جامـــــعة المـــستـقـبـل
AL MUSTAQBAL UNIVERSITY

كلية العلـــوم
قـســـــــم الادلة الجنائية

المحاضرة الثانية

Introduction to Organic chemistry

المادة : عضوية
المرحلة : الثانية
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Acids and Bases

Acid-base theories:-

1) Arrhenius Theory (H^+ and OH^-):-

Acid:-any substance that ionizes (partially or completely) in water to give hydrogen ion (which associate with the solvent to give hydronium ion H_3O^+):

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

Base:-any substance that ionizes in water to give hydroxyl ions. Weak (partially ionized) to generally ionize as follows:-

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

While strong bases such as metal hydroxides (e.g. NaOH) dissociate as

$$M(OH)n \leftrightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

2) Bronsted-Lowry Theory (taking and giving protons, H^+):-

Acid:-any substance that can donate a proton.

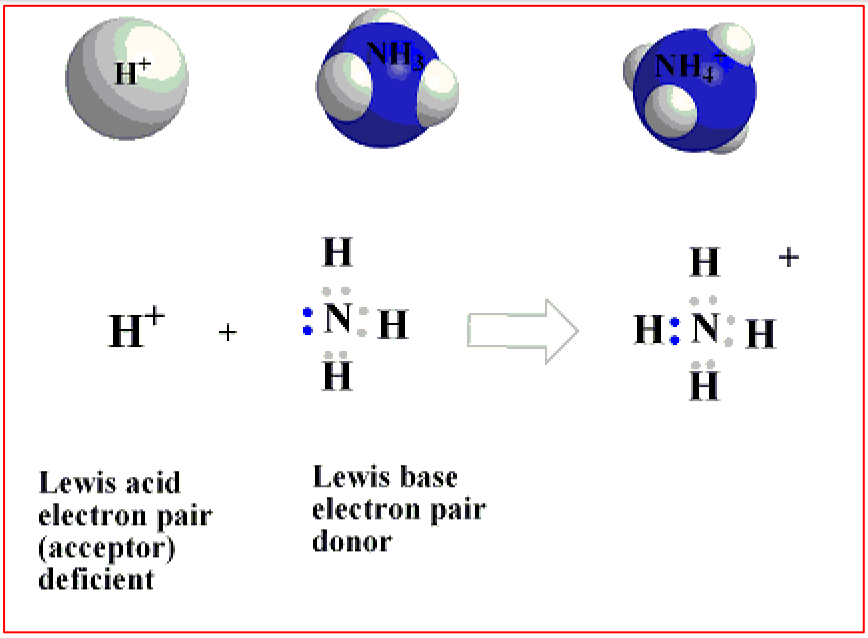
Base:-any substance that can accept a proton. Thus, we can write a half reaction:

$$\textbf{Acid} = \mathbf{H^+} + \textbf{Base}$$

3) Lewis Theory (taking and giving electrons):-

Acid:-a substance that can accept an electron pair.

Base:-a substance that can donate an electron pair.



Strong acids: - H_2SO_4, $HClO_4$, HNO_3, HI and HCl .

Strong bases: - LiOH, KOH, NaOH and $Ca(OH)_2$.

Lewis acids can be classified as follows:

1- their acidity increases with:

a. Increasing positive charge on the cation.

b. Increasing nuclear charge from one atom to another across a horizontal period in the periodic table.

c. Decreasing ionic radius.

d. Decreasing number of electronic shells in the cation.

This means that the Lewis acidity of simple cations increases in the periodic table from left to right and from bottom to top. Examples include:

$$Fe^{++} < Fe^{+++}$$

$$K^{+} < Na^{+} < Li^{+}$$

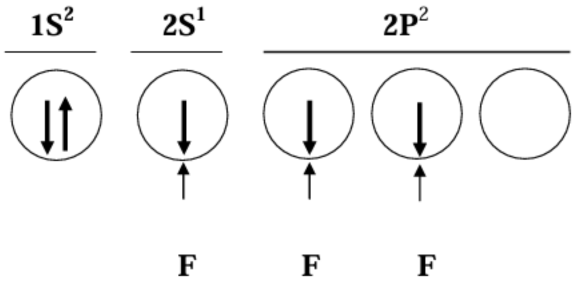
$$Li^{+} < Be^{++} < B^{+++}$$

2- Molecules with a central atom deficient in octet

This type is considered the most important class of Lewis acids. Examples include:

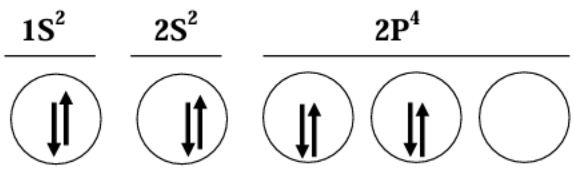
BF_3, BCl_3, $AlCl_3$ If we follow the electronic configuration of boron:

$$_{5}B = 1S^2\ 2S^2\ 2P^1$$
$$= 1S^2\ 2S^1\ 2P^2$$



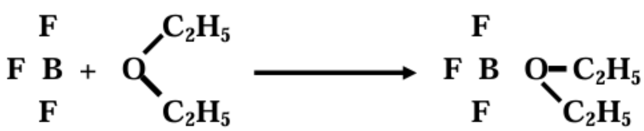
Then, it shares three fluorine atoms to saturate the three unpaired orbitals, and the result is:

an empty orbital in BF_3, which gives it the property of a Lewis acid because it has the ability to accept an electron pair.



As shown in the following reaction, the empty orbital in boron accepts the lone pair of electrons on the oxygen atom in the ether molecule.

$$BF_3 + (C_2H_5)_2O \longrightarrow BF_3O(C_2H_5)_2$$



The acidity of these molecules increases with:

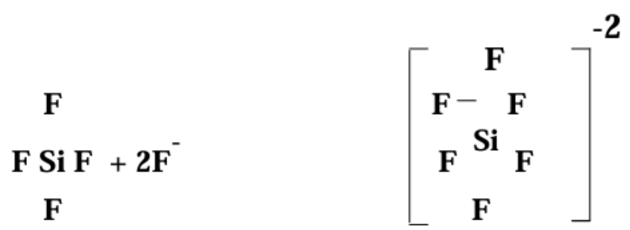
a. Increasing the nuclear charge of the central atom.

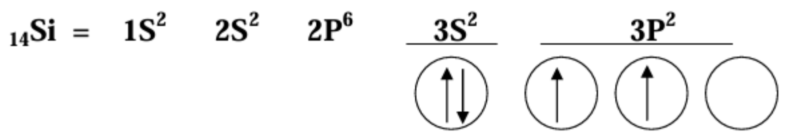
b. Decreasing the atomic radius of the central atom.

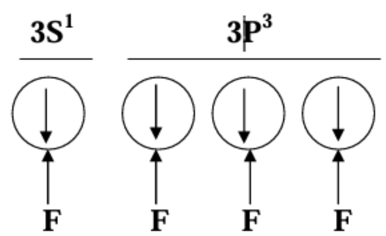
c. Decreasing the number of electronic shells in the central atom.

3- Molecules with a central atom that has an expandable octet

The reactivity of SiF_4 and $SiCl_4$ compared to CCl_4 is attributed to the silicon atom containing empty orbitals of type (d), thus allowing it to act as a Lewis acid. This is clear from the reaction of silicon tetrafluoride with the fluoride ion to form fluosilicate:







At first glance, it seems
that SiF_4 has bonded and its outer shell is satisfied with electrons after being bonded to four fluorine atoms. However, the reality indicates the presence of five d-orbitals in the silicon atom (considering that silicon belongs to the third period of the periodic table, which contains the d subshell). This allows it to accept electrons via its empty d-orbitals,

which gives it the property of a Lewis acid. As for CCl_4 and CF_4 compounds, they are not considered Lewis acids because the central atom, Carbon (C), belongs to the second period and does not have the d subshell.

4- Molecules with a Multiple Polar Covalent Bond (e.g., CO_2)

It initially appears that this molecule does not conform to the Lewis concept. However, in reality, bases also attack the centers with lower electronegativity. In this molecule, the two oxygen atoms pull the bonding electron pairs (the double bonds) between them and the carbon atom towards themselves (as they are stronger in electronegativity), leaving an electron deficiency on the carbon atom. This deficiency is then filled by the electron pairs from the base.

$$\overleftarrow{O=}C\overrightarrow{=O}$$

Note the direction of electron density pull towards the oxygen atoms.