

**B.Sc. (Honours) Part-I**  
**Paper-IA**

**Topic: Hard-and-Soft-Acids-and-Bases**

**UG**

**Subject-Chemistry**

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## **HARD AND SOFT ACIDS AND BASES (HSAB)**

### **Pearson's classification of Lewis acids and Lewis bases into hard and soft acids and bases.**

R. G. Pearson (1963) has classified the Lewis acids and Lewis bases as hard and soft acids and bases. R. G. Pearson extended and generalized the qualitative correlation between Lewis acids and Lewis bases by classifying them into two categories Hard and Soft.

The class –‘a’ metals which are small and less polarizable, prefer to combine with non- metals or ligands which are also small and not very polarizable , pearson called such metals as Hard Acids and the corresponding ligands as soft Bases.

Similarly the class ‘b’metals having large size ,more or easily polarisable, prefers to combine with non-metals or ligands having similar properties Pearson called such metals as soft acids and the ligands as soft base The attempt of classification of acidsand bases as hard and soft by Pearson is known as Hard and soft Acids and Bases .(HSAB) or pearson's concept Principle of Pearson's concept :

Pearson suggested a simple rule (Sometimes called Pearson's principle ) for predicting the stability of complexes formed between hard and soft acids and bases. “Hard acids prefer to bind (co-ordinate) with hard bases and soft acids prefer to bind with soft bases and gives stable complex compound ”. It should be noted that the statement given above is not a theory or an

explanation but it is simple rule of thumb which enables us to predict the relative stabilities of acid-bases adducts qualitatively.

Third categories whose characteristics are intermediate between those of hard and soft acids/bases are called borderline acids/bases.

<b>Hard acids</b>	<b>Soft acids</b>
d-orbitals are either vacant or non-existent	Nearly full d-orbitals
Smaller in size	Larger in size
Not so easily polarizable	Easily polarizable
These are mostly light metal ions generally associated with high positive oxidation state.	These are mostly heavy metal ions generally associated with low (or even zero) positive oxidation state.

<b>Hard Acids</b>	<b>Borderline Acids</b>	<b>Soft Acids</b>
H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Be <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Mn <sup>2+</sup> , Al <sup>3+</sup> , Ga <sup>3+</sup> , In <sup>3+</sup> , La <sup>3+</sup> , Lu <sup>3+</sup> , Cr <sup>3+</sup> , Co <sup>3+</sup> , Fe <sup>3+</sup> , As <sup>3+</sup> , Si <sup>4+</sup> , Ti <sup>4+</sup> ,	Fe <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> Pb <sup>2+</sup> , Sn <sup>2+</sup> , Sb <sup>3+</sup> , Bi <sup>3+</sup> ,	Cu <sup>+</sup> , Ag <sup>+</sup> , Au <sup>+</sup> , Tl <sup>+</sup> , Hg <sup>+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup> , Pt <sup>2+</sup> , Hg <sup>2+</sup> , Pt <sup>4+</sup> , TI <sup>3+</sup> , BH <sub>3</sub> ,

$U^{4+}$ , $Ce^{3+}$ , $Sn^{4+}$ , $VO^{2+}$ , $UO_2^{2+}$ , $MoO_3^{3+}$ , $BF_3$	$Rh^{3+}$ , $SO_2$ , $NO^+$ , $GaH_3$	$GaCl_3$ , $InCl_3$ , carbenes $\pi$ - acceptor ligands $I^+$ , $Br^+$ , O, Cl, Br, I, N Zero valent metal atoms.
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Hard bases	Soft bases
Donor atoms having low polarisabilities and high electronegativity	Donor atoms that can be easily polarized and have low electronegativity.

Hard Bases	Borderline Bases	Soft Bases
$H_2O$ , $OH^-$ , $F^-$ , $CH_3COO^-$ , $PO_4^{3-}$ , $SO_4^{2-}$ , $Cl^-$ , $CO_3^{2-}$ , $ClO_4^-$ , $NO_3^-$ , $ROH$ , $RO^-$ , $R_2O$ , $NH_3$ , $NH_2$ , $N_2H_4$	$C_6H_5NH_2$ , $C_6H_5N$ , $N_3^-$ , $NO_2$ , $SO_3^{2-}$ , $N_2$ , $Br^-$	$R_2S$ , $RSH$ , $RS^-$ , $I^-$ , $SCN^-$ , $S_2O_3^{2-}$ , $R_3P$ , $R_3As$ , $CN^-$ , $RCN$ , $CO$ , $C_2H_4$ , $C_6H_6$ , $H^-$

According to HSAB principle, hard acids form stable complexes with hard bases and soft acids with soft bases.

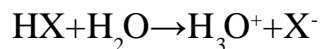
## APPLICATIONS OF HSAB PRINCIPLE

With the help of HSAB a large number of chemical reactions can be understood.

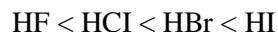
### 1. Relative strength of Hydracids HF, HCl, HBr and HI :

In aqueous solution the relative strength of HF, HCl, HBr and HI can be predicted.

The reaction of acids with water is:



The hardest base  $\text{F}^-$  will be most successfully and strongly bonded to the hard acid  $\text{H}^+$ . Hence HF will be highly stable. It is therefore least dissociated. Hence acid strength increases as :



### 2. Relative stabilities of complexes in Aqueous Solutions :

HSAB entails that  $[\text{Cd}(\text{CN})_4]^{2-}$  is more stable than  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ . According to HSAB principle hard prefers hard and soft prefers soft. Hence the soft acid  $\text{Cd}^{2+}$  will prefer to coordinate soft base  $\text{CN}^-$ . It is clear from the  $K_{\text{inst}}$  constants where cyano complex has  $K_{\text{inst}} = 1.4 \times 10^{-19}$  while for ammine complex it is  $7.5 \times 10^{-8}$ . Thus cyano is stable.

### 3. To Predict the Course of Reaction :



The reaction (i) goes to right as the hard acid  $\text{H}^+$  binds strongly to hard base  $\text{OH}^-$  to produce stable product  $\text{H}_2\text{O}$ .

On the other hand the reaction (ii) is favoured to left where soft base  $\text{SH}^-$  will tend to remain combined with soft acid  $\text{CH}_3\text{Hg}^+$  instead of joining to hard acid  $\text{H}^+$ .

## LIMITATIONS OF HSAB PRINCIPLE

Hard and soft classification is useful concept no doubt but it has some tricky limitations as pointed out below.

1. The prime limitation of the HSAB concept is that it is widely general and has no any direct quantitative scale of acid base strength .
2. The inherent acid base strengths are not accounted for e.g.OH<sup>-</sup> and F<sup>-</sup> ions are both hard bases where OH<sup>-</sup> is nearly  $10^{13}$  times stronger base than F ions .Correlation between hardness and inherent acid base strength is yet to be developed.