Environmental Chemistry and Microbiology
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Lecture -09
Chemical Equilibrium-IV

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Professor Anjali Pal. We are both from Civil Engineering Department, IIT Kharagpur. This is module two and, in this module, Chemical Equilibrium-IV will be covered. We have divided this course into two parts the first part is Environmental Chemistry, which is covered by me and the second part is Environmental Microbiology, which will be taught by Professor Sudha Goel. Now, I am coming to my ninth lecture and this is on the chemical equilibrium.

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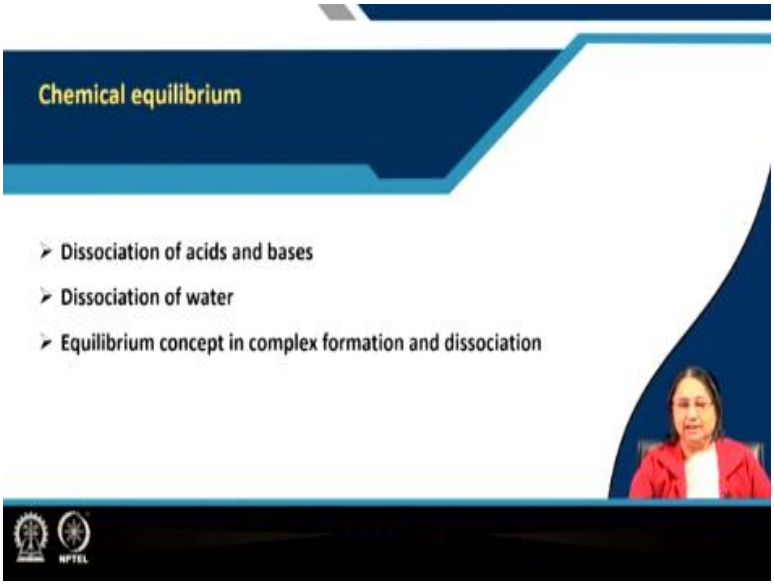

The topics covered in this lecture will be dissociation of acids and bases, dissociation of water, equilibrium concept in complex formation and dissociation.

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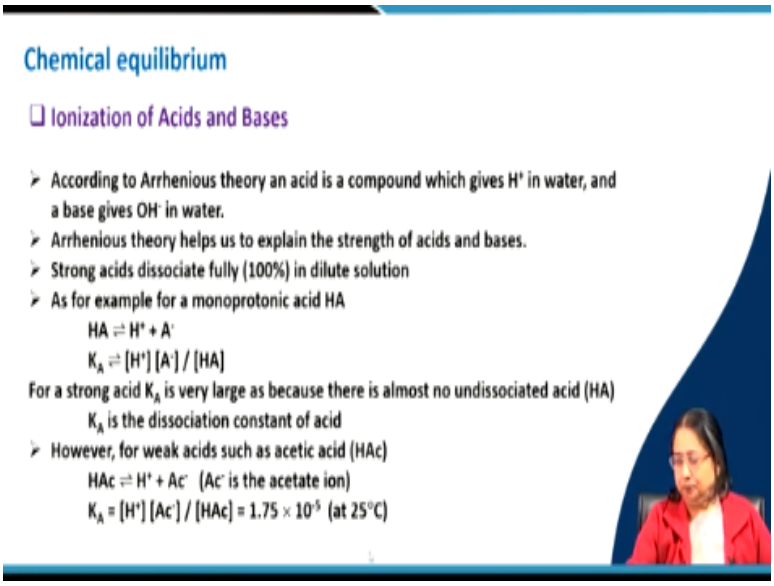

Ionization of acids and bases:

We have already seen in the acid-base chapter and we all know that according to Arrhenius theory an acid is an is a compound which gives H^+ ion in water and a base give OH^- ions in water. So, Arrhenius theory helps us to explain the strength of acids and bases. We know that strong acids fully dissociated (100% dissociation) in dilute solution and for example, we have seen that HA, which is a monoprotic acid or monoprotonic acid which gives H^+ ion and A^- ion. In case of acid dissociation, we always write K_A as follows:

$$K_A = \frac{[H^+][A^-]}{[HA]} \quad \text{.....(1)}$$

Now what information we will get if K_A value is low or high. For a strong acid the K_A value is very large. It is so because this [HA] is very low since almost no portion is undissociated. On the other hand, in case of weak acids say for example acetic acid decomposes into H^+ and Ac^- ion and then in that case we can write

$$K_A = \frac{[H^+][Ac^-]}{[HAc]} \quad \text{.....(2)}$$

At 25^0C the value of K_A for acetic acid is 1.75×10^{-5} (very low). So, it is a weak acid. It dissociates only a very small fraction.

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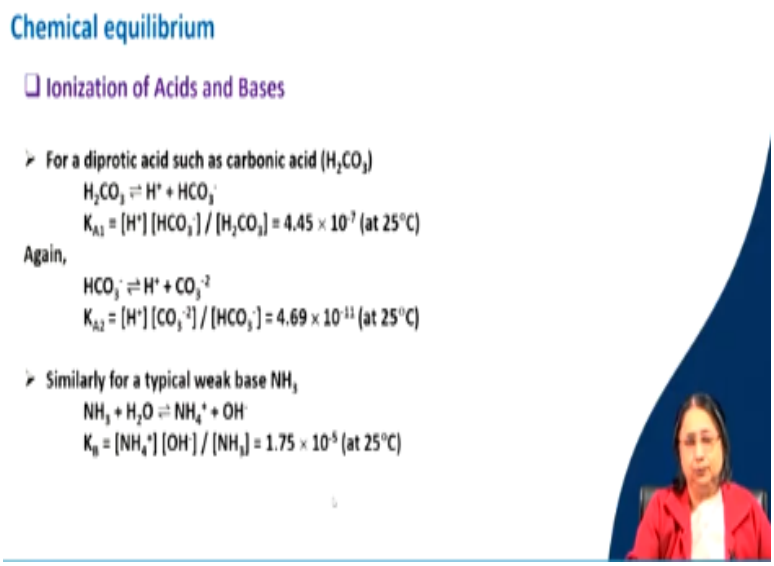

Now in case of diprotic acid let us consider the case of the carbonic acid:

$H_2CO_3 \leftrightharpoons H^+ + HCO_3^-$.....(3)

$$K_{A1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7} \text{ (at } 25^0 \text{ C)}.....(4)$$

Reactions expressed by (3) and (4) explain the case of first dissociation of carbonic acid. Since carbonic acid is a diprotic acid so second dissociation can be expressed as follows:

$HCO_3^- \leftrightharpoons H^+ + CO_3^{-2}$.....(5)

$$K_{A2} = \frac{[H^+][CO_3^{-2}]}{[H_2CO_3]} = 4.69 \times 10^{-11} \text{ (at } 25^0 \text{ C)}.....(6)$$

From the K_{A2} value it is very evident that carbonic acid is a very weak acid.

If we know the pK_A value (minus log of K_A) then we will see it is just below 7. And from this pK_A value we easily tell that it is a very weak acid. Now in the second deprotonation occurs from the bicarbonate ion. This bicarbonate ion will give H^+ ion and carbonate ion (CO_3^{-2}) and then in that case, K_{A2} is can be written in by the expression (6) and the value of K_{A2} is 4.69×10^{-11}. It is very low and in that case from pK_A we can see that it is in the alkaline range.

Now for ammonia, which is a typical weak base similarly we can write:

$NH_3 + H_2O \leftrightharpoons NH_4^+ + OH^-$.....(7)

$$K_B = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5} \text{ (at } 25^0 \text{ C)}.....(8)$$

Ammonia and water give NH_4^+ and OH^- ion and in this case we can write K_B as expressed by equation (8) and pK_B value can be easily obtained from K_B value.

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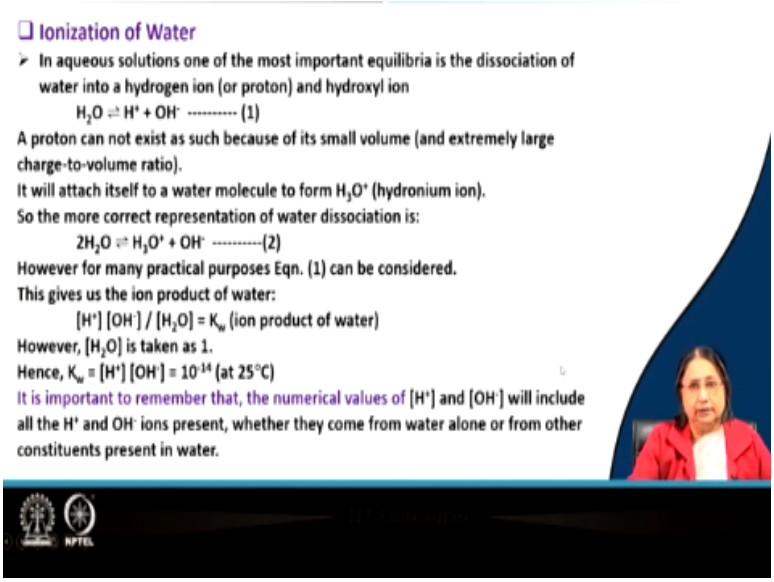

Now let us recall the ionization of water. This has already been explained in acid base chapter and then here again it is written just to recapitulate. In aqueous solution the most important equilibrium is the dissociation of water into H^+ ion and OH^- ion. A proton cannot exist because it has very small volume. So, due to its extremely large charge to volume ratio immediately it reacts with another water molecule, to form the hydronium ion or hydroxonium ion. So basically, it is better to write the following equation (9):

$2H_2O \leftrightharpoons H_3O^+ + OH^-$.....(9)

But for simplicity purposes we always use the following dissociation expression (10):

$H_2O \leftrightharpoons H^+ + OH^-$.....(10)

Now, equilibrium constant (ion product of water) is expressed as (11):

$$K_W = \frac{[H^+][OH^-]}{[H_2O]} \text{.....(11)}$$

But $[H_2O]$ is equal to 1 and therefore ion product of water is equal to $[H^+][OH^-]$ and its value at 25^0C is equal to 10^{-14}. It is important to remember that the numerical values of $[H^+]$ and $[OH^-]$ will include all the H^+ and OH^- ions present, whether they come from water alone or from other constituents present in water. This is very important. On the other day I have shown you by seesaw diagram, that if H^+ ion goes up then OH^- ion goes down.

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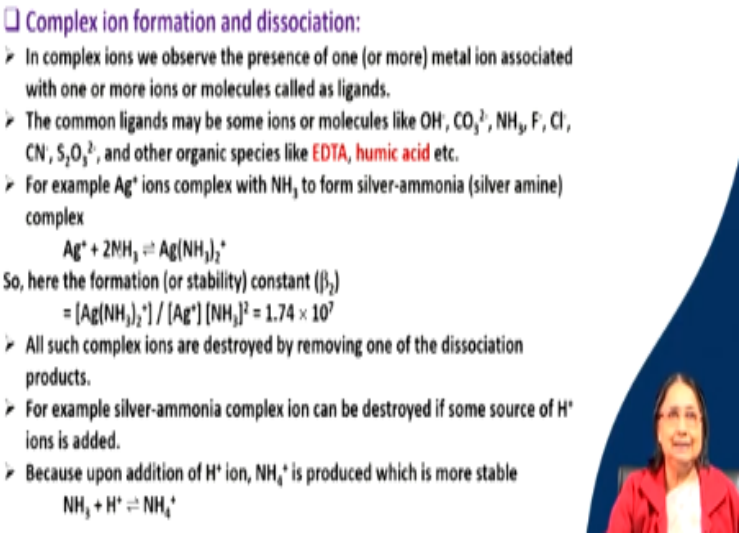

Now let us see complex ion formation and dissociation. It is also very important to know the complex ion. If some complex is formed then how we should write and what you should consider? If you consider complex ions for example $Ag(NH_3)_2^+$ what we see? We see that there is a metal ion and this metal ion is complexed with something. It is associated with one or more ions or molecule. So here in this case it is molecule but some cases it will be ion also. These ions or molecules are called ligands. Some common ligands are OH^-, CO_3^{2-}, ammonia, fluoride, chloride, cyanide, thiosulphate and some species like ethylene diamine tetra acetic acid (EDTA), humic acid. Humic acid is a natural ligand in the humus substances. We always see it is a natural color forming agent. It has a very complex structure and they also can combine with metal ion to form the complex. For example, the Ag^+ ion forms a complex with ammonia to give silver ammonia or sliver amine complex. Now so, how do we express? In case of acid, we say it is dissociation constant, in case of weak base (ammonia) it is also dissociation constant, and then in case of water we write the ion product of water K_w. So, in case of this complex we write the formation constant or stability constant (β) as follows:

$$Ag^+ + 2NH_3 \leftrightharpoons Ag(NH_3)_2^+ \quad \text{.....(12)}$$

$$\beta = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.74 \times 10^7 \quad \text{.....(13)}$$

So here also such complex ions are destroyed by moving one of the dissociation products. Taking this example, silver amine complexes are produced from sliver ion and ammonia, then

this complex may be broken down. Now you have some idea about the shifting the equilibrium. So, if I want to make this reaction in the go to backward reaction then how we will do it? If you want to remove ammonia that is produced, then how will you remove it? We put some acid. Then in presence of acid this ammonia will form the ammonium ion which is very stable and then ammonia will go to solution and slowly the reaction will go to the backward reaction. All such complexes are destroyed by removing one of the dissociation products.

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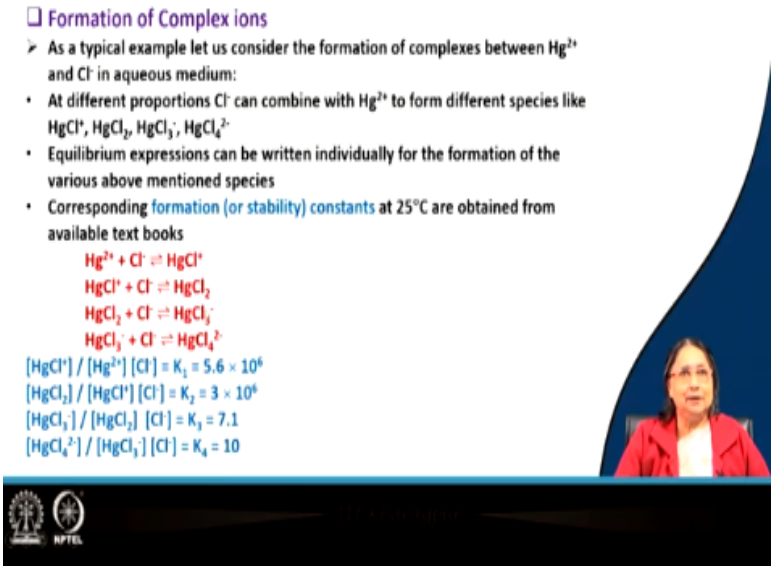

Now let us see the formation of a complex. Let us consider the formation of complexes between Hg^{2+} and Cl^-. It is complex because chloride can be added in various proportions as shown below:

$Hg^{2+}+Cl^- \leftrightharpoons HgCl^+$.....(14)

$HgCl^+ + Cl^- \leftrightharpoons HgCl_2$.....(15)

$HgCl_2 + Cl^- \leftrightharpoons HgCl_3^-$.....(16)

$HgCl_3^- + Cl^- \leftrightharpoons HgCl_4^{2-}$.....(17)

Similarly, four equilibrium constants can be written as follows:

$$K_1=\frac{[HgCl^+]}{[Hg^{2+}][Cl^-]}=5.6\times10^6 \text{.....(18)}$$

$$K_2=\frac{[HgCl_2]}{[HgCl^+][Cl^-]}=3\times10^6 \text{.....(19)}$$

$$K_3=\frac{[HgCl_3^-]}{[HgCl_2][Cl^-]}=7.1 \text{.....(20)}$$

$$K_4=\frac{[HgCl_4^{2-}]}{[HgCl_3^-][Cl^-]}=10 \text{.....(21)}$$

Now it is also possible to consider the overall reaction by combining the stepwise reaction.

$Hg^{2+}+Cl^- \leftrightharpoons HgCl^+$ .....(22)

$Hg^{2+}+2Cl^- \leftrightharpoons HgCl_2$ .....(23)

$Hg^{2+}+3Cl^- \leftrightharpoons HgCl_3^-$ .....(24)

$Hg^{2+}+4Cl^- \leftrightharpoons HgCl_4^{2-}$ .....(25)

Similarly, four equilibrium constants can be written as follows:

$$\frac{[HgCl^+]}{[Hg^{2+}][Cl^-]}=\beta_1 \text{.....(26)}$$

$$\frac{[HgCl_2]}{[Hg^{2+}][Cl^-]^2}=\beta_2=K_1K_2 \text{.....(27)}$$

$$\frac{[HgCl_3^-]}{[Hg^{2+}][Cl^-]^3}=\beta_3=K_1K_2K_3 \text{.....(28)}$$

$$\frac{[HgCl_4^{2-}]}{[Hg^{2+}][Cl^-]^4}=\beta_4=K_1K_2K_3K_4 \text{.....(29)}$$

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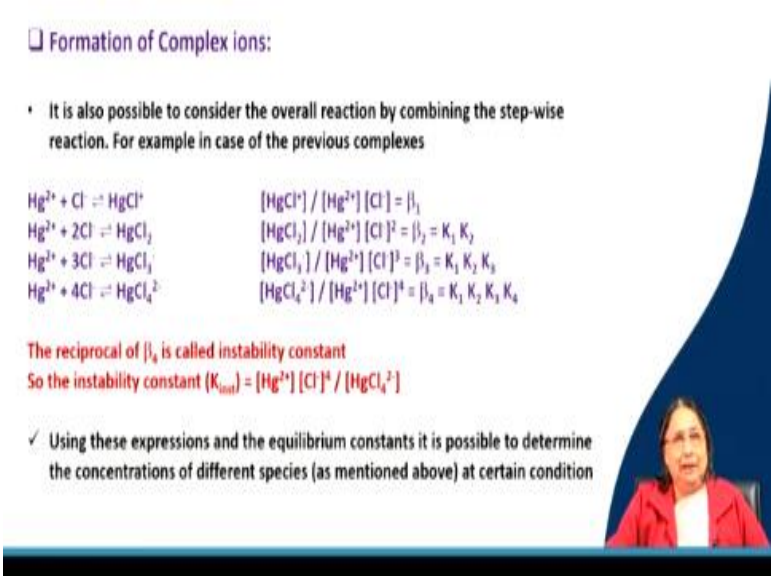

Reciprocal of β_4 is called instability constant.

You can see that by using these expressions and the equilibrium constant values it is possible to determine the concentrations of different species as mentioned above at certain conditions. Say for example you have a system where $[Hg^{2+}]$ is known and chloride concentration is known. Then you are able to tell me how much is there as a $HgCl^{+}$, how much is there as a $HgCl_2$, how much is there $HgCl_3^{-}$.

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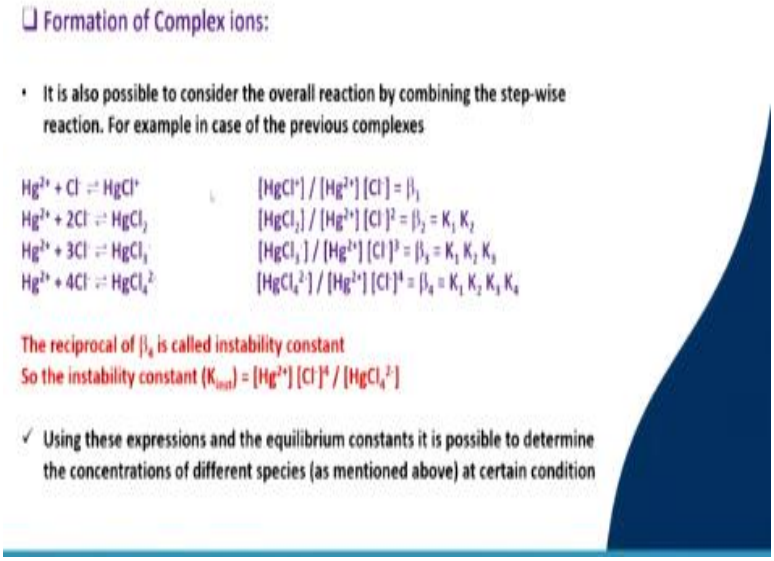

Now as a reference you can follow General and Inorganic Chemistry by Dutt P. K. and Dutt P. K. Moreover, for the mercuric chloride problem you can see Sawyer McCarty. There is one example also shown. As I told in the previous slide using these expressions and equilibrium

constant values you can determine the different species. There is a very nice example which you can solve it. You can solve it by yourself because you know the concept now and finally you can see that whether you have done it correctly or not. If you can do it correctly without seeing the book (the solved problem), then I will know that you have understood know what is explained here. So please try that. This is a very good example to learn and I hope that you can solve it without seeing the solved problem. Thank you.