ACIDS AND BASES

Acids and Bases Definition

> An acid is any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance. A base is a molecule or ion able to accept a hydrogen ion from an acid.

Acidic substances are usually identified by their sour taste. An acid is basically a molecule which can donate an H^+ ion and can remain energetically favourable after a loss of H^+. ***Acids are known to turn blue litmus red.***

Bases, on the other hand, are characterized by a bitter taste and a slippery texture. A base that can be dissolved in water is referred to as an alkali. When these substances chemically react with acids, they yield salts. ***Bases are known to turn red litmus blue.***

Bronsted-Lowry Acid

The Bronsted-Lowry acid is a substance which donates a proton or H^+ ion to the other compound.

$Acid \rightleftharpoons Proton + Conjugatebase$
A conjugate base can accept a proton and acid reforms.

$$HF \rightleftharpoons H^+ + F^-$$
$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$NH_4^+ \rightleftharpoons H^+ + NH_3$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$F^- + H^+ \rightleftharpoons HF$$

Bronsted-Lowry Base

The Bronsted-Lowry base is a substance which accepts a proton or H+ ion from other compounds.

$Base + Proton \rightleftharpoons Congatedacid$
A conjugated acid can donate a proton and base reforms.

$$OH^- + H^+ \rightleftharpoons H_2O$$
$$S^{2-} + H^+ \rightleftharpoons HS^-$$
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

The Bronsted-Lowry theory of an acid-base reaction involves the transfer of protons or H^+ ions between the acid and base.

Consider a reaction in which ammonia (base) is dissolved in water (acid). Ammonia takes a proton from water and the reaction is as follows,

$$H_2O(l)) + NH_3(Aq)) \rightleftharpoons OH^-(Aq) + NH_4^+$$
$$Acid + Base \rightleftharpoons Conjugatebase + conjugateacid$$

Example 2:

A reaction between acetic acid and water, acetic acid donates a proton and acts like acid and water molecule (base) takes a proton.

$$CH_3CO_2H(aq) + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$
$$Acid + Base \rightleftharpoons conjugatebase + conjugateacid$$

Note:

- *Strong Bronsted-Lowry acids are those which have a strong tendency to give a proton and their corresponding conjugate base is weak.*
- *Weak Bronsted-Lowry acids will have a little tendency to donate a proton and their corresponding conjugated base is strong.*

Lewis Acid

Lewis Acids are the chemical species which have empty orbitals and are able to accept electron pairs from Lewis bases. This term was classically used to describe chemical species with a trigonal planar structure and an empty p-orbital. An example of such a Lewis acid would be BR_3 (where R can be a halide or an organic substituent).

Water and some other compounds are considered as both Lewis acids and bases since they can accept and donate electron pairs based on the reaction.

Examples of Lewis Acids

Some common examples of Lewis acids which can accept electron pairs include:

- H^+ ions (or protons) can be considered as Lewis acids along with onium ions like H_3O^+.
- The cations of d block elements which display high oxidation states can act as electron pair acceptors. An example of such a cation is Fe^{3+}.
- Cations of metals such as Mg^{2+} and Li^+ can form coordination compounds with water acting as the ligand. These aquo complexes can accept electron pairs and behave as Lewis acids.

Lewis Base

Atomic or molecular chemical species having a highly localized HOMO (The Highest Occupied Molecular Orbital) act as Lewis bases. These chemical species have the ability to donate an electron pair to a given Lewis acid in order to form an adduct, as discussed earlier.

The most common Lewis bases are ammonia, alkyl amines, and other conventional amines. Commonly, Lewis bases are anionic in nature and their base strength generally depends on the pK_a of the corresponding parent acid. Since Lewis bases are electron-rich species that have the ability to donate electron-pairs, they can be classified as nucleophiles. Similarly, Lewis acids can be classified as electrophiles (since they behave as electron-pair acceptors).

Examples of Lewis Bases

Examples of Lewis bases which have an ability to donate an electron pair are listed below.

- Pyridine and the derivatives of pyridine have the ability to act as electron pair donors. Thus, these compounds can be classified as Lewis bases.
- The compounds in which Oxygen, Sulphur, Selenium, and Tellurium (which belong to group 16 of the Periodic Table) exhibit an oxidation state of -2 are generally Lewis bases. Examples of such compounds include water and ketones.

Lux-Flood concepts for acid and base:

According to this theory, acid and base are defined as acid being an oxide acceptor and the base being an oxide donor.

Example: Calcium oxide(CaO)(CaO)(CaO) reacts with silicon dioxide(SiO_2) (SiO2)(SiO_2)to form calcium silicate(CaSiO3)(CaSiO_3)($CaSiO_3$).

$CaO + SiO_2 \longrightarrow CaSiO_3$

In this reaction, CaO is an oxide donor. So, CaO acts as the base while SiO_2 is an oxide acceptor. So, SiO_2 acts as an acid.

Hard and Soft Acids and Bases (HSAB) Theory

Hard and Soft Acids and Bases (HSAB) Theory is a qualitative concept introduced by Ralph Pearson to explain the stability of metal complexes and the mechanisms of their reactions.

However it is possible to quantify this concept based on Klopman's FMO analysis using interactions between HOMO and LUMO.

According to this theory, the Lewis acid and bases can be further divided into hard or soft or border line types.

Hard Acids	Soft Acids
Small ionic radii, High positive charge, Strongly solvated, Empty orbitals in the valence shell High energy LUMOs.	Large ionic radii, Low positive charge, Completely filled atomic orbitals Low energy LUMOs.
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+} **Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+},**	**Cu^+, Ag^+, Au^+, Hg^+ , Cs^+ , Tl^+ , Hg^{2+} Pd^{2+}, Cd^{2+} , Pt^{2+}**

Hard Bases	**Soft Bases**
Small ionic radii, Highly electronegative, Weakly polarizable, Strongly solvated, High energy LUMOs.	Large ionic radii, Intermediate electronegativity, highly polarizable Low energy LUMOs.
H_2O, OH^-, F^-, Cl^-, $CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, NO_3^-, ClO_4^-, ROH, RO^-, R_2O, NH_3,	**RSH, RS^-, R_2S, I^-, CN^-, SCN^-, $S_2O_3^-$, R_3P, R_3As $(RO)_3P$, RNC, CO, C_2H_4, C_6H_6, R^-, H^-**

The **Border line** Lewis acids and bases have intermediate properties.

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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.**

Problems

1. State the protonic definition of acids and bases.
   Show that for aqueous solutions, the protonic definition of acids is practically equivalent to the Arrhenius definition; but for bases, the protonic definition covers more compounds.
2. According to which of the various definitions of acids and bases is (a) HCl an acid in water, (b) HCl(*g*) an acid, (c) NH_4Cl an acid, (d) H_2SO_4 a base, (e) $NH_3(g)$ a base and (f) BF_3 an acid?
3. What are conjugate acids and bases? Write down the conjugate acids of:
   H_2O, NH_3, Cl^-, HS^-, S^{2-}, CO_3^{2-}, PO_4^{3-}, OH^-.
   Write down the conjugate bases of:
   H_2O, HCl, HS^-, NH_3, HCO_3^-, H_2SO_4, NH_4^+, HNO_3.
4. What do you mean by levelling effect of a solvent? Explain the statement: "Acetic acid exerts less levelling effect on the strengths of acids than water."
5. State, with reason, which one among each pair of the following should be a stronger acid or stronger base?
   (i) $H_2O - H_3O^+$, (ii) $NH_3 - NH_4^+$, (iii) $H_2S - H_2Se$,
   (iv) $HCO_3^- - CO_3^{2-}$, (v) $H_2SO_3 - H_2SO_4$, (vi) $KOH - Ba(OH)_2$,
   (vii) $Be(OH)_2 - Sr(OH)_2$, (viii) $Fe(OH)_2 - Fe(OH)_3$, (ix) HCl – HI,
   (x) HOCl – HOI (xi) $H_3PO_3 - H_3PO_4$ (xii) $HClO_3 - HClO_4$.
6. Explain/Justify:
   (a) F^- ion is a strong base.
   (b) HNO_3, HCl and H_2SO_4 appear equally strong in water but their strengths differ in acetic acid medium.
   (c) HSO_3^- may be considered both as an acid and a base.
   (d) Metal cations are good Lewis acids.

SUGGESTED READINGS/REFERENCES:

1. Lee, J. D., Concise Inorganic Chemistry
2. R.P. Sarkar, General and Inorganic Chemistry