E-Content Study Material

B. Sc. Chemistry (H)

2nd Year

Paper II B

Inorganic Chemistry

Chapter VII: Acids and Bases

Topic: Lux-Flood and Lewis Concept of Acids and Bases

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Lux-Flood Concept of Acids and Bases.

This concept was proposed by Lux and extended by Flood. It considers the acid-base reaction in terms of the specific reaction of the oxide ion and is mainly used for molten oxides at high temperatures. According to this concept, an acid is a substance which accepts the oxide ion and a base is a substance which donates the oxide ion. In other words, an acid is an oxide ion-acceptor and a base is an oxide ion-donor. For example, in the reaction

$$\underset{\text{Base}}{CaO} + \underset{\text{Acid}}{SiO_2} \longrightarrow CaSiO_3$$

Calcium oxide is a base and silicon dioxide is an acid, Similarly, in the reaction

$$PbO + SO_3 \longrightarrow PbSO_4$$

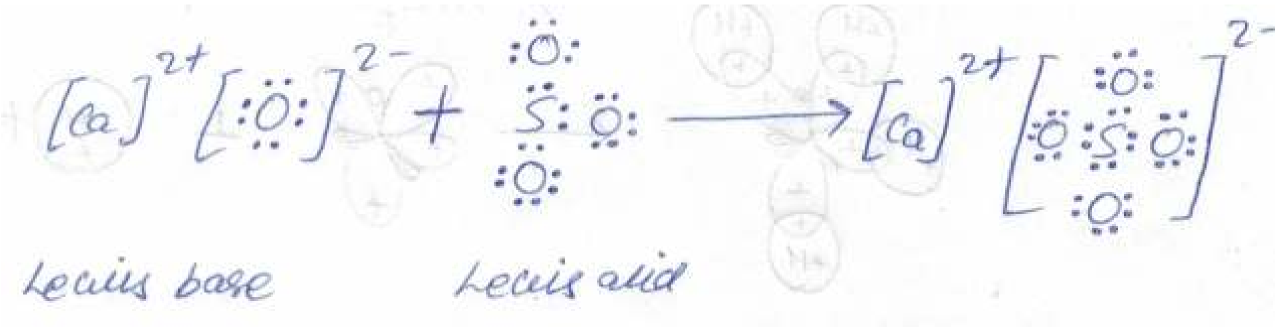
PbO is a base while SO_3 is an acid.

This concept, however, has only a limited scope.

Lewis Concept of Acids and Bases.

In 1923, G.N. Lewis, in order to cover all types of neutralization reactions, gave more broad based definitions of acids and bases. According to Lewis concept, a base is defined as a substance which can donate electrons whereas an acid is a substance which can accept electrons. In other words, while a base is an electron-donor, an acid is an electron-acceptor.

In the light of these definitions, the combination of calcium oxide with sulphur trioxide to form calcium sulphate is represented as below:



A lone pair of electrons from oxide ion of calcium oxide is donated to sulphur trioxide.

Lewis definition of a base covers all substances which have unshared electrons in the outer energy levels. These would also be classed as bases according to Lowry-Bronsted's concept. On the hand, Lewis acids include all substances which have vacant orbitals to accept electrons. These include the following types of substances:

1. All cations are regarded as Lewis acids because they can accept electrons. While larger cations such as Na^+, K^+, Ba^{2+}, Ca^{2+}, etc., behave as weak Lewis acids, smaller cations such as H^+, Ag^+, Fe^{2+}, etc., behave as strong Lewis acids. The smallest cation, H^+ ion, behaves as the strongest Lewis acid.

$$H^+ \quad + \quad NH_3 \longrightarrow NH_4^+$$

2. Electron – deficient compounds in which the central atom can expand their valence shells are regarded as Lewis acids.

   For example, in molecules such as BF_3, BCl_3, $AlCl_3$, etc., the central atoms have only six electrons around them and, therefore, have a tendency to accept an electron pair to complete their octet.

   For example,

$$F_3B \; + \; :NH_3 \longrightarrow F_3B : NH_3$$

3. Molecules in which the central atoms have vacant d orbitals may also behave as Lewis acids by extending their valency shells beyond the octet. For example, in molecules such as $SnCl_{4}$, SiF_{4}, SbF_{5}, etc., the central atoms have vacant d orbitals and, therefore, they extend their valency shells beyond the octet, as shown below:

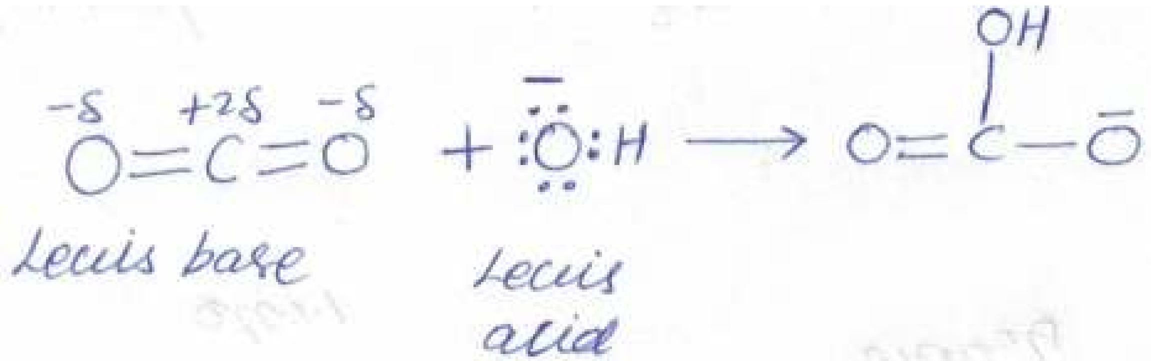
$$\underset{\text{Lewis acid}}{SiF_4} + \underset{\text{Lewis base}}{2F^-} \longrightarrow [SiF_6]^{2-}$$

$$SnCl_4 + 2Cl^- \longrightarrow [SiCl_6]^{2-}$$

$$SbF_5 + F^- \longrightarrow [SbF_6]^-$$

4. Molecules in which the central atom is bonded to atoms of different electronegativities through one or more multiple bonds also behave as Lewis acids. For example, C atom in CO_2 behaves as a Lewis acid because in this molecule, carbon is bonded to more electronegative oxygen atoms through double bonds. As the Lewis base approaches the less electronegative carbon atom, the pi electron charge density gets displaced away

from the carbon atom towards oxygen atoms. This result in development of a partial positive charge on carbon atom and a partial negative charge on oxygen atoms. In other words, the electron charge density on carbon atom decreases and, therefore, carbon atom in carbon dioxide acts as an electron-acceptor.



Similarly, S atoms in SO_2 acts as a Lewis acid towards OH^- ion.

Sulphur trioxide also acts as a Lewis acid. Its electronic structure is as shown before. It has a double bond between S and one of the O atoms. The oxygen atom, being more electronegative than sulphur atom, pulls the pi electrons towards itself leaving a partial positive charge on sulphur atom which, thereby, acts as an electron-deficient centre. As a result, a Lewis base like O^{2-} would donate its electron pair to S atom of SO_3 leading to the formation of SO_4^{2-} ion, as mentioned before.

Limitations of Lewis Concept.

The Lewis concept has several limitations, the most significant of which are discussed below:

1. The Lewis concept is too general and includes all reactants which can form coordination bonds. Even metals in their zero oxidation state (e.g., Fe, Ni, Co, Mn) are termed as Lewis acids in their complexes with pi acceptor ligands such as CO, cyclopentadiene and olefins.
2. The relative strengths of acids and bases cannot be explained on the basis of Lewis concept.