UNIT-1 : HARD SOFT ACID BASE (HSAB)

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CONTENTS OF SYLLABUS :

1) Introduction
2) Hard, Soft Acid -Base
3) HSAB Theory / Pearson's concept/principle
4) Applications of HSAB
5) Limitations of HSAB

T. Y. B. Sc. Part-III

Inorganic Chemistry

Academic Year: 2019-20 Sem-V Paper-X

University Questions:

1)	State Pearson's /HSAB principle. Explain different applications of HSAB	5M April-10
2)	Write short note on 'Limitations of HSAB'	5M April-13
3)	Write short note on 'Applications of HSAB concept'	

"Success and Excuses do not talk together.
If you want Excuses, forget about Success.
If you want Success, do not give Excuses..!"

Q.1) Write short note on 'HSAB principle'

HSAB concept:- (Pearson's Concept)

Statement:- Hard acids prefers to bind with hard bases and soft acids prefers to bind with soft bases.

Pearson's classified hard & soft acids & bases as follow;

① Hard acids:-

~~It is~~ They are Lewis acids with acceptor center of-

i) low polarizability
ii) small size
iii) high electronegativity
iv) high +ve charge v) absence of d $\bar{e}^s$.

eg. H^+, Na^+, Li^+, Mg^{++} etc.

② Soft acids:- They are Lewis acids with acceptor center of —

i) high polarizability
ii) Large size
iii) low electronegativity iv) with nearly full d $\bar{e}^s$.

eg. Cu^+, Ag^+, Au^+ etc.

same

③ Hard bases:- They are lewis bases with donor center of —

i) low polarizability
ii) small size
iii) high electronegativity
~~iv) no low energy empty d-orbitals,~~

eg. H_2O, NH_3, F^-, OH^- etc.

iv) presence of filled orbitals; empty orbitals may exist at high energy level

(4) Soft bases :- They are Lewis bases with donor center of —
i) high polarizability
ii) large size
iii) low electronegativity
iv) partially filled orbitals, empty orbitals may exist at low energy level.

eg. CN^-, H_2S, etc.

* Applications of HSAB :-

1. To determine relative strength of HX
2. To predict stability of complexes
3. To predict reactivity w.r.t. soft-soft & hard-hard combination
4. To explain certain catalytic reactions
5. To determine relative stabilities of complexes in aqueous solutions.
6. To explain solubility of solute
7. To predict the course of reaction
8. To predict rate of reaction
9. Occurence of minerals.
10. To study symbiosis
11. To explain linkage of Ambidentate ligand (SCN^-) to metal atoms.
12. To predict site preference in organic reactions.

* Limitations of HSAB :-

1. HSAB has not quantitative scale of measurements.
2. It fails to explain relative quantitative measurements of acid-base strength
3. It fails to explain hard-soft combinations which occur in many cases also.
4. HSAB fails to explain (justify) breaking between ethanol & acetic acid during esterification
5. HSAB fails to explain proceeding of reaction in forward or backward direction.

Applications of HSAB:-

① To determine the relative strength of HX:-

In aqueous sol^n, $HX + H_2O \longrightarrow H_3O^+ + X^-$

where X = F, Cl, Br, I

Here, hardest base F^- will be most successfully & strongly bonded to the hard acid H^+. Hence HF will be highly stable. as compared with HCl, HBr & HI. Therefore, acid strength increases as,

eg. HF < HCl < HBr < HI

HF ↑ Hardest base; HI ↑ softest Base

HF (Highly stable) —— Relative stability decreases / degree of dissociation increases ——→ HI (Less stable)

② To predict reactivity w.r.t. soft-soft & hard-hard combination.

eg. Li-I + Cs-F ⟶ Li-F + Cs-I

Hard-soft   soft-Hard   Hard-Hard   soft-soft

Here, reaction between LiI & CsF is due to the soft-soft & Hard-Hard combination/interaction.

③ To predict stability of complexes

eg. It explains stability of AgI_2^- because of soft-soft interaction while AgF_2^- is unstable due to soft-hard interaction.

AgI_2^- soft-soft (Stable) AgF_2^- soft-Hard (unstable)

4) To explain certain catalytic reactions
eg. soft metal adsorbs soft bases

5) To determine relative stabilities of complexes in aqueous solutions.

eg. $[Cd(CN)_4]^{2-}$ (soft – soft) — more stable; $[Cd(NH_3)_4]^{2+}$ (soft – hard) — less stable

According to HSAB, soft acid Cd^{2+} prefers to bind with soft base CN^- easily & form more stable complex $[Cd(CN)_4]^{2-}$ whereas Cd^{2+} difficult to bind with hard base NH_3

6) To explain solubility of solute
eg. Hard solvent is expected to dissolve hard solute

7) To predict the course of the reaction
Let's consider,

i) $H^+ + CH_3Hg^+OH^- \longrightarrow H_2O + CH_3Hg^+$
(H^+: Hard; CH_3HgOH: soft acid – Hard base)

ii) $H^+ + CH_3Hg^+SH^- \longrightarrow H_2S + CH_3Hg^+$
(H^+: Hard; CH_3HgSH: soft acid – soft base)

Reaction-(i) is favoured to right side because hard acid H^+ prefers to binds strongly to hard base OH^- to produce stable product H–OH (Hard – Hard)

Reaction (ii) is favoured to left side because soft base SH^- will tend to remain combined with soft acid CH_3Hg^+ instead of joining (binding) to the hard acid H^+.

(8) To predict rate of reaction

Rates of chemical reactions in electrophile as well as nucleophilic substitution reaction, can be corelated ~~to~~ with hard-soft nature of acids & bases.

(9) Occurrence of minerals.

eg. i) Hard acids such as Mg^{2+}, Ca^{2+} & Al^{+3} occuring in nature as metal carbonates or oxides. This is because hard acid cation reacts with hard anions such as CO_3^{2-} & O^{2-}

ii) Whereas soft acids such as Cu^+, Ag^+, Hg^{2+} etc. react with soft base S^{2-} to form corresponding sulphides.

(10) To study symbiosis:

soft ligands have tendency to combine with a center already having soft ligands while hard ligands have tendency to combine with a center already having hard ligands. This phenomenon is known as 'Symbiosis'.

eg. 1) F^- hard Ligand combines with BF_3 to form stable complex BF_4^-

$$\underset{\text{Hard Ligand}}{F^-} + \underset{\text{Hard}}{BF_3} \longrightarrow \underset{\text{stable complex}}{BF_4^-}$$

ii) H^- soft ligand combines with B_2H_6 to form stable complex BH_4^-

$$\underset{\text{soft}}{B_2H_6} + \underset{\text{soft}}{2H^-} \longrightarrow \underset{\text{stable complex}}{2BH_4^-}$$

(11) To explain linkage of Ambidentate ligand (SCN^-) to metal atoms.

eg. Ambidentate ligand SCN^- can bind either by S-end or N-end to the metal atom. According to HSAB, soft metal (eg. Pt^{2+}) binds SCN^- through S-atom (soft base) whereas hard metal (eg. Cr^{+3}) binds SCN^- through N-atom (hard base).

(12) To predict site preference in organic reactions.

i) $\underset{\text{Hard}}{CH_3\overset{+}{C}O\,X^-} + SCN^- \longrightarrow \underset{\text{acyl isothiocyanate}}{CH_3\overset{O}{\overset{\|}{C}}-NCS} + X^-$

ii) $CH_3^+X^- + SCN^- \longrightarrow \underset{\text{methyl thiocyanate}}{CH_3-SCN} + X^-$

$CH_3C\overset{+}{O}$ (hard acid) reacts with N-end of SCN^- whereas CH_3^+ (soft acid) reacts with S-end.

* Limitations of HSAB:-

(1) HSAB has not quantitative scale of measurement.

(2) HSAB ~~has difficulty~~ fails to explain relative quantitative measurement of Acid-Base strength.

eg. OH^- & F^- ions are both hard bases whereas OH^- is nearly 1013 times stronger base than F^- ions.

(3) HSAB fails to explain Hard-soft combinations which occur in many cases.

eg. $SO_3^{2-} + HF \longrightarrow HSO_3^- + F^-$

soft base; HF: Hard acid (H^+), Hard base (F^-); HSO_3^-: Hard-soft; F^-: Hard base

Here, soft base SO_3^{2-} has replaced hard base F^- & combines with hard acid H^+.

(4) This theory is unable to determine the relative strengths of acids & bases.

(5) Hard-soft factors are independent of the acidic or basic character of compounds.

eg. $CH_3^+ + H_2 \longrightarrow CH_4 + H^+$

CH_3^+: soft; H_2 (H^+-H^-): Hard soft; CH_4 (CH_3-H): soft-soft; H^+: Hard.

This reaction must favoured due to soft-soft combination betn CH_3^+ & H^-. But this combination is endothermic by about +360 kJ mol^{-1}. This unfavourable entropy change does not allow to proceed this reaction.

(6) HSAB fails to explain (justify) breaking between ethanol & acetic acid during esterification.

There are two possibilities in breaking;

Break-I : $CH_3COO^-H^+ + C_2H_5^+OH^- \longrightarrow CH_3COOC_2H_5 + H_2O$ (ester)

Break-II : $CH_3CO^+OH^- + C_2H_5O^-H^+ \longrightarrow CH_3COOC_2H_5 + H_2O$ (ester).

The hard-hard combination of H^+ with OH^- for both break is justifible. But it fails to explain breaking betn ethanol & acetic acid during esterification.

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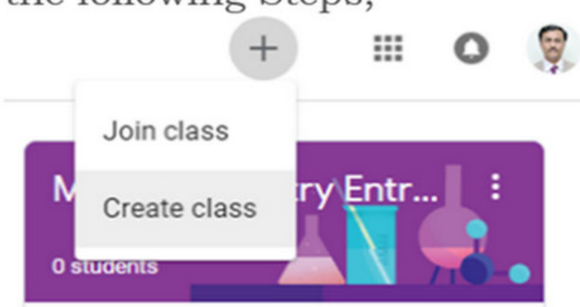

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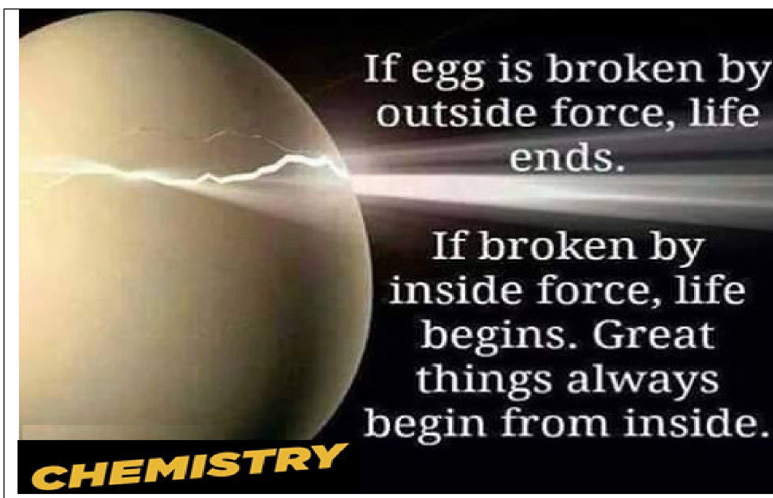

"Without Your Involvement You Can't Succeed.

With Your Involvement You Can't Fail.

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