in nature & undergo auto ionisⁿ.

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Eg → $2H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$

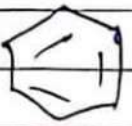
$2NH_3 \rightleftharpoons NH_4^{\oplus} + NH_2^{\ominus}$

$2HF \rightleftharpoons HF^{\oplus} + F^{\ominus}$

$2SO_2 \rightleftharpoons SO_2^{+2} + SO_3^{-2}$

(b) Non ionising solvent

They are non polar or non-ionising in nature.

Eg →  , CCl_4 etc.

Classifⁿ based on relation with water :-

(a) Aqous solvent (only water come in this category)

(b) Non Aqous solvent

except

~~Except~~ water other liquid which have capacity to dissolve other comp'd are K/a Non - Aq/s solvent

Eg → liq. NH_3, liq SO_2, HF, H_2SO_4, BrF_3 etc.

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Physical properties of solvent :-

① M.P & B.P →

Most of the reacⁿ take place in liq. state. The Tr b/w M.P & B.P of any liq. is k/as its liq. Tempr field or liq. range.

The liq range of water is b/w 0°C to 100°C & that of the liq ammonia is b/w -77°C to -33°C.

② Dipole moment →

Solvent having higher value of d.M dissolve the polar substance easily.

This is because of the fact the greater the polarity of a solvent, energy released on dissolution of substance is higher

Eg → Water (D.M = 1.84) is better solvent for ionic compⁿd in comparison of liq NH_3 (D.M = 1.46)

③ Dielectric constant →

Dielectric constant is defined as the capacity of a solvent to weaken e⁻ static force of attracⁿ of ions

present in a ionic comp^{n}d.

$$f = \frac{q^+ q^-}{D r^2} \qquad f \propto \frac{1}{D}$$

(D = dielectric Medium) $\qquad D \uparrow \; f \downarrow$

$H_2O \rightarrow 78.5$
$NH_3 \rightarrow 22$

A solvent having high value of dielectric constant will weaken the force holding the ions of ionic crystal together. And ultimately will dissolve the ionic crystal in it.

Water which have greater value of dielectric constant (78.5) then liq NH_3 (22) is better solvent for dissolving ionic comp^{n}d.

④ Electrical conductance →
Ionising solvent undergoes self ionis^{n} to give cation and anion. The limit of self ionis^{n} of the solvent can be determine by the Electrical conductivity.

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greater is the ionisⁿ, easier it is for acid base rxn to occur in the solvent.

⑤ Viscosity →
Some solvents are highly ~~flood~~ fluid. i.e water, low molecular weight alcohol, liq NH_3.

While some others are viscous like H_2SO_4 high molecular weight alcohol.

The solvents with low viscosity are better for chemical processes like pptⁿ crystallizⁿ, filterⁿ etc.

⑥ Proton affinity →
It is defined as the tendency to accept proton.

$$A: + H^{\oplus} \longrightarrow A^{\oplus}H + \text{energy}$$

↑ Proton affinity

Proton affinity is measurement of basicity.

$\overset{\ominus}{CH_3}$ $\overset{\ominus}{NH_2}$ $\overset{\ominus}{OH}$ $\overset{\ominus}{F}$

$:NH_3$ $H_2\ddot{O}:$ ⟶

E·N ↑, l·p donating tendency ↓, H^+ accepting tendency ↓

P·A ↓

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$F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$ ↓

Size ↑, Stability ↑
l.p donating tendency ↓
H^+ accepting tendency ↓
P.A ↓

Proton affinity is applicable for protonic solvent only. It greatly affect the behaviour of a solute in a given solvent system.

Eg → Acetamide behave as weak base in aq. soln while behave as acid in liq NH_3.

- $CH_3-C(=O)-NH_2 + H_2O \longrightarrow CH_3-C(=O)-\overset{\oplus}{N}H_3 + \overset{\ominus}{O}H$

(Base)

- $CH_3-C(=O)-NH_2 + NH_3 \text{ (liq.)} \longrightarrow CH_3-C(=O)-\overset{\ominus}{N}H + \overset{\oplus}{N}H_4$

(Acid)

Properties of Some Ionising Solvent :

Rxn's in liquid ammonia :-

① Acid - Base Rxn

2012 Acid + Base $\xrightarrow{liq.\ NH_3}$ Salt + Solvent

Ammonium salt act as acids in liq NH_3 whereas Amide, Imide, nitrides behave as base.

$NH_4Cl + NaNH_2 \xrightarrow{''} NaCl + 2NH_3$

$2NH_4NO_3 + PbNH \xrightarrow{''} Pb(NO_3)_2 + 3NH_3$

$3NH_4I + AlN \xrightarrow{''} AlI_3 + 4NH_3$

$3NH_4I + BiN \xrightarrow{''} BiI_3 + 4NH_3$

Rxn of Ammono Acid

The ammono acid are the substance which gives NH_4^+ ion in liq. NH_3

It can react with various substance like metals, metal hydroxide and metal oxide.

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(a) $Na + NH_4^{\oplus} \xrightarrow{liq\ NH_3} Na^+ + NH_3 + \frac{1}{2}H_2$

(b) $2NH_4Cl + Na_2O \xrightarrow{''} 2NaCl + 2NH_3 + H_2O$

(c) $NH_4Cl + NaOH \xrightarrow{''} NaCl + NH_3 + H_2O$

Some comp'd do not donate proton in water but give proton in liq. NH_3

Eg → 2015

Behaviour of urea in liq. NH_3

$NH_2-\underset{\underset{O}{||}}{C}=NH_2 + liq\ NH_3 \Rightarrow NH_2-\underset{\underset{O}{||}}{C}-\overset{\ominus}{N}H + \overset{\oplus}{N}H_4$

(Acid)

$CH_3-\underset{\underset{O}{||}}{C}-NH_2 + liq\ NH_3 \longrightarrow CH_3-\underset{\underset{O}{||}}{C}-\overset{\ominus}{N}H + \overset{\oplus}{N}H_4$

Rxn of ammono base

Many metal salt react with ammono bases to give ppt of amide, Imide nitrides.

(a) $AgNO_3 + KNH_2 \xrightarrow{liq\ NH_3} AgNH_2\downarrow + KNO_3$

(b) $PbI_2 + 2KNH_2 \xrightarrow{''} PbNH\downarrow + 2KI + NH_3$

(c) $BiI_3 + 3KNH_2 \xrightarrow{''} BiN\downarrow + 3KI + 2NH_3$

② Amonation rxn and formⁿ of Ammoniates

In these rxn one or more molecules of liq NH_3 are attached with solute species containing acceptor atom and give product known as ammoniates.

$BF_3 + NH_3 \longrightarrow [\ddot{N}H_3 \rightarrow BF_3]$ or $NH_3 \cdot BF_3$

$SiF_4 + 2NH_3 \longrightarrow SiF_4 \cdot 2NH_3$

NH_3 is better lewis base than water Hence NH_3 is replaced water molecule from complexes.

$[Cu(H_2O)_4]^{+2} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{+2}$

$[Ag(H_2O)_2]^{+} + 2NH_3 \longrightarrow [Ag(NH_3)_2]^{+}$

2019

③ PPtⁿ rxn

(i) Most of the chloride (except Na, Be, NH_4^+) 2016 are insoluble in liq NH_3

$KI + NH_4Cl \xrightarrow{liq.NH_3} KCl\downarrow + NH_4I$

(ii) When solⁿ of various nitrates are mixed with NH_4Br, NH_4I then ppt of metallic bromide or iodide is form.

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$Sr(NO_3)_2 + 2NH_4Br \xrightarrow{liq\ NH_3} SrBr_2 \downarrow + 2NH_4NO_3$

$Zn(NO_3)_2 + 2NH_4I \xrightarrow{\quad "\quad} ZnI_2 \downarrow + 2NH_4NO_3$

(iii) Ammonium Sulphide $[(NH_4)_2S]$ can ppt the sulphide of various metal like as Zn, Mg, Cd, Bi, Co, Ag, Pb, Hg

$(NH_4)_2S + AgNO_3 \xrightarrow{\quad "\quad}$ Black $Ag_2S \downarrow + NH_4NO_3$

$(NH_4)_2S + Zn(NO_3)_2 \xrightarrow{\quad "\quad}$ White $ZnS \downarrow + "$

$(NH_4)_2S + Cd(NO_3)_2 \xrightarrow{\quad "\quad}$ Yellow $CdS \downarrow + "$

$(NH_4)_2S + Mn(NO_3)_2 \xrightarrow{\quad "\quad}$ Buff color $MnS \downarrow + "$

(4) Ammonia as proton acceptor

2018 Reason for NH_3 is better proton acceptor.

Liq NH_3 has a strong tendency to pick up proton even from neutral as weak base substance

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

2018 (i) Acetic acid is weak acid in aq. soln but behave as strong acid in liq NH_3. (Reason)

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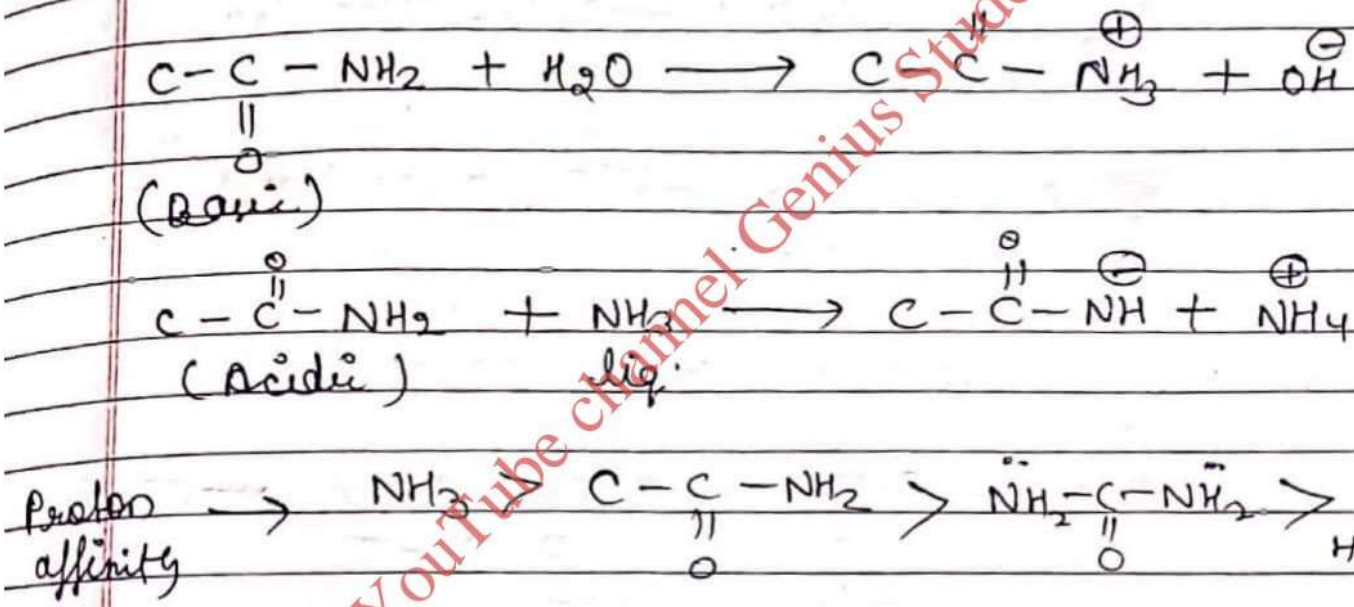
$CH_3COOH + NH_3 \longrightarrow CH_3COO^- + \overset{\oplus}{NH_4}$

proton donor (S.A) ↑ more proton affinity so accept all proton

(W.A) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^{\oplus}$

proton donor

(ii) Acetamide and urea behave as W.B in aqs soln but show acidic property in liq NH_3.



(Basic)

(Acidic)

Proton affinity → NH_3 > >

(5) 2019 Ammonolysis

(i) Ammonolysis of inorganic halide

$BCl_3 + 6NH_3 \xrightarrow{liq} B(NH_2)_3 + 3NH_4Cl$

$SO_2Cl_2 + 4NH_3 \xrightarrow{liq} SO_2(NH_2)_2 + 2NH_4Cl$

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$TiCl_4 \xrightarrow[-NH_4Cl]{liq\ NH_3} TiCl_3(NH_2) \xrightarrow{liq\ NH_3} TiCl_2(NH_2)_2$

$TiCl_2(NH_2)_2 \xrightarrow{liq.\ NH_3} TiCl(NH_2)_3 \xrightarrow[NH_3]{liq.} Ti(NH_2)_4$

Hg_2Cl_2 and $SnCl_4$ are not completely ammonolysed.

$$Hg_2Cl_2 + liq.2NH_3 \longrightarrow Hg + HgCl(NH_2) + NH_4Cl$$

Mercurous chloride / corrosive Sublimate

$$SnCl_4 + \underset{6NH_3}{liq} \xrightarrow{-63^\circ C} SnCl(NH_2)_3 + 3NH_4Cl$$

(II) Ammonolysis of organic halide

$$R-X + \underset{liq}{2NH_3} \longrightarrow R-NH_2 + NH_4Cl$$

(P.A)

$$R-NH_2 + X-R \xrightarrow[NH_3]{liq} R_2NH + NH_4Cl$$

(S.A)

$$R_2NH + X-R \underset{}{\overset{liq\ NH_3}{\rightleftharpoons}} R_3N + NH_4X$$

(III) Ammonolysis of alkali metal hydride & oxide

$$NaH + liq\ NH_3 \longrightarrow NaNH_2 + \frac{1}{2}H_2\uparrow$$

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$Na_2O + liq.\ 2NH_3 \longrightarrow 2NaNH_2 + H_2O$

⑥ Complex formation Reaction

$Zn(OH)_2 + 2KOH \xrightarrow{liq\ NH_3} K_2[Zn(OH)_4]$

insoluble — Soluble hydroxo complex

$Zn(NH_2)_2 + 2KNH_2 \xrightarrow{liq\ NH_3} K_2[Zn(NH_2)_4]$

insoluble — soluble amide complex

Aluminium amalgam reacts similarly to form a soluble complex

$Al^{+3} + 3NH_2^- \xrightarrow{liq\ NH_3} Al(NH_2)_3$

KNH_2 — insoluble

$Al(NH_2)_3 + NH_2^- \xrightarrow{\quad\quad} [Al(NH_2)_4]^{\ominus}$

soluble

$SnCl_4 + 6NH_3\ (liq) \xrightarrow{-63^\circ C} Sn(NH_2)_3Cl + 3NH_4Cl$

Ammonolysis product

$\xrightarrow{-36^\circ C}$

$(NH_4)_2[SnCl_3(NH_2)_3] + NH_4Cl$

⑦ Redox Reaction

→ When gaseous oxygen passed slowly through soln of metallic sodium in liq ammonia the product are hydroxide & amide followed later by further oxidn in which amide converted into nitride.

$$2Na + NH_3 + \tfrac{1}{2}O_2 \longrightarrow NaOH + NaNH_2$$

$$4NaNH_2 + 3O_2 \longrightarrow 2NaOH + 2NaNO_2 + 2NH_3$$

→ Soln of alkali & alkali earth metal in liq ~~and~~ NH_3 act as e^- donar (reducing agent). Hence they can react with e^- acceptor (O.A)

Oxidn — Redun

$$Na + NH_4Br \xrightarrow{liq\ NH_3} NaBr + NH_3 + \tfrac{1}{2}H_2$$

$$CuI_2 + 2Na \xrightarrow{//} Cu + 2NaI$$

Redun — Oxidn

→ Catalytic Oxidn of NH_3 to NO

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

$0 \rightarrow +2$ oxidn

2018

Metal ammonia soln & their rxn

Metals that have low I.E and sublimn energy and high energy of hydrn like alkali metals, alkaline earth metals, Al, Europium (Eu) and Yb readily dissolves in liq NH_3 and give metal ammonia soln.

These are blue in color in dilute and bronze color in conc. soln.

* The bronze colored soln have electrical conductance like metals while blue colored have electrical conductance like electrolytic soln.

The blue metal ammonia dilute soln are paramagnetic in nature indicating the presence of unpaired electron

$$M \longrightarrow M^+ + e^-$$

$$M^+ + x\,NH_3 \longrightarrow [M(NH_3)x]^+$$

ammonated cation

$$e^- + y\,NH_3 \longrightarrow [e(NH_3)y]^-$$

ammonated electron

$$M + x + y(NH_3) \longrightarrow [M(NH_3)x]^+ + [e(NH_3)y]^-$$

or $M \underset{\longleftarrow}{\overset{\text{liq } NH_3}{\longrightarrow}} \underset{(am.)}{M^+} + \underset{(am.)}{e^-}$

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(ammoniated)

On Passing conc^n solvated e^- or solvated cation and ~~solvated~~ electron may formed pair Hence paramagnetic nature lose

$$2[e(NH_3)_y]^- \longrightarrow [e_2(NH_3)_y]^{-2} + yNH_3$$

$$[e(NH_3)_y]^- + [M(NH_3)_x]^+ \longrightarrow$$

$$[M(NH_3)_x \cdot e(NH_3)_y]$$

All metal ammonia sol^n, upon long standing or in presence of suitable catalyst (Fe_2O_3) / Pt black undergoes decompon and give H_2 gas and metal amide

$$Na + \underset{liq}{NH_3} \xrightarrow[\text{or}]{Fe_2O_3} \underset{Pt\ Black}{} NaNH_2 + \frac{1}{2}H_2\uparrow$$

Rxn of metal ammonia sol^n :-

Since the blue metal NH_3 sol^n contain highly mobile ammonated e^- So such sol^n can act as strong reducing agent.

① Rxn of non metallic elements

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$O_2 + e^- \longrightarrow O_2^- \xrightarrow{H^+} HO_2$ (superoxide)

$O_2 + 2e^- \longrightarrow O_2^{-2} \xrightarrow{H^+} H_2O_2$ (Peroxide)

$S + 2e^- \longrightarrow S^{-2} \xrightarrow{H^+} H_2S$

② Metal ammonia soln are quickly decolourised by ammonium salt

$NH_4^+ + e^-_{(am.)} \longrightarrow NH_3 + \frac{1}{2}H_2\uparrow_{(g)}$

③ Reduction of Organic Compⁿd

$R-C\equiv C-H \xrightarrow{Na/liq.\,NH_3} R-C\equiv C^{\ominus}\,Na^{\oplus} + \frac{1}{2}H_2\uparrow$

Sodium alkylide

CHEMICAL RXN in liq SO_2 :-

① Acid + Base RXN

Autoionisⁿ of SO_2 take place as following

$SO_2 + SO_2 \rightleftharpoons \underset{\text{thionyl ion (act as acid)}}{SO^{+2}} + \underset{\text{sulphite ion (Act as base)}}{SO_3^{-2}}$

* thionyl salt + sulphite salt → Salt + Solvent

$SO^{+2} + SO_3^{-2} \longrightarrow 2SO_2$ (liq.)

Acid + Base ⟶ Salt + Solvent

$SOCl_2 + Cs_2SO_3 \longrightarrow 2CsCl + 2SO_2$ (1)

$SoBr_2 + [N(CH_3)_4]SO_3 \longrightarrow 2[N(CH_3)_4]Br + 2SO_2$

tetra methyl ammonium sulphite

$SO(SCN)_2 + K_2SO_3 \longrightarrow 2K(SCN) + 2SO_2$

② Redox reaction

Gaseous SO_2 may behave either as an oxidising agent or as a reducing agent depending on the nature of substance with which gaseous SO_2 reacts.

On the other hand liq SO_2 does not have oxidising or reducing property although it may serve as medium for redox reaction.

$3SbCl_5 + 6KI \xrightarrow[SO_2]{liq.} 2K_3[SbCl_6] + SbCl_3 + 3I_2$

$FeCl_3 + KI \xrightarrow{''} FeCl_2 + KCl + I_2$

$CH_3-\underset{\underset{O}{\|}}{C}-BF_4 + CH_3COOK \xrightarrow{''} (CH_3CO)_2O + KBF_4$

(acetyl fluoro borate)

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(3) Complex formⁿ

Complex formⁿ occurs in 2 ways :-

(i) Solubility of a ppt in an ~~excess~~ excess of its own anion

(ii) Complex formⁿ not involving any pptⁿ

$AlCl_3 + NaOH \xrightarrow{H_2O} Al(OH)_3 \downarrow$ pptⁿ

$Al(OH)_3 + NaOH \longrightarrow [Al(OH)_4]^-$ (excess)

$2AlCl_3 + 3SO_3^{-2} \longrightarrow Al_2(SO_3)_3 \downarrow + 6Cl^-$ pptⁿ

$Al_2(SO_3)_3 + 3SO_3^{-2} \longrightarrow 2[Al(SO_3)_3]^{-3}$ (insoluble) (excess)

$SbCl_3 + 3KCl \xrightarrow{liq\ SO_2} K_3[SbCl_6]$

$SbCl_5 + NOCl \xrightarrow{\quad''\quad} NO[SbCl_6]$

$KI + I_2 \xrightarrow{\quad''\quad} KI_3$

$HgI_2 + 2KI \xrightarrow{\quad''\quad} K_2[HgI_4]$

④ Solvolysis Reaction

$$PCl_5 + \underset{liq.}{SO_2} \longrightarrow POCl_3 + SOCl_2$$

$$PBr_5 + SO_2 \longrightarrow POBr_3 + SOBr_2$$

$$SbCl_5 + SO_2 \longrightarrow SbOCl_3 + SOCl_2$$

$$WCl_6 + SO_2 \longrightarrow WOCl_4 + SOCl_2$$

⑤ Solvation Reaction

2015

Many of the most soluble salt form the addⁿ compⁿd with the solvent ~~and form~~ this addⁿ compⁿd are called solvates which are analogus to hydrates and ammoniates formed in water and liq NH_3 respectively.

$$NaI + \underset{liq}{4SO_2} \longrightarrow NaI \cdot SO_2$$

$$KI + 4SO_2 \longrightarrow KI \cdot 4SO_2$$

$$LiI + 2SO_2 \longrightarrow LiI \cdot 2SO_2$$

$$AlCl_3 + SO_2 \longrightarrow AlCl_3 \cdot SO_2$$

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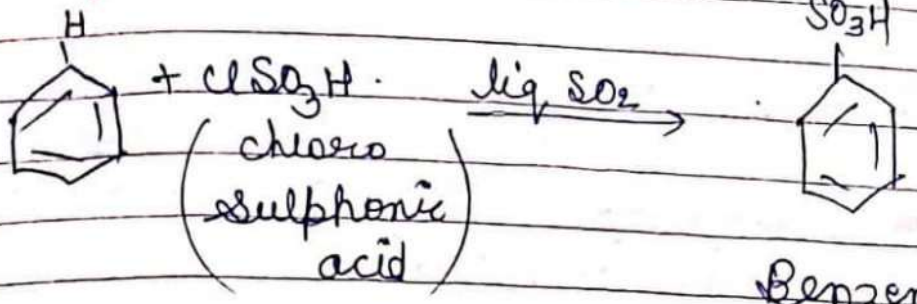
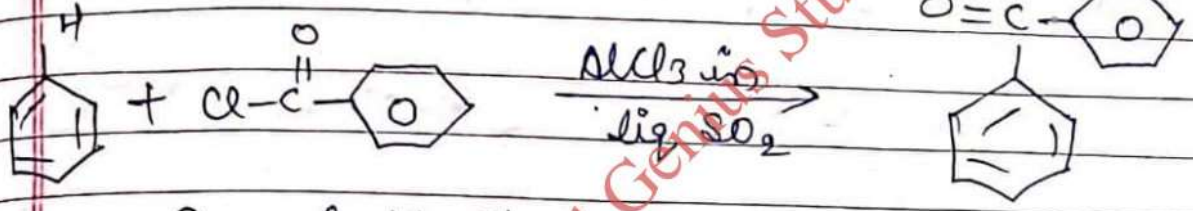
⑥ Reaction with Organic comp^{n}d

(i) Sulphonation



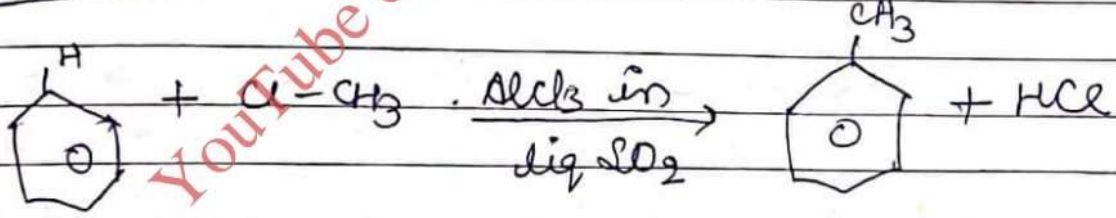
Benzene sulphonic acid

(ii) Friedal craft RXN



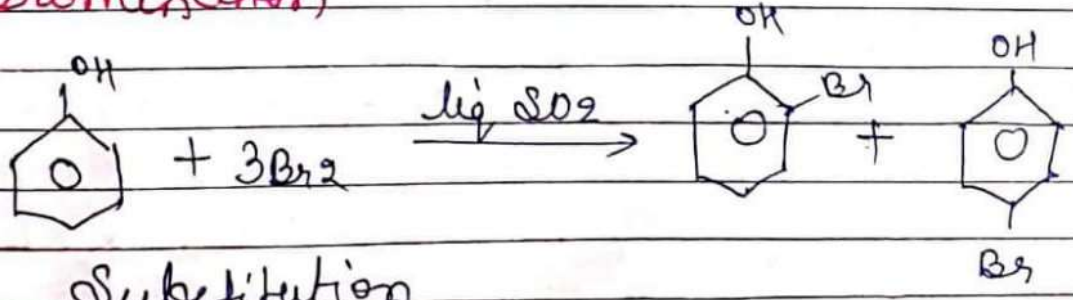
Benzoyl chloride — Benzophenone

ACYLATION → Benzoylat^{n} (above RXN)



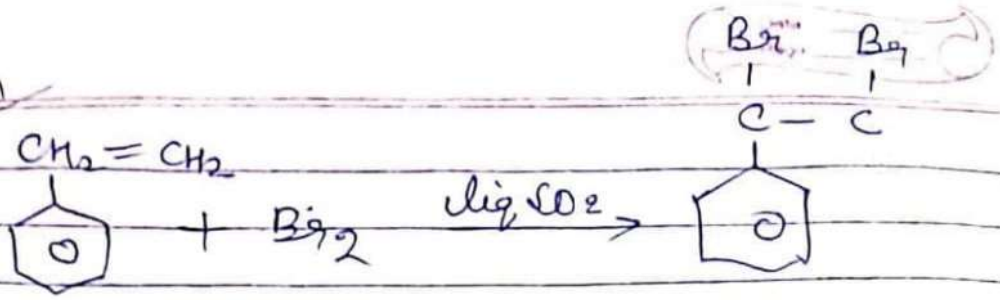
ALKYLATION

(iii) Bromination



Substitution

Addition



(7) Pptⁿ rxn

Pptⁿ rxn in liq SO_2 have been studied by Tender.

$BaI_2 + Zn(CNS)_2 \xrightarrow{liq\ SO_2} Ba(CNS)_2\downarrow + ZnI_2$

(soluble) $SbCl_3 + 3LiI \xrightarrow{''} SbI_3\downarrow + 3LiCl$

$AlCl_3 + NaI \xrightarrow{''} NaCl\downarrow + AlI_3$

A large no of thionyl derivates have been prepared from the miscible soln of $SOCl_2$ in liq SO_2

$Ag(CH_3COO) + SOCl_2 \xrightarrow{''} AgCl\downarrow + SO(CH_3COO)_2$
(thionyl acetate)

$2KBr + SOCl_2 \xrightarrow{''} 2KCl\downarrow + SOBr_2$
(thionyl Bromide)

$2KI + SOCl_2 \xrightarrow{''} 2KCl\downarrow + SoI_2$
(thionyl iodide)

2017

Advantage of using liq NH_3 as Solvent

① One of the ~~bravest~~ greatest advantage of liq NH_3 as solvent is that it dissolves alkali metals without reacting with that.

The dissolved alkali metal can be recovered simply by evaporating the solvent.

② Liq NH_3 has lesser tendency than water to undergo solvolysis RXN with dissolv solute.

③ It can ppt salts like $BaCl_2$, AgF_2, which are soluble in water.

④ For strong reducing agent water cannot be used as solvent for eg They will react with water to liberate H_2 in such cases liq NH_3 is most suitable solvent.

Disadvantage " " :-

① It is extremely hydroscopic nature Hence a great care has to be taken to prevent atmospheric moisture.

② Pure ammonia has B.P of ~~-33°C~~ -33.38°C

therefore it is necessary to work at low temp to avoid high pressure

③ Elaborate equipments and special techniques are required to use liq NH_3 as solvent.

Ques Why ceric sulphate is used in redox rxn?

Ans The ceric ion (Ce^{+4}) is a strong oxidising especially under acidic cond^n. That's why ceric sulphate is used in analytical chemistry for redox titration.

The Ce(IV) only exist just because it has the noble gas configur^n at this oxid^n state contributing in its stability

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