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Class: Semester-2

Paper: C3T: Inorganic Chemistry

Topic: Acid-Base Reaction

PART 2

Comments: Go through the whole lesson thoroughly.

[N.B.**-** Acknowledgement of indebtedness to Mr. Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

$CO(NH_2)_2 + NH_3 \rightleftharpoons NH_4^+ + NH_2CONH^-$ ---- (vii)

$HCOOH + CO(NH_2)_2 \rightleftharpoons NH_2-\underset{O}{\overset{\|}{C}}-NH_3^+ + HCOO^-$ ---- (viii)

From the above table following points are important. From equation (i) and (ii)

(1) HSO_4^- may behave both as an acid and a base. The same remark applies to HCO_3^- and HS^-. The conjugate acids of HCO_3^-, HS^- and HSO_4^- are H_2CO_3, H_2S and H_2SO_4 respectively.

(2) Equation (iii) explains why an aqueous sol^n of NaHS will be basic and smell of H_2S.

(3) From equ^n (iv) it is clear that HNO_3 acts as a base in anhydrous HF, though it is an acid in aqueous sol^n.

(4) From equ^n (v) and (vi) it can say that HF and H_2SO_4 act as basics in presence of $HClO_4$.

(5) From equ^n (vii) and (viii) it is cleared that urea may behave both as an acid or a base in liq. NH_3.

Q. Advantages of Bronsted-Lowry concept:-

(i) This concept is superior to Arrhenius concept, since Arrhenius concept can explain the acidic/basic character of a substance only in H_2O medium while Bronsted-Lowry concept can explain the acidic/basic nature of a substance in H_2O as well as in other protonic solvants like liq. NH_3, liq. HF etc.

(ii) Acid-base reactions taking place in gaseous phase can also be explained by this concept. e.g; in the reaction between HCl (g) and NH_3 (g) is an acid-base reaction in gaseous phase.

⇒ Limitations of Bronsted-Lowry concept:-

(i) This concept can not explain the acid-base reaction taking place in non-protonic solvants like liq. SO_2, liq. BrF_3 etc. in which no transfer of protons takes place.

$acid_1 + base_2 \rightleftharpoons acid_2 + base_1$

$SOCl_2 + Na_2SO_3 \rightleftharpoons 2NaCl + 2SO_2$

Q. All Arrhenius acids are Bronsted acids but all Arrhenius bases are not Bronsted bases :- Explain.

Let us consider the behavior of HCl in the following two reactions,

i) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$; (ii) $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$

In reaction (i), HCl gives H_3O^+ ion when dissolved in water, hence HCl is acid according to Arrhenius concept.

In reaction (ii) HCl loses a proton which combines with NH_3 to form NH_4^+ ion. Hence HCl acts as a Bronsted acid.

From the above two reactions it is clear that the same substance (HCl) behaves as Arrhenius acid and Bronsted acid. Therefore we can say that all Arrhenius acids are also Bronsted acids.

According to Arrhenius concept a substance that gives OH^- ions in aqueous soln is called Arrhenius base.

e.g; NaOH gives OH^- ions in aqu. soln. hence it is an Arrhenius base. Such a substance (NaOH) can not accept a proton and hence according to Bronsted-Lowry concept NaOH can not act as a Bronsted base. Thus we can say all Arrhenius bases are not Bronsted bases.

4. Lewis Concept of Acids and Bases :-

According to Lewis concept, an acid is any specis that can accept an electron pair to form a co-ordinate bond and a base is any specis that can donate an electron pair to the formation of a co-ordinate bond. Thus in this concept, an acid is an electron pair accepter and a base is an electron pair donor i.e, neutralisation is the formation of a co-ordinate bond between an acid and a base. The neutralisation product termed as co-ordinate complex or adduct.

Q. Classification of Lewis Acids :-

Lewis acids may be classified as.

1) cations with empty or partially filled orbitals:

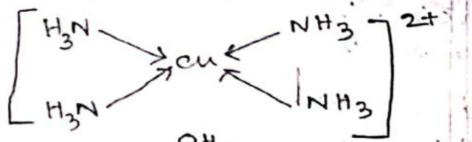
Ions of transition metals (Cu^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ag^{+} etc) are good examples of this type of Lewis acid. Co-ordination of such ions by different donor ligands may be looked upon as an acid-base interaction.

e.g:

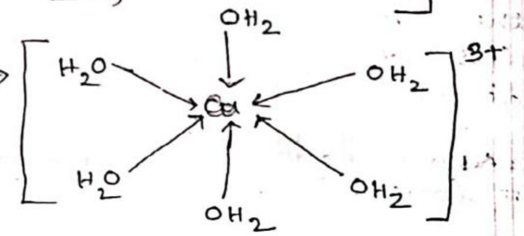
Lewis acid + Lewis base ⟶ Adduct

$Ag^{+} + 2NH_3 \longrightarrow [H_3N \rightarrow Ag \leftarrow NH_3]^{\oplus}$

$Cu^{2+} + 4NH_3 \longrightarrow$



$Co^{3+} + 6H_2O \longrightarrow$



2) Molecules containing a central atom with an incomplete valence shell:-

The examples of this class of acids are electron deficient molecules such as alkyls and halydes of Be, B and Al. Some reactions of this type of Lewis acids with Lewis bases are shown below.

Lewis acid + Lewis base ⟶ Adduct

$BF_3 + O(C_2H_5)_2 \longrightarrow [F_3B \leftarrow O(C_2H_5)_2]$

$AlCl_3 + C_5N_5N \longrightarrow [Cl_3Al \leftarrow NC_5H_5]$

$Me_3B + N_2H_4 \longrightarrow [Me_3B \leftarrow NH_2-NH_2]$

3) Molecules containing a central atom with vacent d-orbitals:-

The central atom of this halydes SiX_4, SnX_4, $TiCl_4$, PCl_5, SF_4 have vacent d orbitals. These substances can accept an electron pair from the Lewis base to accomodate in their vacent 'd' orbital and can form adducts with a number of halydes ions and organic bases.

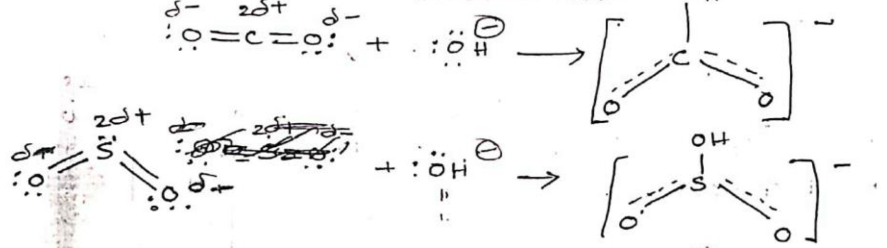
$SiF_4 + 2F^- \longrightarrow SiF_6^{=}$

$SnCl_4 + 2Cl^- \longrightarrow SnCl_6^{=}$

4) Molecules having a multiple bond between atoms of dissimilar electro negativity:-

The examples of molecules falling in this class of Lewis acids are; CO_2, SO_2 and SO_3. In these compounds the oxygen atoms are more electronegative than 'S' or 'C' atom. As a result, the electron density of π electrons is displaced away from carbon or sulpher atoms towards the 'O' atom. The 'C' or 'S' atom becomes electron defficient and is able to accept an electron pair from a Lewis base such as OH^- ions to form the bond.

Lewis acid + Lewis base



Bi-sulphite ion.

5) Elements with an electron sextent :-

'O' and 'S' atoms contain six electrons in their valence shell and can be regarded as Lewis acids. The oxidation of SO_3^{2-} to SO_4^{2-} ion by 'O' and to $S_2O_3^{=}$ ion by 'S' are the acid-base reactions.

Lewis acid + Lewis base → Adduct

$$:\ddot{O} + SO_3^{=} \longrightarrow SO_4^{=}$$

$$:\ddot{S} + SO_3^{=} \longrightarrow S_2O_3^{=}$$

B. Classification of Lewis bases :-

Lewis bases can be classified as

1) All negative ions :-

All anions are bases. Greater the charge density stronger is the base strength. The reactions of the some Lewis bases are shown below,

Lewis acid + Lewis base → Adduct

$$BF_3 + F^- \longrightarrow BF_4^-$$

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

$$I_2 + I^- \longrightarrow I_3^-$$

2) Molecules having an atom with one or more unshared pairs of electrons :-

H_2O, NH_3, $R-NH_2$, R_2O etc. are well known examples of such ~~reactions~~ molecules,

e.g; Lewis acid + Lewis base = Adduct

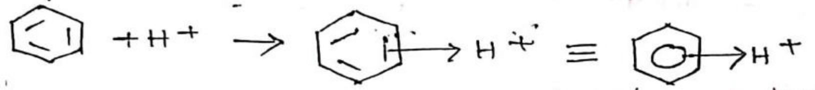
$Co^{3+} + 6H_2O = [Co(H_2O)_6]^{3+}$

$BF_3 + NH_3 = F_3B \leftarrow NH_3$

$H^+ + R-NH_2 = R-NH_3^+$

3) Compounds containing c–c multiple bonds :-

Alkene, alkyne, aromatic compound having high π-electron densities are the examples of such catagory. The donation of an electron pair from a π bond to Lewis acid results in the formation of π complexes.



(π- complex)

4) Halides :-

The halides that can make halide ion available behave as Lewis bases. Examples of such halides are, XeF_2, XeF_4, XeF_6 etc. In the following reaction these halides act as Lewis bases.

Lewis acid + Lewis base ⟶ Adduct

$AsF_5 + XeF_2 \longrightarrow [XeF]^+[AsF_6]^-$

$SbF_5 + XeF_4 \longrightarrow [XeF_3]^+[SbF_6]^-$

Q. Utility of Lewis concept :-

(i) This concept includes those reactions in which no protons are involved i.e, BF_3, $AlCl_3$, Cu^{2+} are acids.

(ii) In this concept acid-base behavior is not dependent in the presence or absence of a solvant.

(iii) It explains the basic proparties of metallic oxides and acidic proparties of non-metallic oxides.

(iv) This theory also includes many reactions, such as gas phase, high temperature reaction as neutralisation processes.

(v) This concept is of great value in cases where the protonic concept is in-applicable.

e.g; In reaction between acidic and basic oxides in the fused state.

Q. Limitations of Lewis concept:-

(i) The conventional protonic acids (H_2SO_4, HCl, HNO_3 etc) are not covered under Lewis concept, as they do not form co-ordinate bond by accepting electron pairs.

(ii) The relative acid-base strength of the substances can not be determined. The strength is reaction dependent i.e, a substance may acts as a strong acid or base in one reaction while weak in other.

Q. Difference between protonic concept and Lewis concept of acids and bases

Protonic concept	Lewis concept.
(i) Acids are proton donor & bases are proton acceptors.	(i) Acids are electron pair acceptors, bases are electron pair donor.
(ii) Acid-base neutralisation results in the formation of conjugate acid-base pair.	(ii) Acid-base neutralisation results in the formation of one or more co-ordinate bonds.
(iii) Acids must have H atom to donate as H^+ ion.	(iii) Acids may not have H atom.
(iv) Relative strength of acid or base can be determined.	(iv) Relative strength of acid or bases can not be determined.

Q. Lux-Flood concept of acid and bases:-

According to this concept an acid is an acceptor of oxide ion and a base is a donor of oxide ion.

i.e base $\rightleftharpoons$ acid + $O^=$

e.g; $CaO \rightleftharpoons Ca^{2+} + O^{2-}$

$SiO_2 + O^{2-} \rightleftharpoons SiO_3^{2-}$

$CaO + SiO_2 \rightleftharpoons CaSiO_3$

base acid salt.

$PbO + SO_3 \rightleftharpoons PbSO_4$

$CaO + CO_2 \rightleftharpoons CaCO_3$

$6Na_2O + P_4O_{10} \rightleftharpoons 4Na_3PO_4$

This view is particularly useful in high temperature chemistry as in the fields of ceramics and metallurgy.

Similarly ores ([illegible])(TiO_2) Ti are dissolved in sodium pyrosulphate around 800°c are the acid base reactions.

$TiO_2 + Na_2S_2O_7 \rightleftharpoons Na_2SO_4 + (TiO)SO_4$

base acid salt

ZnO shows amphoterism as it can both donate or accept oxide ions.

$Na_2O + ZnO \rightleftharpoons Na_2ZnO_2$

acid

$S_2O_7^= + ZnO \rightleftharpoons Zn^{2+} + 2SO_4^=$

base

Q. Usanovich concept of acids and bases:-

Usanovich proposed a very wide definition of acids and bases. According to this concept an acid is any chemical species which

i) Reacts with a base or
ii) Accepts anions or electrons or
iii) Furnishes cations and

A base is any chemical species ~~that~~ which

i) Reacts with an acid or

ii) Accepts cations or

iii) Furnishes anions or electrons to give a salt.

Some examples of acid base reactions are given below:

i) SO_3 (acid) + Na_2O (base) → Na_2SO_4 (Salt)

$Na_2O \rightleftharpoons 2Na^+ + O^{2-}$

Na_2O gives O^{2-} anion and hence acts as a base.

$SO_3 + O^{2-} \rightleftharpoons SO_4^{=}$

SO_3 accepts O^{2-} anion and hence behaves as an acid.

(ii) SO_2 (acid) + Na_2O (base) → Na_2SO_3 (salt):

$Na_2O \rightleftharpoons 2Na^+ + O^{2-}$

Na_2O gives O^{2-} ion and hence acts as a base.

$SO_2 + O^{2-} \rightleftharpoons SO_3^{2-}$

SO_2 accepts O^{2-} anion and hence it behaves as an acid.

(iii) Cl_2 (acid) + 2Na (base) → 2NaCl (salt)

$2Na \rightarrow 2Na^+ + 2e$

Since 'Na' furnishes electrons, it acts as a base.

$Cl_2 + 2e \rightarrow 2Cl^-$

'Cl' atom accept electron and it acts as an acid.

(iv) $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$
acid base salt.

$4KCN \rightleftharpoons 4K^+ + 4CN^-$

KCN acts as a base, since it gives CN^- anion.

$Fe(CN)_2 + 4KCN^- \rightleftharpoons Fe(CN)_6^{4-}$

$Fe(CN)_2$ behaves as an acid as it accepts CN^- anion.