Environmental Chemistry and Microbiology
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Lecture-01
Acids, Bases and Salts –I

Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Anjali Pal. We are both from Civil Engineering Department of IIT Kharagpur. We have divided this course into 2 parts, the first part Environmental Chemistry will be covered by me and the second part Environmental Microbiology will be taught by Professor Sudha Goel.

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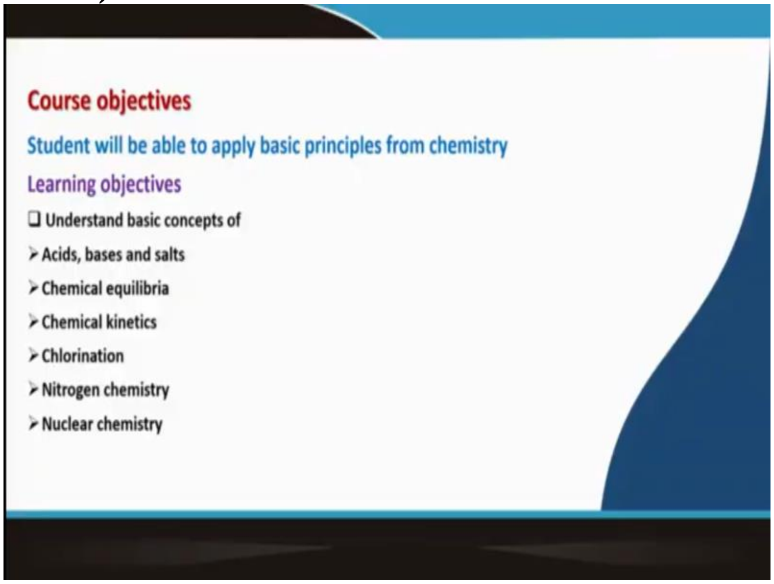

Course objectives

Student will be able to apply basic principles from chemistry

Learning objectives

❑ Understand basic concepts of

- Acids, bases and salts
- Chemical equilibria
- Chemical kinetics
- Chlorination
- Nitrogen chemistry
- Nuclear chemistry

The objective of this Environmental Chemistry is shown:

Students will be able to apply basic principles of chemistry. The course will be covered by the following topics: acids, bases and salts, chemical equilibria, chemical kinetics, chlorination, nitrogen chemistry and nuclear chemistry.

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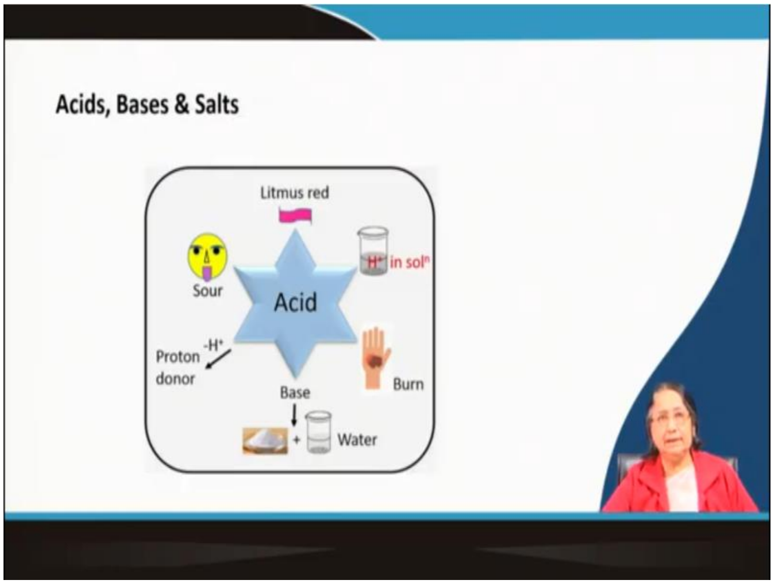

Acids, Bases & Salts

So, in my first lecture, I will start with acids, bases and salts. The old concept of acids is that some people told that acid should turn blue litmus red, somebody told it is sour and some people told that it reacts with bases to form salt and water. It burns the skin. It can donate proton. But all these properties were very old and it is not explained by the modern concepts.

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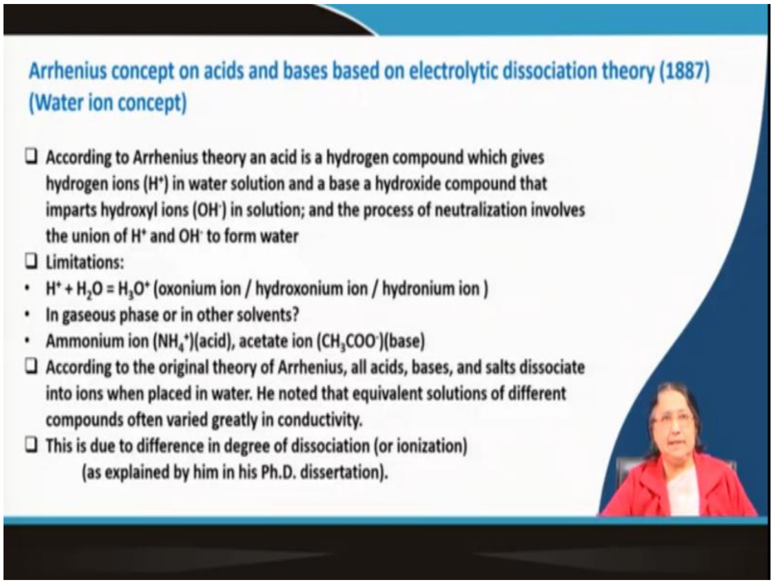

Arrhenius concept on acids and bases based on electrolytic dissociation theory (1887) (Water ion concept)

❑ According to Arrhenius theory an acid is a hydrogen compound which gives hydrogen ions (H^+) in water solution and a base a hydroxide compound that imparts hydroxyl ions (OH^-) in solution; and the process of neutralization involves the union of H^+ and OH^- to form water

❑ Limitations:

- $H^+ + H_2O = H_3O^+$ (oxonium ion / hydroxonium ion / hydronium ion)
- In gaseous phase or in other solvents?
- Ammonium ion (NH_4^+)(acid), acetate ion (CH_3COO^-)(base)

❑ According to the original theory of Arrhenius, all acids, bases, and salts dissociate into ions when placed in water. He noted that equivalent solutions of different compounds often varied greatly in conductivity.

❑ This is due to difference in degree of dissociation (or ionization) (as explained by him in his Ph.D. dissertation).

The first modern concept was given by Arrhenius and he said that, the acid is something which gives hydrogen ions in water solution and a base is something which gives hydroxide compound and the neutralization process is nothing but the union of H^+ and OH^- to form the water. This is also called water ion concept and it was first given by Arrhenius in his dissertation (PhD dissertation).

And he explained it as electrolytic dissociation theory in 1887. But this theory has several limitations. Say, for example, we all know now, that proton H^+ cannot stay as such, because of its high hydration energy, it immediately combines with the water molecule to form H_3O^+, which is oxonium ion, it is also called hydroxonium ion, and also it can be called as hydronium ion.

Second thing is that, in this concept, it is mentioned that acid is a proton donor in aqueous solution that means, water medium and base is something which gives the hydroxide ion in water. But an acid should be defined not in terms of any medium, but it should be told by itself. Say, for example, in gaseous phase or in other solvents, what happens for acids and what happens for bases? It also could not explain the properties of ammonium ion which shows an acidic property and acetate ion is basic, showing basic property.

So, this has some limitations. But at that time, it was quite sufficient and in aqueous medium it is quite good to explain the acidic and basic properties

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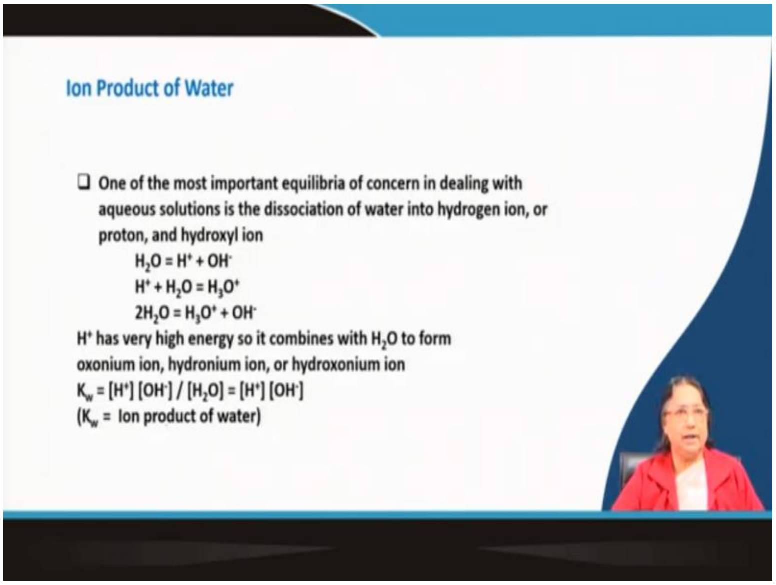

Ion Product of Water

☐ One of the most important equilibria of concern in dealing with aqueous solutions is the dissociation of water into hydrogen ion, or proton, and hydroxyl ion

$H_2O = H^+ + OH^-$

$H^+ + H_2O = H_3O^+$

$2H_2O = H_3O^+ + OH^-$

H^+ has very high energy so it combines with H_2O to form oxonium ion, hydronium ion, or hydroxonium ion

$K_w = [H^+] [OH^-] / [H_2O] = [H^+] [OH^-]$

(K_w = Ion product of water)

It is very important to know the ion product of water. We all know that water dissociates into H^+ and OH^-. Of course, H^+ cannot stay as such, and it immediately combines with water to form hydroxonium ions. So, in terms of the formation of hydroxonium ions, we can tell that the actual equation for water dissociation is given by.

$2H_2O = H_3O^+ + OH^-$ …………………(1)

Water dissociates very slightly and the ion product of water which is called as K_w is nothing but the equilibrium constant of this equation.

It is nothing but $[H^+]$ multiplied by $[OH^-]$ followed by division by $[H_2O]$. Because $[H_2O]$ is unity, so, we can tell it is nothing but $[H^+][OH^-]$and this is called as the ionic product of water. It is nothing but the equilibrium constant of the dissociation of water molecule.

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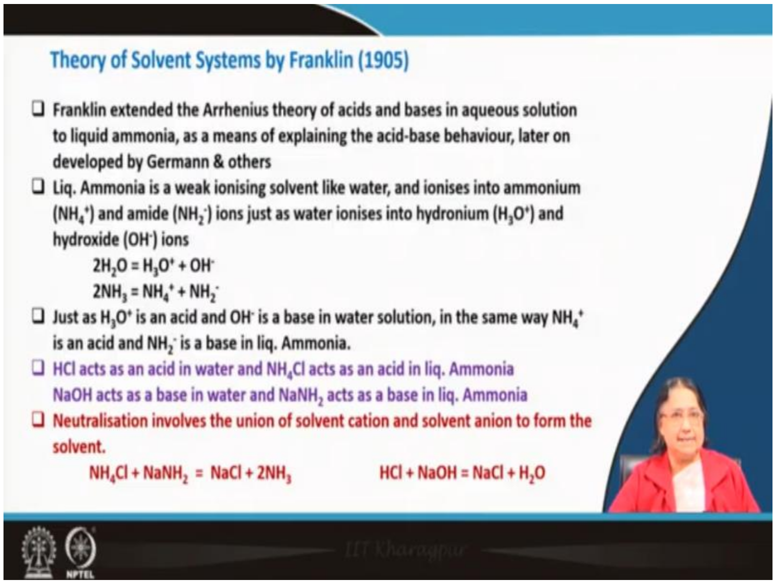

Theory of Solvent Systems by Franklin (1905)

- ☐ Franklin extended the Arrhenius theory of acids and bases in aqueous solution to liquid ammonia, as a means of explaining the acid-base behaviour, later on developed by Germann & others
- ☐ Liq. Ammonia is a weak ionising solvent like water, and ionises into ammonium (NH_4^+) and amide (NH_2^-) ions just as water ionises into hydronium (H_3O^+) and hydroxide (OH^-) ions

$$2H_2O = H_3O^+ + OH^-$$
$$2NH_3 = NH_4^+ + NH_2^-$$

- ☐ Just as H_3O^+ is an acid and OH^- is a base in water solution, in the same way NH_4^+ is an acid and NH_2^- is a base in liq. Ammonia.
- ☐ HCl acts as an acid in water and NH_4Cl acts as an acid in liq. Ammonia
  NaOH acts as a base in water and $NaNH_2$ acts as a base in liq. Ammonia
- ☐ Neutralisation involves the union of solvent cation and solvent anion to form the solvent.

$$NH_4Cl + NaNH_2 = NaCl + 2NH_3 \qquad HCl + NaOH = NaCl + H_2O$$

Now, this concept, which Arrhenius told in aqueous medium, it was then extended by Franklin in 1905. He extended this theory in another solvent which is liquid ammonia. We know that in liquid ammonia many reactions are carried out and he said that just like water molecules, ammonia can give ammonium ion and amide ion. So, NH_4^+ is a cationic part and NH_2^- is an anionic part and he said in a very similar way to the Arrhenius concept.

He said that something in liquid ammonia which gives ammonium ion is an acid and which gives amide ion is a base. But remember that this is extended in liquid ammonia. And he could explain many things say for example, HCl, we know that it acts as an acid in water and ammonium chloride acts as an acid very similar way in liquid ammonia. So, HCl gives H^+ ion in water medium that is why it is an acid in water and ammonium chloride in liquid ammonia gives NH_4^+. So, it is an acid.

So, it is very similar and if we extend this thing in terms of the acid base reaction, we know that in aqueous condition reaction between HCl and NaOH gives salt and water (shown by the following equation).

$HCl+NaOH=NaCl+H_2O$ ………………(2)

Similarly, ammonium chloride and sodium amide reacts to give NaCl and NH_3 (shown by the following equation).

$NH_4Cl+NaNH_2=NaCl+2NH_3$ ………………….(3)

So, these types of reactions could be explained by Franklin very nicely.

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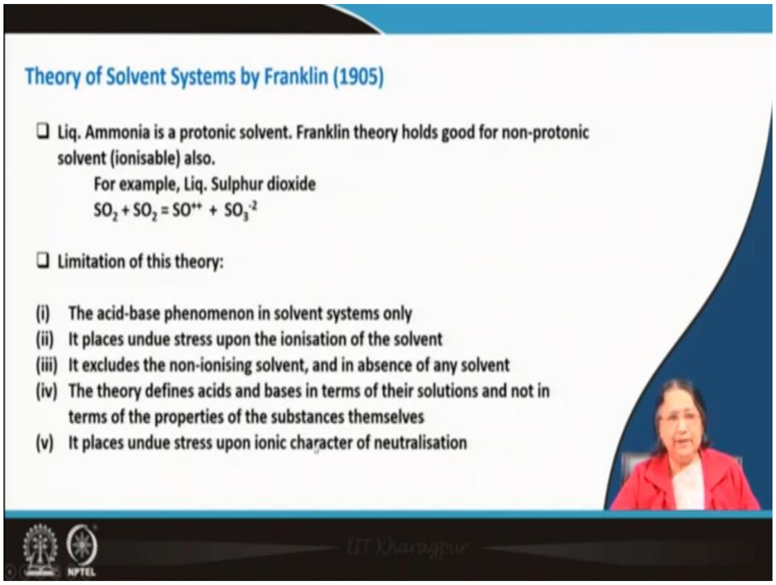

Theory of Solvent Systems by Franklin (1905)

❑ Liq. Ammonia is a protonic solvent. Franklin theory holds good for non-protonic solvent (ionisable) also.

For example, Liq. Sulphur dioxide

$SO_2 + SO_2 = SO^{++} + SO_3^{-2}$

❑ Limitation of this theory:

(i) The acid-base phenomenon in solvent systems only
(ii) It places undue stress upon the ionisation of the solvent
(iii) It excludes the non-ionising solvent, and in absence of any solvent
(iv) The theory defines acids and bases in terms of their solutions and not in terms of the properties of the substances themselves
(v) It places undue stress upon ionic character of neutralisation

Also, we know that ammonia is a protonic solvent. But there are some solvents we know that it is non protonic say for example, liquid sulphur dioxide. In liquid sulphur dioxide, we do not have any proton. So, what will happen to this, it is also explained by Franklin. So, something which gives the cationic part of sulphur dioxide that is thionyl group (SO^{++}) that will be an acid and something which will give in liquid sulphur dioxide the sulphite ion that is nothing but a SO_3^{-2} that will be called as a base.

The limitation of Franklin's theory is that the acid base phenomena in solvent system only has been explained here just similar to Arrhenius concept. So, it is placing undue stress upon the ionization of solvent and also it excludes the non-ionizing solvent and in absence of any solvent.

So, for example, in gaseous phase it could not explain the properties of acids and bases. The theory defines acids and bases in terms of their solutions and not in terms of the properties of the substance themselves. And it places undue stress upon the ionic character of neutralization also. So, every theory has some limitations.

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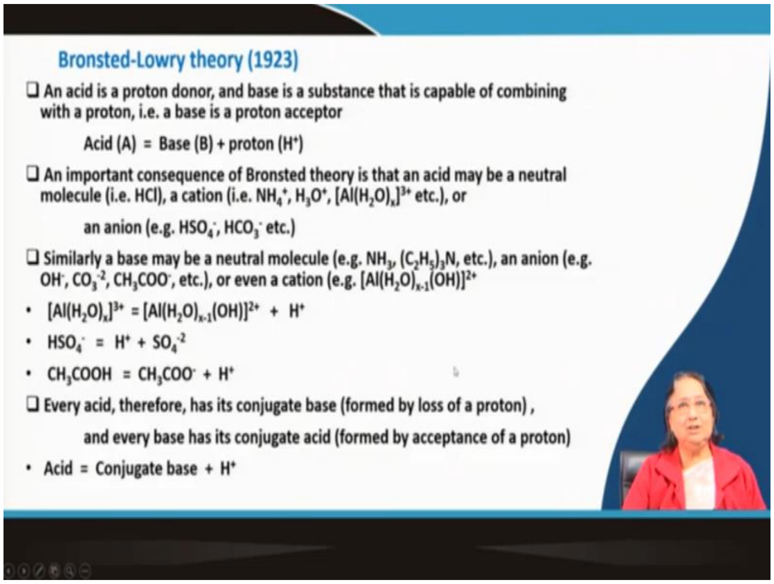

Bronsted-Lowry theory (1923)

❑ An acid is a proton donor, and base is a substance that is capable of combining with a proton, i.e. a base is a proton acceptor

Acid (A) = Base (B) + proton (H^+)

❑ An important consequence of Bronsted theory is that an acid may be a neutral molecule (i.e. HCl), a cation (i.e. NH_4^+, H_3O^+, $[Al(H_2O)_x]^{3+}$ etc.), or an anion (e.g. HSO_4^-, HCO_3^- etc.)

❑ Similarly a base may be a neutral molecule (e.g. NH_3, $(C_2H_5)_3N$, etc.), an anion (e.g. OH^-, CO_3^{-2}, CH_3COO^-, etc.), or even a cation (e.g. $[Al(H_2O)_{x-1}(OH)]^{2+}$

- $[Al(H_2O)_x]^{3+} = [Al(H_2O)_{x-1}(OH)]^{2+} + H^+$
- $HSO_4^- = H^+ + SO_4^{-2}$
- $CH_3COOH = CH_3COO^- + H^+$

❑ Every acid, therefore, has its conjugate base (formed by loss of a proton), and every base has its conjugate acid (formed by acceptance of a proton)

- Acid = Conjugate base + H^+

But at that time, it could explain the properties of acids and bases very nicely in water and other solvents. Now comes Lowry-Bronsted theory and it has been stated in 1923 that, an acid is a proton donor and a base is a substance that is capable of combining with a proton. That means here it is not told that base is a substance which can give OH^-. Instead, it said that base is something which can take up the proton.

So, here it is shown (in the slide next page) that if A is an acid and B is a base, then acid A gives H^+, and that H^+ will be taken up by the base B to form some type of acid. This is more general and it can can explain many things beyond the Arrhenius and Franklin concept. Say for example, by this Bronsted theory, we can explain the acid / base behavior of several molecules. Say, for example, if it is a neutral molecule like HCl then we can explain why it is an acid?

If it is a cation say, for example, ammonium ion or hydronium ion or even some aqua complexes of aluminium then also we can explain why it is an acid or even some anions like bisulphate or bicarbonate that also can be explained. Because you know this bisulphate can give proton, bicarbonate can give proton. So, it is an acid. Ammonium ion can give proton, hydronium ion can give proton. So, these are acids.

Now, similarly, in case of base say for example, neutral molecule NH_3 it can take up a proton to form ammonium ion. So, it is a base. An anion, say for example, OH^-, it can take up a proton to form water. So, it is a base. Even a cation, say for example, complexes like $[Al(H_2O)_{x-1}(OH)]^{2+}$, which can take up a proton to give back $[Al(H_2O)_x]^{3+}$ is a base. So, this way the property of acid or base can be explained by Bronsted-Lowry theory.

It has been shown here by means of the following equations why something is an acid and why something is a base.

$[Al(H_2O)_x]^{3+} = [Al(H_2O)_{x-1}(OH)]^{2+} + H^+$ ………………….(4)

$HSO_4^- = H^+ + SO_4^{2-}$ ……………………………………….(5)

$CH_3COOH = CH_3COO^- + H^+$ …………………….……...(6)

Now, from this we can easily understand that every acid therefore, has its conjugate base. When an acid gives a proton, it forms another compound which is nothing but its conjugate base. So, it is formed by the loss of a proton and every base has its conjugate acid formed by the acceptance of a proton. So, it is also called conjugate acid base theory.

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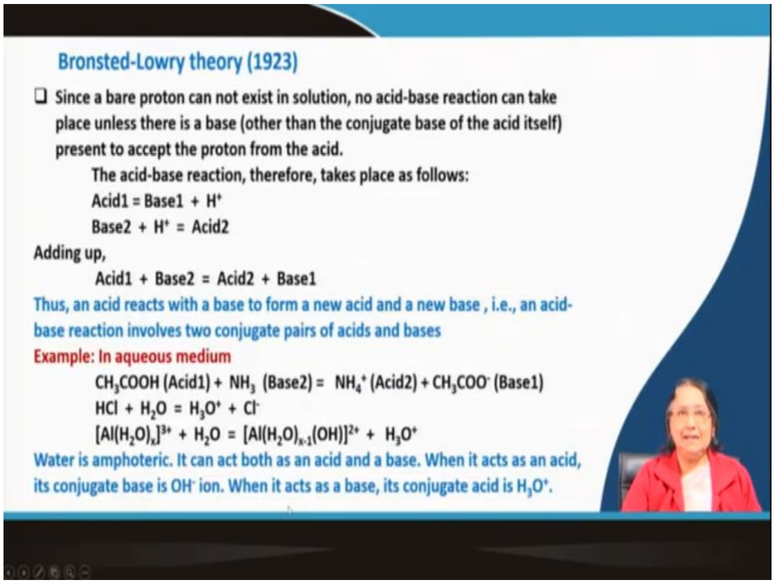

Bronsted-Lowry theory (1923)

☐ Since a bare proton can not exist in solution, no acid-base reaction can take place unless there is a base (other than the conjugate base of the acid itself) present to accept the proton from the acid.

The acid-base reaction, therefore, takes place as follows:

Acid1 = Base1 + H^+

Base2 + H^+ = Acid2

Adding up,

Acid1 + Base2 = Acid2 + Base1

Thus, an acid reacts with a base to form a new acid and a new base , i.e., an acid-base reaction involves two conjugate pairs of acids and bases

Example: In aqueous medium

CH_3COOH (Acid1) + NH_3 (Base2) = NH_4^+ (Acid2) + CH_3COO^- (Base1)

$HCl + H_2O = H_3O^+ + Cl^-$

$[Al(H_2O)_x]^{3+} + H_2O = [Al(H_2O)_{x-1}(OH)]^{2+} + H_3O^+$

Water is amphoteric. It can act both as an acid and a base. When it acts as an acid, its conjugate base is OH^- ion. When it acts as a base, its conjugate acid is H_3O^+.

Now, this theory is very nice because it can explain the acid / base behavior of many molecules or ions. So, here you can see since a bare proton cannot exist in solution, so, no acid base reaction can take place unless there is a base. Why so? Because, some acid will give up some proton, but there must be some taker of that proton. So, it is nothing but a base. Because proton cannot exist in solution it must be combined with something to form something.

So, who will take up this proton? Base will take up this proton. The whole phenomenon is represented here by means of following two equations:

$\text{Acid1}=\text{Base1}+H^+$ ………(7)

$\text{Base2}+H^+=\text{Acid2}$ ……….(8)

Adding (7) and (8),

$\text{Acid1}+\text{Base2}=\text{Acid2}+\text{Base1}$…………(9)

Thus, an acid reacts with a base to form a new acid and a new base i.e., an acid base reaction involves two conjugate pairs of acids and bases.

Here in the example (equation (10)) you see acetic acid, which is acid 1, then the ammonia molecule which is base 2 can produce ammonium ion and acetate ion.

$CH_3COOH(\text{Acid1})+NH_3(\text{Base2})=NH_4^+(\text{Acid2})+CH_3COO^-(\text{Base1})$ ……………….(10)

So, this acetic acid gives the proton which is taken up by ammonia to form the ammonium ion and then acetic acid is converted to a base which is nothing but the acetate ion. So, acid 1 and base 1, and base 2 and acid 2 they are the two pairs. So, in this way we can explain acid-base reactions and we also know that water is amphoteric.

So, water can act both as an acid and a base. When it acts as an acid, its conjugate base is OH^-, and when it acts as a base, its conjugate acid is hydronium ion.

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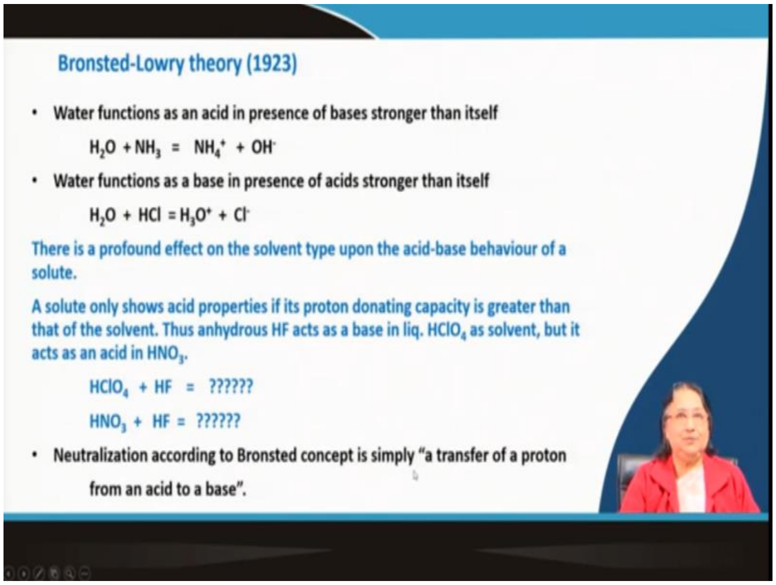

Bronsted-Lowry theory (1923)

- Water functions as an acid in presence of bases stronger than itself

$H_2O + NH_3 = NH_4^+ + OH^-$

- Water functions as a base in presence of acids stronger than itself

$H_2O + HCl = H_3O^+ + Cl^-$

There is a profound effect on the solvent type upon the acid-base behaviour of a solute.

A solute only shows acid properties if its proton donating capacity is greater than that of the solvent. Thus anhydrous HF acts as a base in liq. $HClO_4$ as solvent, but it acts as an acid in HNO_3.

$HClO_4 + HF = $??????

$HNO_3 + HF = $??????

- Neutralization according to Bronsted concept is simply "a transfer of a proton from an acid to a base".

This is very simple. Now, here it is shown (equation (11)) water functions as an acid here.

$H_2O+NH_3=NH_4^+ +OH^-$ ………………………(11)

So, it will give a proton and ammonia will be a base. So, from water OH^- ion is produced and from ammonia, ammonium ion is produced.

Water can function as a base in this reaction (equation (12)).

$H_2O+HCl=H_3O^+ +Cl^-$ ……………………………………….(12)

You can see that because HCl is stronger acid than water. So, everything is relative. You have to think which is a better acid? Which is a better base? Then only you can decide that who will act as an acid and will act as a base.

There is a profound effect which tells us that solvent has enormous effect to decide which will be an acid and which will be a base, that means the acid base behavior of a solute. A very good example of this is the case of perchloric acid. In the liquid perchloric acid, if you put hydrofluoric acid (HF) then who will be the acid and who will be the base that will be decided by who is a stronger acid.

Here you can tell in this reaction (equation (13)) that perchloric acid will be acting as the acid and hydrofluoric acid will be acting as a base.

$HClO_4+HF=$?????…………………………..(13)

But in this case (equation (14)), where perchloric acid is not there, but nitric acid is there it will be opposite, that means nitric acid will be a base and hydrofluoric acid will be an acid.

HNO_3+HF=?????………………………..(14)

And in a similar way neutralization according to Bronsted concept is simply a transfer of a proton from an acid to a base, which has been explained already.

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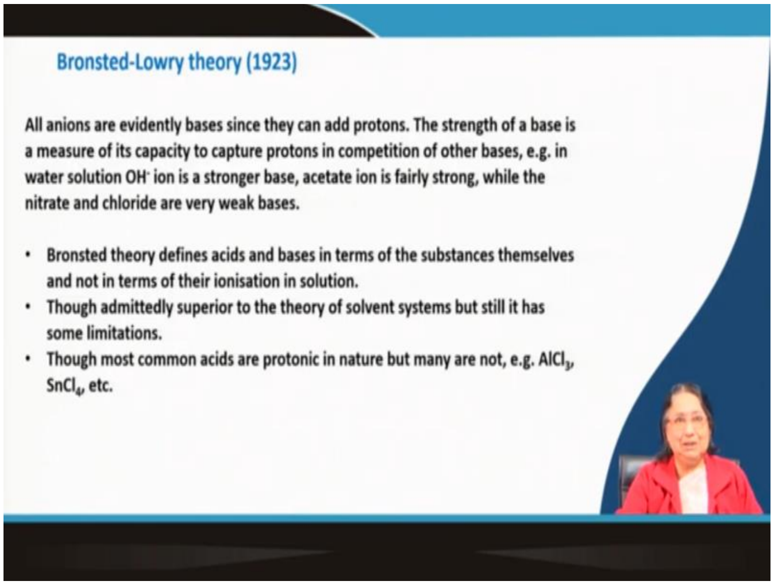

Bronsted-Lowry theory (1923)

All anions are evidently bases since they can add protons. The strength of a base is a measure of its capacity to capture protons in competition of other bases, e.g. in water solution OH^- ion is a stronger base, acetate ion is fairly strong, while the nitrate and chloride are very weak bases.

- Bronsted theory defines acids and bases in terms of the substances themselves and not in terms of their ionisation in solution.
- Though admittedly superior to the theory of solvent systems but still it has some limitations.
- Though most common acids are protonic in nature but many are not, e.g. $AlCl_3$, $SnCl_4$, etc.

Now, all anions are evidently bases. Since they can add protons to the anions. The strength of a base is a measure of its capacity to capture protons in competition with other bases. As for example, in water solution, OH^- is a stronger base, acetate ion is fairly strong, while the nitrate and chloride are very weak bases. In real sense also we know that OH^- is a very strong base, acetate ion is not so strong, though it is basic, and nitrate and chlorides are very weak bases.

Now Bronsted theory defines acids and bases in terms of the substance themselves and not in terms of that ionization in solution. This is the positive point of Bronsted theory. Though admittedly it is superior to the theory of solvent systems, but still it has some limitation. Every theory has some limitation. We all know what is the limitation. The most common acids are protonic in nature, but many are not. Say, for example, aluminium chloride, we know that it is acidic but how it can be explained in terms of Bronsted theory? It is not possible. Again, stannic chloride it is also acidic. How it can be explained by Bronsted theory? So, these are the limitations for Bronsted theory.

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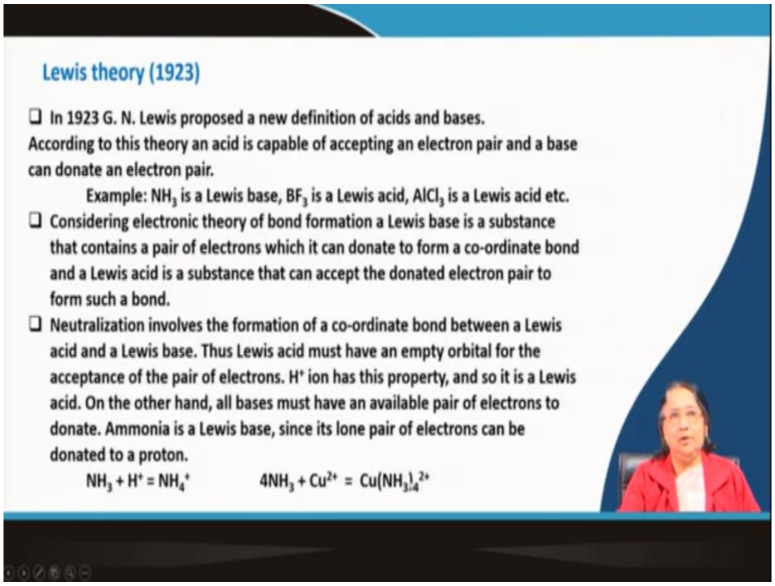

Lewis theory (1923)

☐ In 1923 G. N. Lewis proposed a new definition of acids and bases.
According to this theory an acid is capable of accepting an electron pair and a base can donate an electron pair.

Example: NH_3 is a Lewis base, BF_3 is a Lewis acid, $AlCl_3$ is a Lewis acid etc.

☐ Considering electronic theory of bond formation a Lewis base is a substance that contains a pair of electrons which it can donate to form a co-ordinate bond and a Lewis acid is a substance that can accept the donated electron pair to form such a bond.

☐ Neutralization involves the formation of a co-ordinate bond between a Lewis acid and a Lewis base. Thus Lewis acid must have an empty orbital for the acceptance of the pair of electrons. H^+ ion has this property, and so it is a Lewis acid. On the other hand, all bases must have an available pair of electrons to donate. Ammonia is a Lewis base, since its lone pair of electrons can be donated to a proton.

$NH_3 + H^+ = NH_4^+$ $\quad$ $4NH_3 + Cu^{2+} = Cu(NH_3)_4^{2+}$

Now comes the Lewis theory. It is given in 1923, where G.N. Lewis proposed a new definition of acids and bases. This is very simple. And according to this theory, it is told that the base is something which can donate an electron pair and acid is something which is capable of accepting an electron pair. Something which accepts electron, is an acid and which can give electron that is a base.

So, considering this theory in the bond formation, you know Lewis base is a substance that contains a pair of electrons which can be donated and an acid is something which can take up that electron pair to form a bond. And neutralization is nothing but the formation of the coordinate bond. So, electron pair is given and somebody is taking that electron pair and that is nothing but the coordinate bond between the Lewis acid and Lewis base. So, here you can see (in equation (15) & (16)):

$NH_3+H^+=NH_4^+$ ……………………………………(15)

$4NH_3+Cu^{2+}=Cu(NH_3)_4^{2+}$ ………………………..(16)

Ammonia can combine with H^+ to form ammonium ion.

So, this is nothing but the coordinate bond formation.

Similar way Cu^{2+} can combine with ammonia molecules to form cupramine complex $Cu(NH_3)_4^{2+}$. This is also some type of bond formation and this can be explained very nicely by Lewis theory.

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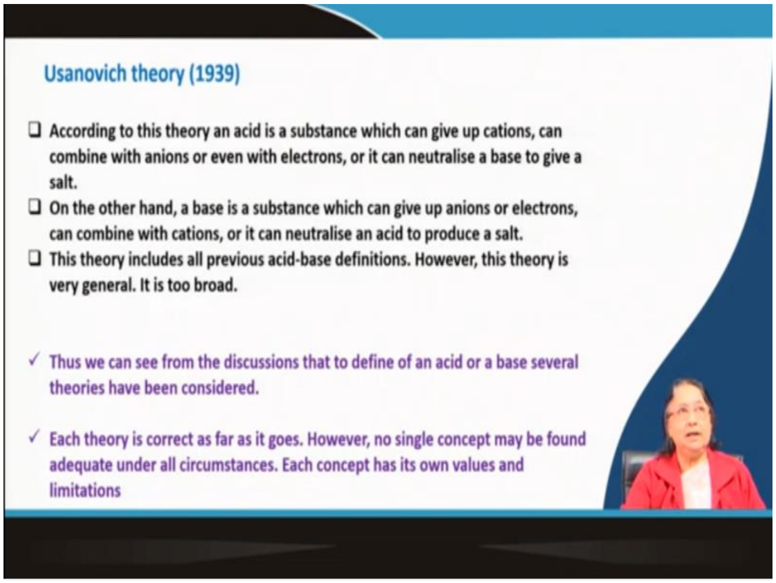

Usanovich theory (1939)

- ☐ According to this theory an acid is a substance which can give up cations, can combine with anions or even with electrons, or it can neutralise a base to give a salt.
- ☐ On the other hand, a base is a substance which can give up anions or electrons, can combine with cations, or it can neutralise an acid to produce a salt.
- ☐ This theory includes all previous acid-base definitions. However, this theory is very general. It is too broad.

- ✓ Thus we can see from the discussions that to define of an acid or a base several theories have been considered.
- ✓ Each theory is correct as far as it goes. However, no single concept may be found adequate under all circumstances. Each concept has its own values and limitations

Now, this is the last one. This is the most general but these can explain maybe everything which is nothing but Usanovich theory. According to this theory, an acid is a substance which can give up cations, can combine with an anion, and even with an electron or it can neutralize a base to give a salt. On the other hand, a base is substances which can give up anions or electrons, can combine with cations or it can neutralize an acid to produce a salt. This theory includes all previous acid base definitions, but it is too general.

Thus, in the first lecture we have discussed that to define an acid or base several theories have been considered. Each theory has some advantages and some limitations. But each one is good and is correct as far as it goes. However, no single concept may be found adequate under all circumstances. Each concept has its own values and limitations.

And you have to decide which one you will use to explain acidity, acidic property or basic property. But you have to remember the solvent. What solvent you are using to explain your things. Thank you.