HSAB Principle :

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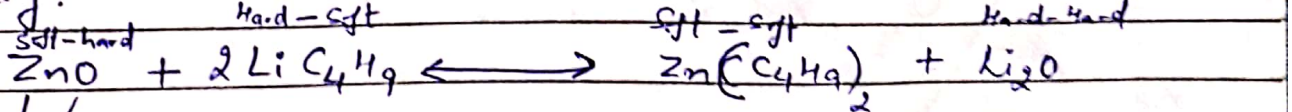
* Hard acids and Bases are small, compact and non-polarizable
* Soft acids and bases are larger, with a more diffuse distribution of electrons
* Hard acids are often metal ions with a higher positive charge and small ionic size. Their d-orbitals are often unavailable to engage in π-bonding.
* Soft acids have lower charge density. Their d-orbitals are available for π-bonding. often 2nd & 3rd row transition metals with +1 or +2 charge (and filled or nearly filled d orbitals) are soft acids
* It is important to realize that hard/soft considerations have nothing to do with acid or base strength.

"An acid or base may be hard or soft and also be either weak or strong"

In a competition rxn between two bases for the same acid, one must consider the relative strength of the bases, and the hard/soft nature of each base and the acid

e.g.



Zn is a strong lewis acid (But soft acid) and oxide ion : a base. (Hard base)

Above rxn proceeds to right as hard/soft considerations override acid-base strength considerations.

Hard Acids: Alkali metal ions, alkaline earth metal ions, light metal ions with no or lesser no. of d-electrons, or metal ions in higher oxidation states e.g.

~~H^+, Li^+, Na^+, K^+~~

Soft acids: Metal ions with bigger size, metal ions in lower oxidation states and metal ions with nearly filled d-orbitals.

Hard acids	Soft acids
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Ti^+, Hg^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	Tl^{3+}, BH_3, GaI_3
Cr^{3+}, Fe^{3+}, As^{3+}	
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	

Hard acids are Lewis acids which are small in size and whose e^- clouds are not so easily polarisable

Soft acids are Lewis acids which are comparatively larger in size and whose e^- clouds are easily polarisable.

HSAB Principle and Its applications?

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(1) Stability of Complexes:

(a) $A + B \longrightarrow A:B$

Lewis acid — Lewis Base — Complex

Complex A:B would be most stable if A and B are either both hard or both soft. eg. AgI_2^- is a stable compound whereas AgF_2^- is not. Because Ag^+ is a soft acid, thus it forms a stable complex with soft base i.e. I^- and not with hard base F^-.

$Ag^+ + 2I^- \longrightarrow AgI_2^-$

Soft acid — Soft Base — (Stable)

$Ag^+ + 2F^- \longrightarrow AgF_2^-$

Soft acid — Hard Base — (Unstable)

(b) Stability of diff types of (natural) ores can also be explained using HSAB Principle

* Most of the 1st row Transition metals are isolated from oxide ores but Copper and Zinc occur naturally in the form of sulphide ores. It is because of increase of soft character of metal ions while going from left to right in the Transition series.

* Due to increase in soft character, most of the 2nd & 3rd row transition elements exist as their sulphides in nature.

(2) Predicting Feasibility of a rxn:

Hard Sft concept can be used to predict whether a given rxn will proceed to the forward (right) or backward (left) side. eg.

$LiI + CsF \longrightarrow LiF + CsI \quad \Delta H = -138\,kJ$

Hard Sft Sft Hard Hard-Hard Sft-Sft

$HgF_2 + BeI_2 \longrightarrow HgI_2 + BeF_2$

Sft Hard Hard Sft

(3) Prediction of hardness and Softness:

Consider a base B whose hardness or softness is to be predicted.

$[BH^+] + [CH_3Mg]^+ \rightleftharpoons [CH_3MgB]^+ + H^+$

Sft acid Hard acid

If the equilibrium shifts to the right, then B is a Sft base and vice-versa.

Basis for Hard-hard and Sft-Sft Interaction

Hard acids and hard bases bind through an ionic bond. Since the electrostatic force of attraction is inversely proportional to the distance between the ions. Therefore smaller the ions lesser would be the internuclear distance and greater would be the electrostatic force of attraction.

But this can't be true in case of Sft-Sft interactions as both of these ions are large

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~~in size.~~ But large sized ions can be easily polarised. & Most of the soft acids have 6-10 d e⁻s which can be easily polarised.

Thus bonding in soft acid - bases is largely covalent in nature.