HARD SOFT ACIDS AND BASES (HSAB)

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CONCEPTS OF ACIDS AND BASES

There are three concepts of acids and bases in current use. Each has its own peculiar advantages.

(a) Arrhenius concept
(b) Bronsted-Lowry concept
(c) Lewis concept

Arrhenius concept

Savante Arrhenius (1884) proposed his concept of acids and bases. According to this concept, **an acid is a compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.**

For example, HCl is an Arrhenius acid and NaOH is an Arrhenius base.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \longrightarrow OH^-(aq) + Na^+(aq)$$

BRONSTED–LOWRY CONCEPT

In 1923 J.N. Bronsted and J.M. Lowry independently proposed a broader concept of acids and bases. According to this theory,

an acid is any molecule or ion that can donate a proton (H^+)

a base is any molecule or ion that can accept a proton

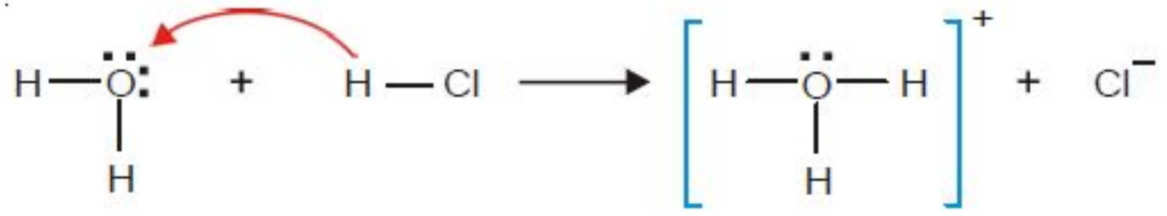
For brevity we can say that an acid is a proton donor while a base is a proton acceptor.

A Bronsted acid is a proton donor and a Bronsted base is a proton acceptor.

BRONSTED–LOWRY CONCEPT

Examples of Bronsted acids and bases

(1) **HCl gas and H_2O.** When dry HCl gas dissolves in water, each HCl molecule donates a proton to a water molecule to produce hydronium ion.



Hydronium ion

Thus HCl gas is a Bronsted acid and water that accepts a proton is a Bronsted base.

(2) **HCl and Ammonia, NH_3.** HCl gas reacts with ammonia (NH_3) to form solid NH_4Cl.

Ammonium ion

HCl is a proton donor and hence a Bronsted acid, while NH_3 is a proton acceptor and a Bronsted base.

LEWIS CONCEPT OF ACIDS AND BASES

In the early 1930s, G.N. Lewis proposed even a more general model of acids and bases. According to Lewis theory,

an acid is an electron-pair acceptor

a base is an electron-pair donor

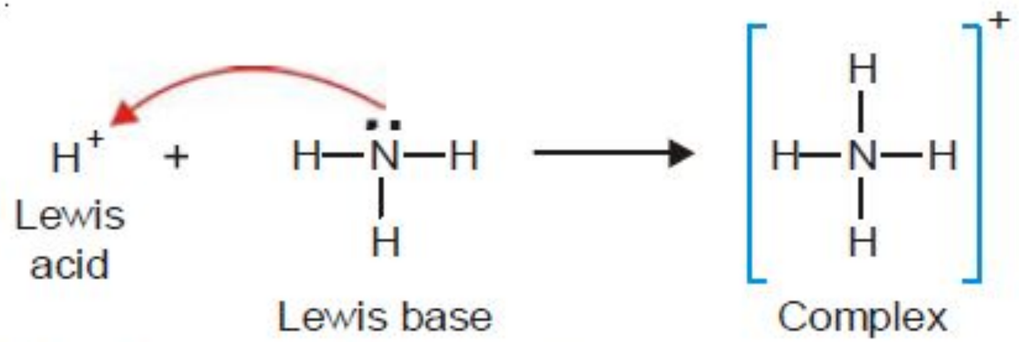
Lewis pictured an acid and base as sharing the electron pair provided by the base. This creates a covalent bond (or coordinate bond) between the **Lewis acid** and the **Lewis base.** The resulting combination is called a **Complex**. If the Lewis acid be denoted by A and the Lewis base by B, then the fundamental equation of the Lewis theory can be written as :

$$\underset{\substack{\text{Lewis}\\ \text{acid}}}{A} \quad + \quad \underset{\substack{\text{Lewis}\\ \text{base}}}{:B} \longrightarrow \underset{\text{Complex}}{A - B}$$

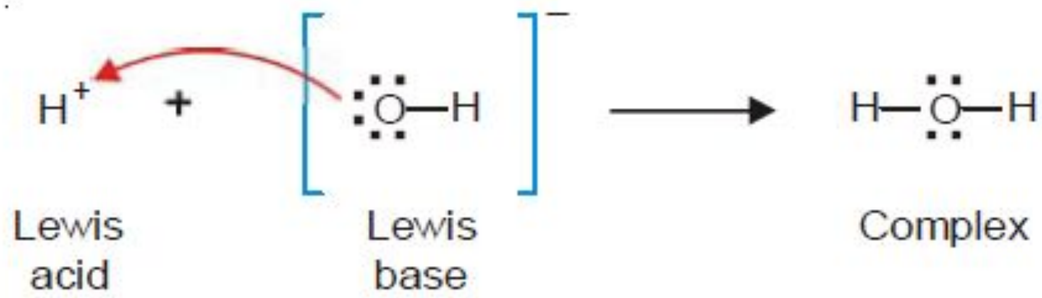
It may be noted that : (1) all cations or molecules short of an electron-pair act as Lewis acids; and (2) all anions or molecules having a lone electron-pair act as Lewis bases.

Examples of Lewis reactions

(1) **Between H^+ and NH_3.** Proton (H^+) is a Lewis acid as it can accept an electron-pair. Ammonia molecule ($:NH_3$) has an electron-pair which it can donate and is a Lewis base. Thus the Lewis reaction between H^+ and NH_3 can be written as :



(2) **Between H^+ and OH^-.** A proton (H^+) is an electron-pair acceptor and, therefore, a Lewis acid. The OH^- is an electron-pair donor and hence a Lewis base. Thus Lewis reaction between H^+ and OH^- can be written as :



SUPERIORITY OF LEWIS MODEL OF ACIDS AND BASES

Superiority of Lewis model of acids and bases

The useful but limited model of Arrhenius was replaced by a more general model of Bronsted and Lowry. Even a more general model was proposed by Lewis. However, the Bronsted-Lowry model is now used in common practice.

TABLE 27.2. THREE MODELS FOR ACIDS AND BASES

Model	Definition of acid	Definition of base
Arrhenius (1884)	H^+ producer	OH^- producer
Bronsted-Lowry (1923)	H^+ donor	H^+ acceptor
Lewis (1939)	electron-pair acceptor	electron-pair donor

The advantages of the Lewis acid-base model

(1) All the Bronsted-Lowry acid base reactions are covered by the Lewis model. It is so because the transfer or gain of a proton is accompanied by the loss or donation of an electron-pair in both types of reactions.

(2) Many reactions which do not involve transfer of a proton *e.g.*,

$$BF_3 + NH_3 \longrightarrow BF_3 - NH_3$$

are also covered by the Lewis theory.

HARD AND SOFT ACIDS AND BASES (HSAB)

- Strength of Lewis acids and bases [Hard (H) and Soft (S) Acid (A) Base (B) Concept = HSAB Concept), 1963].

- Lewis defines acids are electrons acceptor and bases are electron donor. Therefore, the strength of acids and bases is determined by the nature of electron transfer in a particular reaction. Hence, the strength is dependent on a particular reaction. Accordingly, assignment of any single consistent criterion for acid-base strength becomes very difficult in the Lewis definition.
- A qualitative correlation between the various Lewis acids and Bases has been obtained by classifying the acids and bases in to two different groups, known as hard and soft.

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

HARD AND SOFT ACIDS AND BASES (HSAB)

- In 1963, **R. G. Pearson** proposed that hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases. This is known as HSAB concept or theory.

- 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 hard Bases.

- Similarly the class ‘b’ metals having large size, more or easily polarizable, prefers to combine with non-metals or ligands having similar properties; Pearson called such metals as soft acids and the ligands as soft base

HARD AND SOFT ACIDS AND BASES (HSAB)

- 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 a 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.

HARD AND SOFT ACIDS

Hard acids	Soft acids
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.

HARD AND SOFT ACIDS

Hard Acids	Borderline Acids	Soft Acids
H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Si^{4+}, Ti^{4+},	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+},	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pb^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}, Tl^{3+}, BH_3,
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 π - acceptor ligands I^+, Br^+, O, Cl, Br, I, N Zero valent metal atoms.

HARD AND SOFT BASES

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.

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:

$$HX + H_2O \rightarrow H_3O^+ + X^-$$

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

$HF < HCl < HBr < HI$

APPLICATIONS OF HSAB PRINCIPLE

Relative stabilities of complexes in Aqueous Solutions :

HSAB entails that[$Cd(CN)_4]^{2-}$ is more stable that $[Cd(NH_3)_4]^{2+}$ According to HSAB principle hard prefers hard and soft prefers soft.Hence the soft acid Cd^{2+} will prefer to corrdicate soft base CN^-It is clear from the K_{inst} constants where cyano complex has $K_{inst} = 1.4x10^{-19}$ while for ammine complex it is $7.5x10^{-8}$ .Thus cyano is stable.

To Predict the Course of Reaction :

i) $H^+ CH_3HgOH \rightarrow H_2O + CH3Hg^+$

ii) $H^+ + CH^3HgSH \rightarrow H_2S + CH_3Hg^+$

The reaction (i) goes to right as the hard acid H^+ binds strongly to hard base OH^- to produce stable product H_2O

On the other hand the reaction (ii) is favoured to left where soft base SH will tend to remain combined with soft acid CH Hg^+ instead of joining to hard acid H^+

APPLICATIONS OF HSAB PRINCIPLE

1. Recovery of Au

The softest metal ion $Au^+(aq)$ is recovered in mining operations by suspending it in a dilute solution of CN^-, which dissolves the Au.

$$4\,Au(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O \Rightarrow 4\,[Au(CN)_2]^-(aq) + 4\,OH^-$$

2. Why is AgI(s) water-insoluble, but LiI water-soluble?

AgI is a soft acid-soft base combination, while LiI is hard-soft.

The interaction between Li^+ and I^- ions is not strong.

$AgI(s) + H_2O(l) \rightarrow$ essentially no reaction

$LiI(s) + H_2O(l) \rightarrow Li^+(aq) + I^-(aq)$

3. In Hydrogen Bonding:

The strong hydrogen bond is possible in cases of H_2O, NH_3 and HF, since the donor atoms (F, O & N) are HARD BASES and their interactions with partially positively charged H, which is a HARD ACID, are stronger.

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 f 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- and F- ions are both hard bases where OH- is nearly 10^{13} times stronger base than F ions .Correlation between hardness and inherent acid base strength is yet to be developed.

Summary

HSAB Principle: According to HSAB concept,

- **Hard acids prefer binding to the hard bases to give ionic complexes, whereas**
- **Soft acids prefer binding to soft bases to give covalent complexes.**

* The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.

* The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent.

* The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.