

Hard and Soft acids and bases (Pearson's Concept)

Certain ligands tend to form stable complexes with heavier ions such as Ag^+ , Hg^{2+} , Pd^{2+} , Pt^{2+} with nearly full d- electrons, other prefer to form complexes with lighter ions such as Be^{2+} , Al^{3+} , Ti^{4+} with no or less number of d- electrons. Based on their preferential bonding, metal ions as well as ligands have been classified into two categories each :-

1. Alkali metal ions, alkaline earth metal ions, light metal ions with no or less number of d- electrons or metal ion in higher oxidation states are classified as hard acids (all metal ions are Lewis acid). Heavier metal ions with nearly full d- electrons or metal ions in lower oxidation states or metal ions with bigger size are classified as soft acids.
2. Ligands which prefer to form most stable complexes with light metals (i.e hard acids) are classified as hard bases (all ligands are Lewis bases). Ligands which prefer to form stable complexes with heavy metal ions (i.e soft acids) are classified as soft bases.

Hard Acids	Soft Acids
H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ga^{3+} , In^{3+} , La^{3+} , Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ce^{3+} , AlCl_3 , AlH_3 , I^+ , I^{5+} etc.	Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ , Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+} , GaI_3 , SnCl_3 , BH_3 , I^+ , Br^+ etc.

Hard Bases	Soft Bases
NH_3 , RNH_2 , N_2H_4 , H_2O , OH^- , O^{2-} , R-OH , RO^- , CH_3COO^- , CO_3^{2-} , NO_3^- , NCS^- , PO_4^{3-} , SO_4^{2-} , ClO_4^- etc.	H^- , R , C_2H_4 , C_6H_6 , CN^- , RNC , CO , $\text{S}_2\text{O}_3^{2-}$, SCN^- , R_3P , R_3As , I^- etc.

Hard Acids	Soft Acids
1. They have acceptor metal atom of small size. 2. They have acceptor with high positive oxidation charge (state). 3. The valence electrons of the acceptor of these acids cannot be polarised easily. 4. Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} etc.	1. They have acceptor metal atom of large size. 2. They have acceptor with low or zero positive oxidation charge (state) 3. The valence electrons of the acceptor of these acids can be polarised easily. 4. Cu^+ , Ag^+ , Au^+ , Tl^+ etc.

Hard Bases	Soft Bases
1. The donor atom of a hard base has high electronegativity. 2. Holds its valence electrons strongly and hence cannot be polarised easily. 3. NH_3 , RNH_2 , N_2H_4 , H_2O etc.	1. The donor atom of a hard base has low electronegativity. 2. Holds its valence electrons weakly and hence can be polarised easily. 3. H^- , R , C_2H_4 , C_6H_6 etc.

Borderline (Intermediate) acids

The characteristic of borderline acids are intermediate between those of hard acids and soft acids.

E.g. - Fe^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , Sb^{3+} , Bi^{3+} etc.

Borderline (Intermediate) bases

These bases have intermediate properties.

E.g. - $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , Br^- , NO_2^- , SO_3^{2-} , N_2 etc.

Pearson's HSAB Concept and its application

This principle states that a hard acid (Lewis acid) prefer to combine with a hard base (Lewis base) and similarly, a soft acid prefers to combine with a soft base, since this type of combination gives more stable product. The combination of hard acid and hard base occurs mainly through ionic bonding as in $\text{Mg}(\text{OH})_2$, (Mg^{2+} = hard acid, OH^- = hard base) and that of soft acid and soft base take mainly by covalent bonding as in HgI_2 (Hg^{2+} = soft acid, I^- = soft base). This principle, however does not state that hard-soft or soft-hard combination does not or cannot exist. It only state that if there is a choice, a hard-hard or soft-soft combination would be preferred to a hard-soft or soft-hard combination.

1. Stability of a complex compound having the same ligands -

This application can be explained by considering an example. AgI_2 is stable while AgF_2 does not exist. We know that Ag^+ is a soft acid, F^- ion is a hard base and I^- ion is a soft base. Thus, AgI_2 is obtained by the combination of soft acid (Ag^+) and soft base (I^-) and AgF_2 results by the interaction of a soft acid (Ag^+) and a hard base (F^-). Therefore, AgF_2 is stable but AgF_2 does not exist.

2. To predict the nature of bonding in complex ion given by ambidentate ligand -

With the help of HSAB principle, we can predict which atom of an ambidentate ligand will combine with metal ion. SCN^- is an ambidentate ligand since it can co-ordinate to the metal ion either through S-atom or through N-atom. It has been found that Co^{2+} and Pd^{2+} both combine with 4 SCN^- ligand to form complex ion, $[\text{M}(\text{SCN})_4]^{2-}$ ($\text{M} = \text{Co}^{2+}$, Pd^{2+}). With HSAB principle, it can be shown that in $[\text{Co}(\text{SCN})_4]^{2-}$, Co^{2+} is linked with the ligand through N-atom while in $[\text{Pd}(\text{SCN})_4]^{2-}$, Pd^{2+} is co-ordinated with the ligand through S-atom. Thus, the complex ions given by Co^{2+} and Pd^{2+} ions should be represented as $[\text{Co}(\text{NCS})_4]^{2-}$ and $[\text{Pd}(\text{SCN})_4]^{2-}$. The reason is Co^{2+} ion is hard acid and it prefers to co-ordinate with N-atom of the hard ligand NCS^- . On the other hand, Pd^{2+} is a soft acid and hence combines with S-atom of soft ligand, SCN^- .

3. Stability of complex compounds having different ligands -

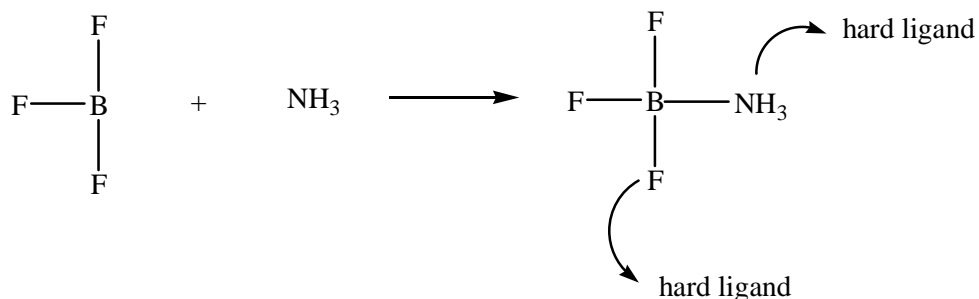
In the compound $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$, both the ligands i.e. NH_3 and F^- ions are hard ligands and hence is a stable complex ion, whereas in $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$, NH_3 is a hard ligand and I^- is a soft ligand, therefore, it is an unstable complex ion. Therefore, complex compound having the same nature of ligand i.e. hard ligand or soft ligand are stable whereas complex compound having ligands of different nature are unstable.

4. Symbiosis -

Soft ligands prefer to get attached with a centre which is already linked with soft ligands. Similarly, hard ligands prefer to get attached with a centre which is already linked with hard ligands. This tendency of ligands is called symbiosis. It can be illustrated with an example -

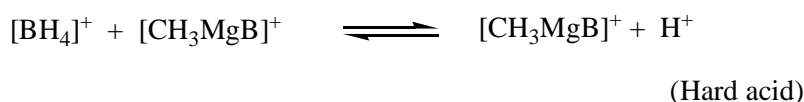
The formation of $(\text{BF}_3 \longleftarrow \text{NH}_3)$ adduct.

Since F^- ions which are already attached with Boron in BF_3 molecules are also hard ligands. Thus -



5. Prediction of hardness and softness -

Consider a base B whose hardness or softness is to be predicted. If the equilibrium shifts towards the right, then B is a soft base because it shows more affinity for the soft acid $[\text{CH}_3\text{Mg}]^+$ (soft-soft interaction).



Basis for Hard-Hard and Soft-Soft Interactions

Several views have been put forth to explain the basis for hard-hard and soft-soft interactions. However, no single view is completely satisfactory. According to the most accepted view, the cause of hard-hard interaction is electrostatic interaction. As discussed, bonding between hard acids and hard bases are predominantly ionic. The electrostatic energy between a positive and negative ion is inversely proportional to the internuclear distance. Therefore, the smaller the ions, the lesser would be the internuclear distance and greater would be the electrostatic attraction between the two ions.

Consequently, in the resulting compound would be highly stable.

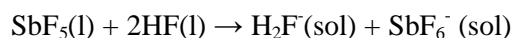
Electrostatic interaction cannot explain the soft-soft interactions because the size of soft species are comparatively very large. Polarisation of the species, however, plays an important role in explaining their interactions. Most of the soft acids have 6 - 10 d-electrons in their electronic configurations. These electrons get easily polarised favouring covalent bonding between them and soft bases which are also easily polarisable (bonding between Li^+ between soft acids and soft bases is assumed to be largely covalent). In soft-soft interactions the contribution of π -bonding is also important. Soft acids are generally metals in low oxidation states and thus have strong tendency to form π bonds with soft bases which are also good π bonding ligands. The polarisability of soft acids and soft bases further favour π -bonding.

Super acids

A superacid is a substance that is a more efficient proton donor than pure H_2SO_4 . Superacids are typically viscous, corrosive liquids and can be up to 10^{18} times more acidic than H_2SO_4 itself. They are formed when a powerful Lewis acid is dissolved in a powerful Bronsted acid. The most common superacids are formed when SbF_5 is dissolved in fluorosulfonic acid, HSO_3F , or anhydrous HF . An equimolar mixture of SbF_5 and HSO_3F is known as 'magic acid', so named because of its ability to dissolve candle wax. The enhanced acidity is due to the formation of a solvated proton, which is a better proton donor than the acid:



An even stronger superacid is formed when SbF_5 is added to anhydrous HF :

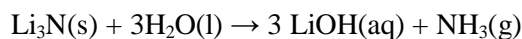


Other pentafluorides also form superacids in HSO_3F and HF and the acidity of these compounds

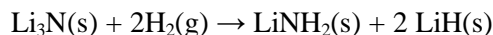
decreases in the order $\text{SbF}_5 > \text{AsF}_5 > \text{TaF}_5 > \text{NbF}_5 > \text{PF}_5$.

Super bases

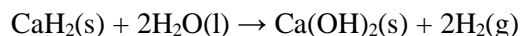
A superbase is a compound that is a more efficient proton acceptor than the OH^- ion, the strongest base that can exist in aqueous solution. Superbases react with water to produce the OH^- ion. Inorganic superbases are usually salts of Group 1 or Group 2 cations with small, highly charged anions. The highly charged anions are attracted to acid solvents such as water and ammonia. For example, lithium nitride, Li_3N , reacts violently with water:



The nitride anion is a stronger base than the hydride ion and deprotonates hydrogen:



Sodium hydride is a superbase that is used in organic chemistry to deprotonate carboxylic acids, alcohols, phenols, and thiols. Calcium hydride reacts with water to liberate hydrogen:



Calcium hydride is used as a dessicant, to inflate weather balloons, and as a laboratory source of pure hydrogen.

Application of acid and base in heterogeneous catalysis

Some of the most important reactions involving the Lewis and Bronsted acidity of inorganic compounds occur at solid surfaces. For example, surface acids, which are solids with a high surface area and Lewis acid sites, are used as catalysts in the petrochemical industry for the interconversion of hydrocarbons. The surfaces of many materials that are important in the chemistry of soil and natural waters also have Bronsted and Lewis acid sites.

Silica surfaces do not readily produce Lewis acid sites because $-\text{OH}$ groups remain tenaciously attached at the surface of SiO_2 derivatives; as a result, Bronsted acidity is dominant. The Bronsted acidity of silica surfaces themselves is only moderate (and comparable to that of acetic acid). However, as already remarked, aluminosilicates display strong Bronsted acidity. When surface OH groups are removed by heat treatment, the aluminosilicate surface possesses strong Lewis acid sites. The best-known class of aluminosilicates is the zeolites, which are widely used as environmentally benign heterogeneous catalysts. The catalytic activity of zeolites arises from their acidic nature and they are known as solid acids.