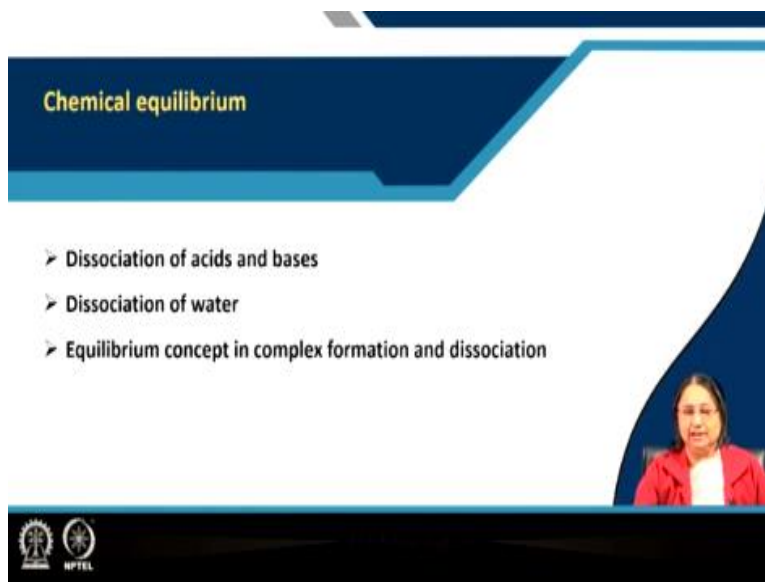


Environmental Chemistry and Microbiology
Dr. Anjali Pal and Dr Sudha Goel
Department of Civil Engineering
Indian Institute of Technology, Kharagpur

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 slide features a dark blue header with the title "Chemical equilibrium" in yellow. Below the header, a list of topics is presented in white text with right-pointing chevrons: "Dissociation of acids and bases", "Dissociation of water", and "Equilibrium concept in complex formation and dissociation". In the bottom right corner, there is a small video inset showing a woman with dark hair wearing a red jacket. At the bottom left of the slide, there are two circular logos: the IIT Kharagpur logo and the NPTEL logo.

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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Chemical equilibrium

□ Ionization of Acids and Bases

- According to Arrhenius theory an acid is a compound which gives H^+ in water, and a base gives OH^- in water.
- Arrhenius theory helps us to explain the strength of acids and bases.
- Strong acids dissociate fully (100%) in dilute solution
- As for example for a monoprotic acid HA

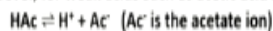


$$K_A = \frac{[H^+][A^-]}{[HA]}$$

For a strong acid K_A is very large as because there is almost no undissociated acid (HA)

K_A is the dissociation constant of acid

- However, for weak acids such as acetic acid (HAc)



$$K_A = \frac{[H^+][Ac^-]}{[HAc]} = 1.75 \times 10^{-5} \quad (\text{at } 25^\circ\text{C})$$



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 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 monoprotic acid which gives H^+ ion and A^- ion. In case of acid dissociation, we always write K_A as follows:

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

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

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

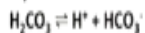
At 25°C the value of K_A for acetic acid is 1.75×10^{-5} (very low). So, it is a weak acid. It dissociates only a very small fraction.

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Chemical equilibrium

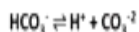
□ Ionization of Acids and Bases

➤ For a diprotic acid such as carbonic acid (H_2CO_3)



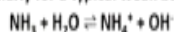
$$K_{A1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.45 \times 10^{-7} \text{ (at } 25^\circ\text{C)}$$

Again,



$$K_{A2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11} \text{ (at } 25^\circ\text{C)}$$

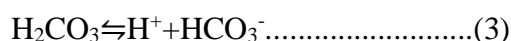
➤ Similarly for a typical weak base NH_3



$$K_B = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.75 \times 10^{-5} \text{ (at } 25^\circ\text{C)}$$

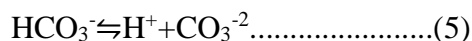


Now in case of diprotic acid let us consider the case of the carbonic acid:



$$K_{A1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.45 \times 10^{-7} \text{ (at } 25^\circ\text{C)} \dots\dots\dots(4)$$

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:

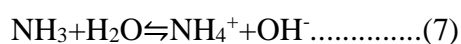


$$K_{A2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]} = 4.69 \times 10^{-11} \text{ (at } 25^\circ\text{C)} \dots\dots\dots(6)$$

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

If we know the $\text{p}K_A$ value (minus log of K_A) then we will see it is just below 7. And from this $\text{p}K_A$ 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 $\text{p}K_A$ we can see that it is in the alkaline range.

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



$$K_B = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.75 \times 10^{-5} \text{ (at } 25^\circ\text{C)} \dots\dots\dots(8)$$

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

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□ Ionization of Water

➤ In aqueous solutions one of the most important equilibria is the dissociation of water into a hydrogen ion (or proton) and hydroxyl ion

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \text{ ----- (1)}$$

A proton can not exist as such because of its small volume (and extremely large charge-to-volume ratio).
It will attach itself to a water molecule to form H_3O^+ (hydronium ion).
So the more correct representation of water dissociation is:

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \text{ ----- (2)}$$

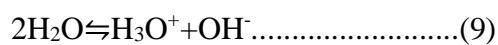
However for many practical purposes Eqn. (1) can be considered.
This gives us the ion product of water:

$$[\text{H}^+][\text{OH}^-] / [\text{H}_2\text{O}] = K_w \text{ (ion product of water)}$$

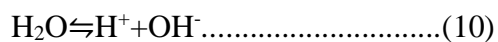
However, $[\text{H}_2\text{O}]$ is taken as 1.
Hence, $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ (at 25°C)

It is important to remember that, the numerical values of $[\text{H}^+]$ and $[\text{OH}^-]$ will include all the H^+ and OH^- ions present, whether they come from water alone or from other constituents present in water.

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):



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



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

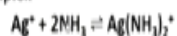
$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \text{(11)}$$

But $[\text{H}_2\text{O}]$ is equal to 1 and therefore ion product of water is equal to $[\text{H}^+][\text{OH}^-]$ and its value at 25°C is equal to 10^{-14} . It is important to remember that the numerical values of $[\text{H}^+]$ and $[\text{OH}^-]$ 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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Complex ion formation and dissociation:

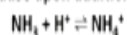
- In complex ions we observe the presence of one (or more) metal ion associated with one or more ions or molecules called as ligands.
- The common ligands may be some ions or molecules like OH⁻, CO₃²⁻, NH₃, F⁻, Cl⁻, CN⁻, S₂O₃²⁻, and other organic species like EDTA, humic acid etc.
- For example Ag⁺ ions complex with NH₃ to form silver-ammonia (silver amine) complex



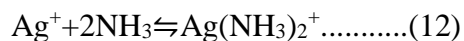
So, here the formation (or stability) constant (β_2)

$$= \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.74 \times 10^7$$

- All such complex ions are destroyed by removing one of the dissociation products.
- For example silver-ammonia complex ion can be destroyed if some source of H⁺ ions is added.
- Because upon addition of H⁺ ion, NH₄⁺ is produced which is more stable



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(NH₃)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⁻, CO₃²⁻, 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 silver 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:



$$\beta = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.74 \times 10^7 \dots\dots\dots(13)$$

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

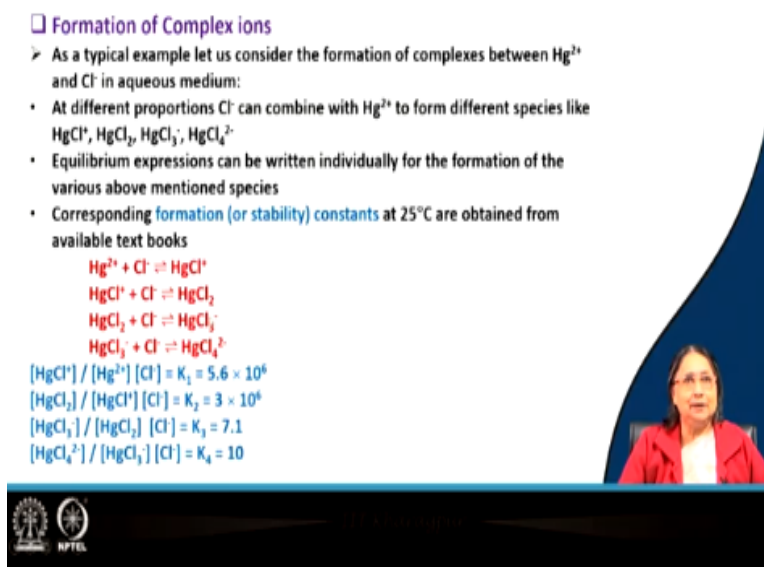
this complex may be broken down. Now you have some idea about the shifting the equilibrium. So, if I want to make this reaction in the go backward reaction then how we will do it? If you want to remove ammonia that is produced, then how will you remove it? We put some acid. Then in presence of acid this 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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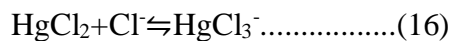
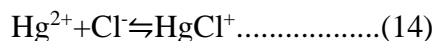
□ Formation of Complex ions

- As a typical example let us consider the formation of complexes between Hg^{2+} and Cl^- in aqueous medium:
 - At different proportions Cl^- can combine with Hg^{2+} to form different species like HgCl^+ , HgCl_2 , HgCl_3^- , HgCl_4^{2-}
 - Equilibrium expressions can be written individually for the formation of the various above mentioned species
 - Corresponding formation (or stability) constants at 25°C are obtained from available text books

$$\begin{aligned} \text{Hg}^{2+} + \text{Cl}^- &\rightleftharpoons \text{HgCl}^+ \\ \text{HgCl}^+ + \text{Cl}^- &\rightleftharpoons \text{HgCl}_2 \\ \text{HgCl}_2 + \text{Cl}^- &\rightleftharpoons \text{HgCl}_3^- \\ \text{HgCl}_3^- + \text{Cl}^- &\rightleftharpoons \text{HgCl}_4^{2-} \end{aligned}$$

$$\begin{aligned} \frac{[\text{HgCl}^+]}{[\text{Hg}^{2+}][\text{Cl}^-]} &= K_1 = 5.6 \times 10^6 \\ \frac{[\text{HgCl}_2]}{[\text{HgCl}^+][\text{Cl}^-]} &= K_2 = 3 \times 10^8 \\ \frac{[\text{HgCl}_3^-]}{[\text{HgCl}_2][\text{Cl}^-]} &= K_3 = 7.1 \\ \frac{[\text{HgCl}_4^{2-}]}{[\text{HgCl}_3^-][\text{Cl}^-]} &= K_4 = 10 \end{aligned}$$


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:



Similarly, four equilibrium constants can be written as follows:

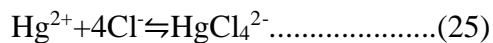
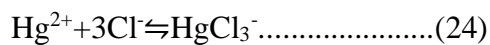
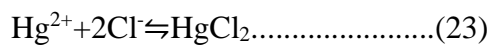
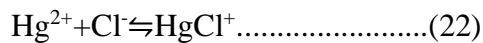
$$K_1 = \frac{[\text{HgCl}^+]}{[\text{Hg}^{2+}][\text{Cl}^-]} = 5.6 \times 10^6 \dots\dots\dots(18)$$

$$K_2 = \frac{[\text{HgCl}_2]}{[\text{HgCl}^+][\text{Cl}^-]} = 3 \times 10^6 \dots\dots\dots(19)$$

$$K_3 = \frac{[\text{HgCl}_3^-]}{[\text{HgCl}_2][\text{Cl}^-]} = 7.1 \dots\dots\dots(20)$$

$$K_4 = \frac{[\text{HgCl}_4^{2-}]}{[\text{HgCl}_3^-][\text{Cl}^-]} = 10 \dots\dots\dots(21)$$

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



Similarly, four equilibrium constants can be written as follows:

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

$$\frac{[\text{HgCl}_2]}{[\text{Hg}^{2+}][\text{Cl}^-]^2} = \beta_2 = K_1 K_2 \dots\dots\dots(27)$$

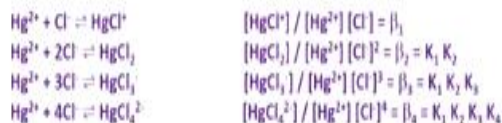
$$\frac{[\text{HgCl}_3^-]}{[\text{Hg}^{2+}][\text{Cl}^-]^3} = \beta_3 = K_1 K_2 K_3 \dots\dots\dots(28)$$

$$\frac{[\text{HgCl}_4^{2-}]}{[\text{Hg}^{2+}][\text{Cl}^-]^4} = \beta_4 = K_1 K_2 K_3 K_4 \dots\dots\dots(29)$$

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Formation of Complex ions:

- It is also possible to consider the overall reaction by combining the step-wise reaction. For example in case of the previous complexes



The reciprocal of β_4 is called instability constant

So the instability constant (K_{inst}) = $[\text{Hg}^{2+}] [\text{Cl}^-]^4 / [\text{HgCl}_4^{2-}]$

- Using these expressions and the equilibrium constants it is possible to determine the concentrations of different species (as mentioned above) at certain condition



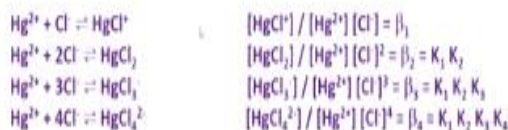
Reciprocal of β_4 is called instability constant.

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 $[\text{Hg}^{2+}]$ 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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Formation of Complex ions:

- It is also possible to consider the overall reaction by combining the step-wise reaction. For example in case of the previous complexes



The reciprocal of β_4 is called instability constant

So the instability constant (K_{inst}) = $[\text{Hg}^{2+}] [\text{Cl}^-]^4 / [\text{HgCl}_4^{2-}]$

- Using these expressions and the equilibrium constants it is possible to determine the concentrations of different species (as mentioned above) at certain condition

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.