

Hard & Soft acids and bases.

(1)

Ahrland, Chatt and Davies classified metals and ligands into two classes.

Class 'a' metals :-

Ions of Alkali metals

Ions of Alkaline earth metals

Lighter metals in higher oxidation state
(e.g. Ti^{4+} , Cr^{3+} , Fe^{3+} and Co^{3+})

Hydrogen ion H^+

Characteristics :-

Small size

High polarizing power

High oxidation state

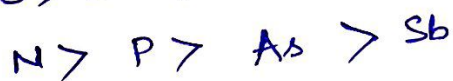
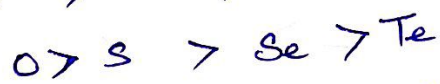
Distortion of outer orbitals (electrons) NOT
easy

Class 'a' ligands

Ligands combining preferentially with
metal ions of class 'a'.

e.g. NH_3 , NR_3 , H_2O and F^-

Tendency of some ligands to form complexes with metals
of 'a' is as given below :-



class 'b' metals :-

Ions of heavier transition metals in lower oxidation states

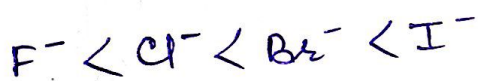
characteristics :-

Large size
Distortion of outer orbitals (electrons) is easy

Class 'b' ligands :- Ligands that combine preferentially with metal ions of class 'b'.

e.g. R_3P , R_2S

Tendency of complexation of ligands with class 'b' metal ions is given hereunder:



R. G. Pearson introduced the terms "hard and soft" for "class a and b" respectively.

class a Metal ions \Rightarrow Hard acid

class a Ligands \Rightarrow Hard base

class b Metal ions \Rightarrow Soft acid

class b Ligands \Rightarrow Soft base

Hence,

Hard acids are those in which the acceptor atoms are small in size, have high electronegativity, low polarisability and have a noble gas configuration.

Soft acids are those in which the acceptor atoms are large in size, have low positive charge and contain unshared pair of electrons (p or d) in valence shell i.e. they have high polarisability and low electronegativity and do not have noble gas configuration.

Hard bases have donor atoms that have low polarisability, high electronegativity and are hard to oxidise.

Soft bases have donor atoms that are easily polarised, have low electronegativity and are easy to oxidise.

However it is important to note that there is no sharp line of demarcation between soft and hard species and a number of borderline cases also exist.

HSAB Principle :- This principle states that "hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases".

It should be noted that hard-soft or soft-hard interactions do also exist. However, given a choice hard-hard or soft-soft interactions are preferred over soft-hard interactions.

The bonding in hard acids and bases is electrostatic and can be explained in terms of ionic or dipole-dipole interactions, whereas bonding in soft acids and bases is covalent and are explained on the basis of polarisation.

Hard and Soft acids and bases

Hard	Borderline case (i.e. intermediate)	Soft
<u>Acids</u> $H^+, Li^+, Na^+, K^+, Be^{2+},$ $Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+},$ $Co^{3+}, Cr^{2+}, Cr^{3+}, Al^{3+},$ $Fe^{3+}, Ti^{4+}, Si^{4+}, Zr^{4+},$ $La^{3+}, Lu^{3+}, Ce^{3+}, Sn^{4+}$ SO_3, BF_3	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},$ $Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+},$ Rh^{3+} SO_2, BBr_3, GaH_3	$Cu^+, Au^+, Ag^+, Tl^+,$ $Hg_2^{2+}, Pd^{2+}, Cd^{2+}, Pt^{2+},$ Hg^{2+} $BH_3, GaCl_3, InCl_3, I^+,$ Br^+, I_2, Br_2
<u>Bases</u> $H_2O, OH^-, F^-, CH_3COO^-,$ PO_4^{3-}, SCN^- $SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-,$ $NO_3^-, ROH, RO^-, R_2O,$ NH_3, RNH_2, N_2H_4	$C_6H_5NH_2, C_5H_5N, Br^-$ NO_2^-, SO_3^{2-}, N_2	$R_2S, RSH, RS^-, I^-,$ $SCN^-, S_2O_3^{2-}, R_3P, R_3As,$ $(RO)_3P, CN^-, RNC, CO,$ C_2H_4, C_6H_6, H^-

* The underlined element represents the bonding site.

Applications of HSAB principle:-

(i) Stability of complexes



The complex AB will be stable if both A and B are either hard acids and bases or soft acids and bases.

e.g. (i) AgI_2^- is stable but AgF_2^- does not exist
(Ag^+ = soft acid; I^- = soft base; F^- = hard base)

(ii) CoF_6^{3-} is more stable than CoI_6^{3-}
(Co^{3+} = hard acid; F^- = hard base; I^- = soft base)

(ii) Predicting feasibility of a reaction



Soft iodide ion prefers to combine with soft caesium ion; hard fluoride ion combines with hard lithium ion.

(iii) Occurrence of minerals Hard acids like Ca^{2+} , Mg^{2+} and Al^{3+} appear as CaCO_3 , MgCO_3 and Al_2O_3 respectively, as the anions CO_3^{2-} and O^{2-} are also hard. These cations are never found as sulphides as S^{2-} is a soft base.

On the other hand, soft acids like Cu^{2+} , Ag^+ & Hg^{2+} combine with soft base S^{2-} and exist as sulphides.

The intermediate acids such as Ni^{2+} , Pb^{2+} and Cu^{2+} are found both as sulphides & carbonates.

The combination of hard acids and hard bases mainly occurs through ionic bonding as in $Mg(OH)_2$ and that of soft acids and soft bases occur mainly through covalent bonding as in HgI_2 .

(iv) for heterogenous catalysis :- HSAB principle says that soft metals adsorb soft bases and for solubility the rule is that hard solute dissolves in hard solvents and soft solute dissolves in soft solvents.

(v) Prediction of donor atom in ambidentate ligand
 $[SCN]^-$ is an ambidentate ligand where N is a hard base and S is a soft base. Therefore, the ligand coordinates through N atom to form $[Co(NCS)_4]^{2-}$ (both Co and N are hard) and through S atom to form $[Pd(SCN)_4]^{2-}$ (both Pd and S are soft).

(vi) Predicting relative strength of halogen acids in aqueous medium :-

HF (hard acid and hard base) being stable, does not dissociate easily in aqueous solution. Hence HF is the weakest acid.

HI (hard acid and soft base) being unstable, dissociates easily and hence is a strong acid.

Relative strength of acids :- $HF < HCl < HBr < HI$
 Weakest acid Strongest acid

The HSAB concept gives only a qualitative idea and does not

offer any quantitative scale of measurement. For example it cannot explain why OH^- is 10^{13} times stronger base than F^- (both are hard bases).