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

Lecture -08
Chemical Equilibrium-III

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 the Civil Engineering Department of IIT Kharagpur. We have divided this course into two parts: Environmental Chemistry and Microbiology. The Environmental Chemistry part will be covered by me and the second part Environmental Microbiology will be taught by Professor Sudha Goel.

This is the module 2 (i.e., chemical equilibrium) and this is the lecture number 8.

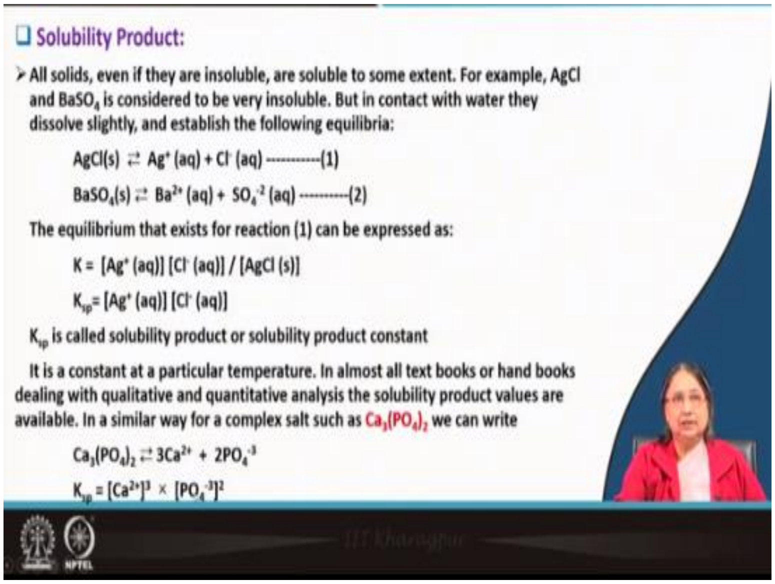
(Refer Slide Time: 01:16)

Chemical Equilibrium

- Solubility product
- Solubility
- Common ion effect
- Application

In this lecture I will cover many important aspects of chemical equilibrium; i.e., the solubility product, solubility, common ion effect and the applications.

(Refer Slide Time: 01:29)



❑ Solubility Product:

- All solids, even if they are insoluble, are soluble to some extent. For example, AgCl and $BaSO_4$ is considered to be very insoluble. But in contact with water they dissolve slightly, and establish the following equilibria:

$AgCl(s) \rightleftarrows Ag^{+}(aq) + Cl^{-}(aq)$ ----------(1)

$BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4^{-2}(aq)$ ----------(2)

The equilibrium that exists for reaction (1) can be expressed as:

$K = [Ag^{+}(aq)]\,[Cl^{-}(aq)] / [AgCl(s)]$

$K_{sp} = [Ag^{+}(aq)]\,[Cl^{-}(aq)]$

K_{sp} is called solubility product or solubility product constant

It is a constant at a particular temperature. In almost all text books or hand books dealing with qualitative and quantitative analysis the solubility product values are available. In a similar way for a complex salt such as $Ca_3(PO_4)_2$ we can write

$Ca_3(PO_4)_2 \rightleftarrows 3Ca^{2+} + 2PO_4^{-3}$

$K_{sp} = [Ca^{2+}]^3 \times [PO_4^{-3}]^2$

We know that solubility product is very important for chemical equilibrium. All solids we know that even if they are very insoluble still, they are to some extent soluble. For example, silver chloride (AgCl) and barium sulphate ($BaSO_4$) are very insoluble but in contact with water they slightly dissolve and they produce the corresponding ions and they establish the following equilibriums:

$AgCl(s) \leftrightharpoons Ag^{+}(aq) + Cl^{-}(aq)$.............(1)

$BaSO_4(s) \leftrightharpoons Ba^{2+}(aq) + SO_4^{-2}(aq)$.....(2)

The equilibrium for (1) can be expressed as follows:

$$K = \frac{[Ag^{+}(aq)][Cl^{-}(aq)]}{[AgCl(s)]} ....(3)$$

But [AgCl(s)] is a constant and therefore we define equilibrium constant by a new term K_{sp} which is called solubility product or solubility product constant as follows:

$$K_{sp} = [Ag^{+}(aq)][Cl^{-}(aq)] ....(4)$$

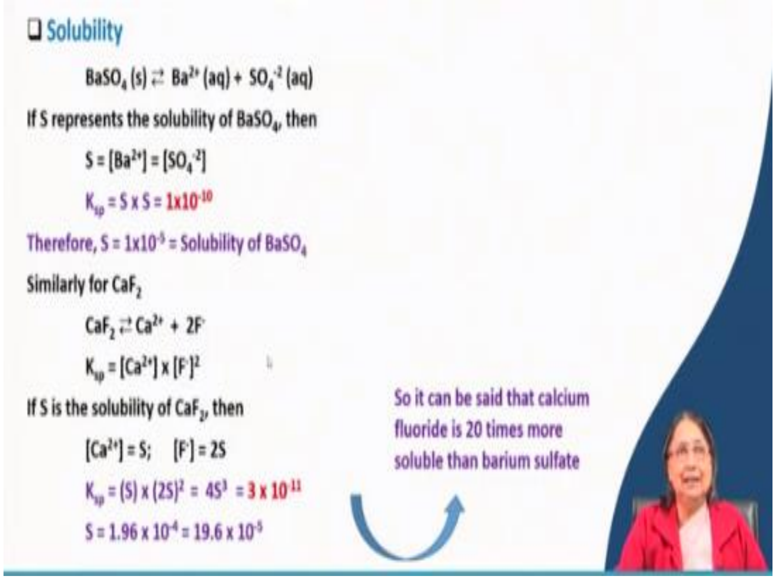
We have seen that in different ways we can express the equilibrium constant. Say for example in case of acid dissociation we write K_a, in case of base dissociation we write base K_b, in case of water dissociation we write K_w. Similarly, here we call equilibrium constant as solubility product and we express in by K_{sp}. This is a very important term for chemical equilibrium. It is constant at a particular temperature. All equilibrium constants are constants at a particular temperature. In almost all textbooks or handbooks dealing with qualitative and quantitative analysis, the solubility product values are available.

You can see it. As a list they show at 25^0C, what is the soluble product values. In a similar way for a complex salt such as calcium phosphate ($Ca_3(PO_4)_2$) equilibrium expression and solubility product can be expressed as follows:

$Ca_3(PO_4)_2 \leftrightharpoons 3Ca^{2+} + 2PO_4^{-3}$...........................(5)

$K_{sp} = [Ca^{2+}]^3 \times [PO_4^{-3}]^2$...................(6)

(Refer Slide Time: 05:25)



❑ Solubility

$BaSO_4\,(s) \rightleftarrows Ba^{2+}\,(aq) + SO_4^{-2}\,(aq)$

If S represents the solubility of $BaSO_4$, then

$S = [Ba^{2+}] = [SO_4^{-2}]$

$K_{sp} = S \times S = 1x10^{-10}$

Therefore, $S = 1x10^{-5}$ = Solubility of $BaSO_4$

Similarly for CaF_2

$CaF_2 \rightleftarrows Ca^{2+} + 2F^-$

$K_{sp} = [Ca^{2+}] \times [F^-]^2$

If S is the solubility of CaF_2, then

$[Ca^{2+}] = S; \quad [F^-] = 2S$

$K_{sp} = (S) \times (2S)^2 = 4S^3 = 3 \times 10^{-11}$

$S = 1.96 \times 10^{-4} = 19.6 \times 10^{-5}$

So it can be said that calcium fluoride is 20 times more soluble than barium sulfate

Now let us come to an important topic called solubility. Till now we have seen about the solubility product. Here we will see what is solubility. Let us take the example of barium sulfate (reaction (2)):

$BaSO_4(s) \leftrightharpoons Ba^{2+}(aq) + SO_4^{-2}(aq)$.....(2)

Now we know that solubility product of barium sulphate at 25^0C is 10^{-10}.

Let the solubility of barium sulfate be S. Therefore, $S=[Ba^{2+}]=[SO_4^{-2}]$

So, $K_{sp}=SxS=10^{-10}$

Therefore, solubility of $BaSO_4$ is $S=10^{-5}$. This was a very simple example and now we will see for calcium fluoride (CaF_2). Similarly, equilibrium expression and solubility product for calcium fluoride can be written as follows:

$CaF_2 \leftrightharpoons Ca^{2+} + 2F^-$..................(7)

$K_{sp} = [Ca^{2+}] \times [F^-]^2$...................(8)

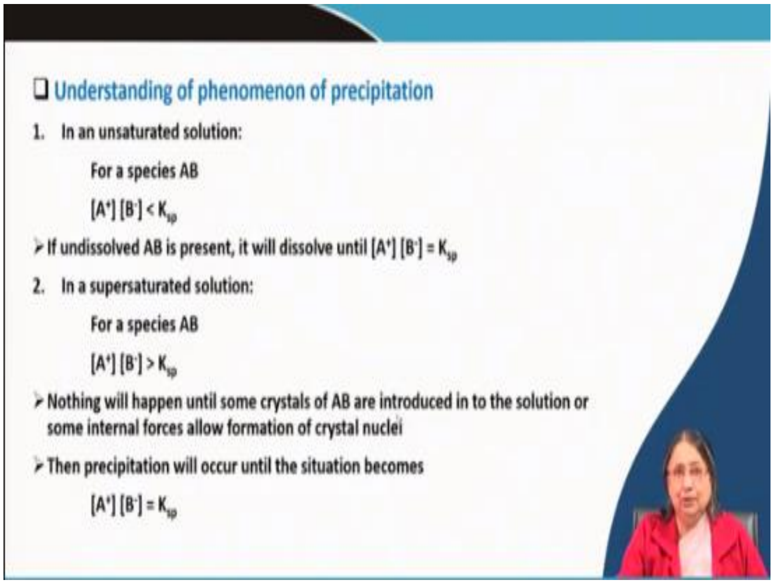
Let the solubility of calcium fluoride be S and from any standard book we will get that the solubility product of calcium fluoride at 25^0C is $3x10^{-11}$.

So, $[Ca^{2+}]=S$, $[F^-]=2S$

$$K_{sp}=(S)\times(2S)^2$$
$$\text{or,}\ 4S^3=3\times10^{-11}$$
$$\text{or,}\ S=19.6\times10^{-5}$$

So, from the above two examples ((2) and (7)) we can see that calcium fluoride is nearly 20 times more soluble than barium sulfate. So, although solubility product of barium sulphate is higher compared to calcium fluoride but solubility of calcium fluoride is higher compared to barium sulphate. So, looking at the solubility product immediately without thinking we can tell that whose solubility product is higher. But it does not always depicts the truth regarding solubility of the compounds.

(Refer Slide Time: 08:25)



❑ Understanding of phenomenon of precipitation

1. In an unsaturated solution:

   For a species AB

   $[A^+]\,[B^-] < K_{sp}$

➢ If undissolved AB is present, it will dissolve until $[A^+]\,[B^-] = K_{sp}$

2. In a supersaturated solution:

   For a species AB

   $[A^+]\,[B^-] > K_{sp}$

➢ Nothing will happen until some crystals of AB are introduced in to the solution or some internal forces allow formation of crystal nuclei

➢ Then precipitation will occur until the situation becomes

   $[A^+]\,[B^-] = K_{sp}$

Now we will understand the phenomena of precipitation. We know that what is saturated solution, what is unsaturated solution and what is super saturated solution. What is unsaturated solution? Let us take a compound AB,

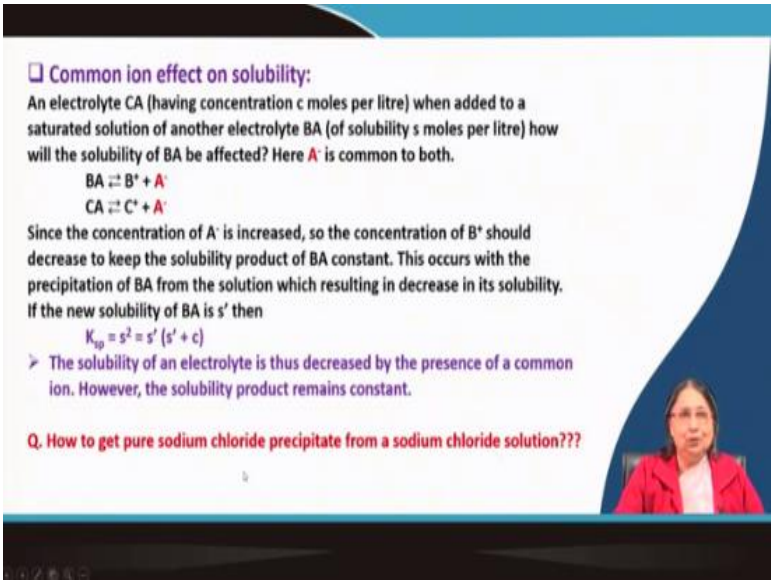
If $[A^+][B^-]<K_{sp}$ then it is an unsaturated solution

If $[A^+][B^-]=K_{sp}$ then it is a saturated solution

If $[A^+][B^-]>K_{sp}$ then it is a supersaturated solution

Precipitation occurs in case of supersaturated solution. These we can see in crystallization. Say for example if you want to make some crystals of something say for example sodium chloride or say sugar. So, you make a very saturated solution (almost super saturated solution). Then you put a single crystal of that material. Then you will see lot of crystals are coming. That is called seeding. It means you are disturbing the super saturated solution so that it will try to remove some crystal from there to get just the saturated solution.

(Refer Slide Time: 10:26)



❑ Common ion effect on solubility:

An electrolyte CA (having concentration c moles per litre) when added to a saturated solution of another electrolyte BA (of solubility s moles per litre) how will the solubility of BA be affected? Here A^- is common to both.

$$BA \rightleftarrows B^+ + A^-$$
$$CA \rightleftarrows C^+ + A^-$$

Since the concentration of A^- is increased, so the concentration of B^+ should decrease to keep the solubility product of BA constant. This occurs with the precipitation of BA from the solution which resulting in decrease in its solubility.

If the new solubility of BA is s′ then

$$K_{sp} = s^2 = s'(s' + c)$$

➢ The solubility of an electrolyte is thus decreased by the presence of a common ion. However, the solubility product remains constant.

Q. How to get pure sodium chloride precipitate from a sodium chloride solution???

Now let us see to the common effect on solubility. Say for example we have an electrolyte BA whose solubility is S moles per liter. Now there is another electrolyte say CA (concentration is c moles per liter). What is interesting feature here in BA and CA is that both these electrolytes contain A^-. It is the common ion. Now let us add CA to BA. Then what will happen? You see initially when BA was alone then solubility is S. But now we are adding CA. After adding CA the solubility will no more be S. It will change. How it will change? Let the new solubility be denoted by S'. Therefore, we can write:

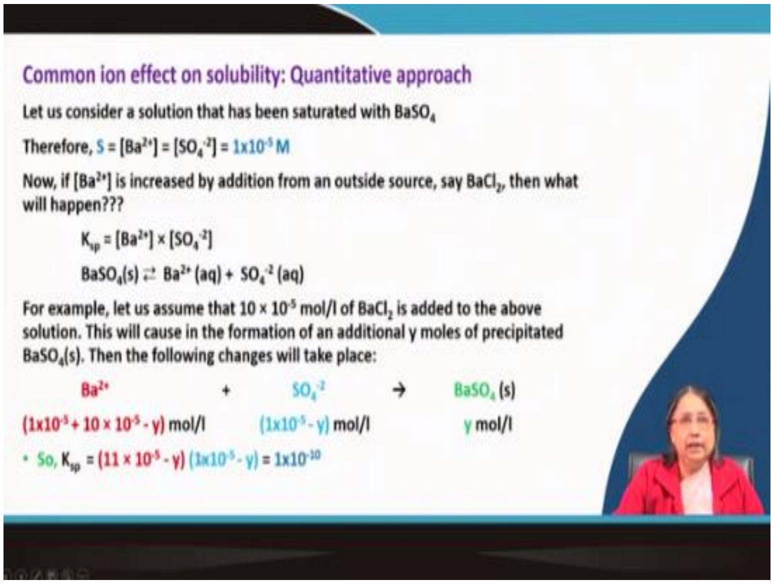
$K_{sp}=S^2=S'(S'+c)$..................(9)

In order to keep K_{sp} constant, S' should be lower than S. The solubility of an electrolyte is thus decreased by the presence of a common ion however the solubility product remains the constant. So, one important question I have given here:

How to get pure sodium chloride precipitate from a a sodium chloride solution?

How will you do it? You take the concentrated sodium chloride solution and then you pass HCl gas through it. Now you are passing HCl where you are adding a common ion which is nothing but chloride ion. So, what will happen? Some sodium will go out of the phase. So, it will be precipitated as sodium chloride. So, you will get pure sodium chloride as a precipitate.

(Refer Slide Time: 13:19)



Common ion effect on solubility: Quantitative approach

Let us consider a solution that has been saturated with $BaSO_4$

Therefore, $S = [Ba^{2+}] = [SO_4^{-2}] = 1x10^{-5}$ M

Now, if $[Ba^{2+}]$ is increased by addition from an outside source, say $BaCl_2$, then what will happen???

$$K_{sp} = [Ba^{2+}] \times [SO_4^{-2}]$$

$$BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4^{-2}(aq)$$

For example, let us assume that 10×10^{-5} mol/l of $BaCl_2$ is added to the above solution. This will cause in the formation of an additional y moles of precipitated $BaSO_4(s)$. Then the following changes will take place:

$$Ba^{2+} + SO_4^{-2} \rightarrow BaSO_4(s)$$

$(1x10^{-5} + 10 \times 10^{-5} - y)$ mol/l　　$(1x10^{-5} - y)$ mol/l　　y mol/l

- So, $K_{sp} = (11 \times 10^{-5} - y)(1x10^{-5} - y) = 1x10^{-10}$

Now I have already told you, what will happen if you add a common ion to some electrolyte. Now we will see the quantitative approach. Let us again consider the case of barium sulfate ($BaSO_4$) (reaction (2)):

$BaSO_4(s) \leftrightharpoons Ba^{2+}(aq) + SO_4^{-2}(aq)$.....(2)

$S=[Ba^{2+}]=[SO_4^{-2}]=10^{-5}M$

Now say for example I am adding barium chloride from outside source say for example barium chloride. So, some concentration of barium was already there. Now we are adding some extra barium iron concentration that is through the application of barium chloride. Barium chloride is strong electrolyte. So, it will dissociate completely. Then what will happen to the barium sulphate? That is shown here. Now K_{sp} is constant.

Now we have added $10x10^{-5}$ moles/liter of barium chloride. This will cause in the formation of an additional y moles of precipitated barium sulphate. When the barium concentration will be increased then some barium sulphate has to be going out of phase. But how much? This can be solved as follows:

$$\begin{array}{cccc} Ba^{2+} & + \quad SO_4^{-2} & \rightarrow & BaSO_4(s) \\ (1x10^{-5}+10x10^{-5}-y)mol/l & (1x10^{-5}-y)mol/l & & ymol/l \end{array}$$

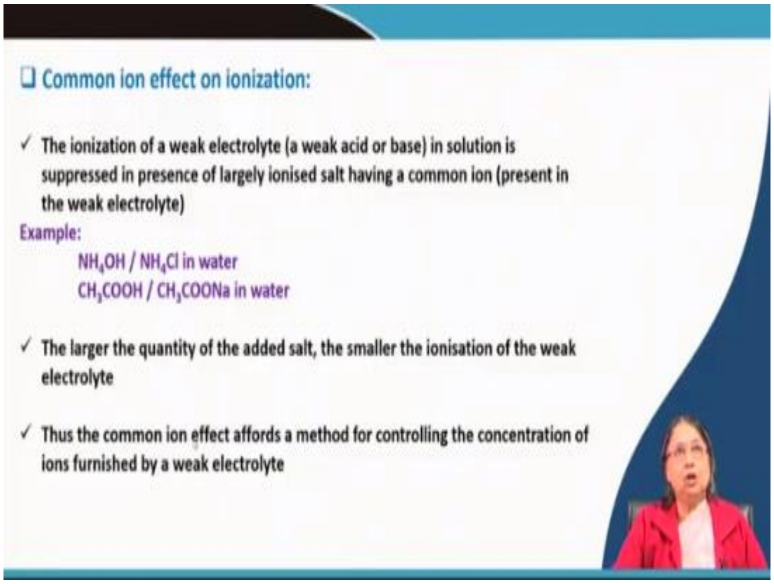
$K_{sp}=(11\times10^{-5}-y)(1\times10^{-5}-y)=1\times10^{-10}$

or, $y=0.9\times10^{-5}mol/l$

So, $[Ba^{2+}]=10.1x10^{-5}$ mol/l

$[SO_4^{-2}]=0.1x10^{-5}$ mol/l

(Refer Slide Time: 16:05)



❑ Common ion effect on ionization:

✓ The ionization of a weak electrolyte (a weak acid or base) in solution is suppressed in presence of largely ionised salt having a common ion (present in the weak electrolyte)

Example:

NH_4OH / NH_4Cl in water

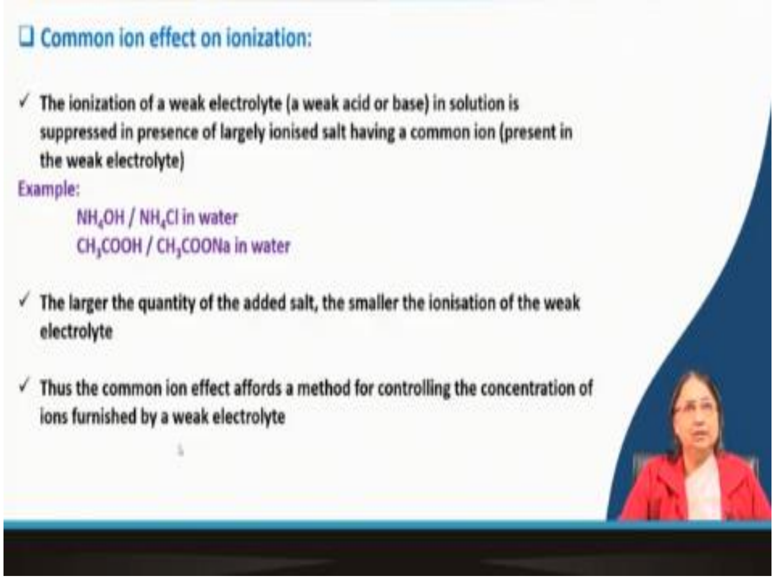
CH_3COOH / CH_3COONa in water

✓ The larger the quantity of the added salt, the smaller the ionisation of the weak electrolyte

✓ Thus the common ion effect affords a method for controlling the concentration of ions furnished by a weak electrolyte

After adding barium chloride, solubility is reduced almost 10 times. So, it is observed that sulphate ion concentration is reduced considerably. This is an application of common ion effect. So, when the sulphate ion concentration is reduced that means lot of barium sulphate has been precipitated. So, in this way sulphate determination is done by adding enough excess amount of barium chloride. This is used extensively in environmental engineering practice and in analytical chemistry to accomplish complete precipitation of the desired ions. This is also true for hardness removal. I told you from the outside we are adding some carbonate or hydroxide to get precipitate the calcium carbonate and magnesium hydroxide to remove the hardness.

(Refer Slide Time: 17:34)



❑ Common ion effect on ionization:

- ✓ The ionization of a weak electrolyte (a weak acid or base) in solution is suppressed in presence of largely ionised salt having a common ion (present in the weak electrolyte)

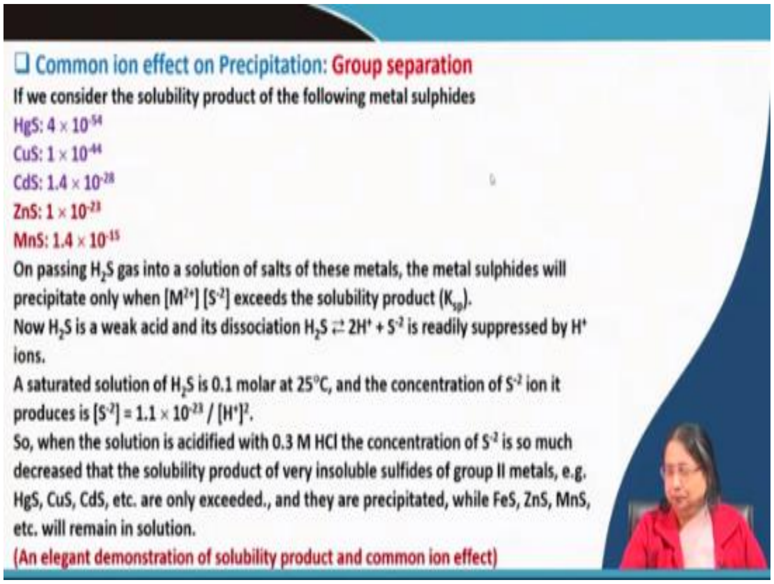
Example:

NH_4OH / NH_4Cl in water
CH_3COOH / CH_3COONa in water

- ✓ The larger the quantity of the added salt, the smaller the ionisation of the weak electrolyte
- ✓ Thus the common ion effect affords a method for controlling the concentration of ions furnished by a weak electrolyte

Now come to the common ion effect on ionization. This is general thing but we have seen in buffer also (ammonium hydroxide ammonium chloride buffer or acetic acid acetate ion buffer). So, what is happening? In case of ammonium hydroxide ammonium chloride buffer dissociation of NH_4OH is suppressed and in case of the other dissociation of acetic acid is suppressed due to the presence of common ion. If we increase the concentration of ammonium chloride still it will be less dissociated. So, degree of dissociation will be less in presence of common ion. Thus, it is of course a method for controlling the concentration of ions furnished by a weak electrolyte.

(Refer Slide Time: 19:18)



❑ Common ion effect on Precipitation: Group separation

If we consider the solubility product of the following metal sulphides

HgS: 4×10^{-54}
CuS: 1×10^{-44}
CdS: 1.4×10^{-28}
ZnS: 1×10^{-23}
MnS: 1.4×10^{-15}

On passing H_2S gas into a solution of salts of these metals, the metal sulphides will precipitate only when $[M^{2+}]$ $[S^{-2}]$ exceeds the solubility product (K_{sp}).

Now H_2S is a weak acid and its dissociation $H_2S \rightleftarrows 2H^+ + S^{-2}$ is readily suppressed by H^+ ions.

A saturated solution of H_2S is 0.1 molar at 25°C, and the concentration of S^{-2} ion it produces is $[S^{-2}] = 1.1 \times 10^{-23} / [H^+]^2$.

So, when the solution is acidified with 0.3 M HCl the concentration of S^{-2} is so much decreased that the solubility product of very insoluble sulfides of group II metals, e.g. HgS, CuS, CdS, etc. are only exceeded., and they are precipitated, while FeS, ZnS, MnS, etc. will remain in solution.

(An elegant demonstration of solubility product and common ion effect)

Common ion effect on group separation has enormous applications in many cases, say for example in group separation. Those who are in chemistry background they will see it in group separation. what is there? Here solubility product of some sulphide salts is considered:

Salt	Solubility product
HgS	$4x10^{-54}$
CuS	$1x10^{-44}$
CdS	$1.4x10^{-28}$
ZnS	$1x10^{-23}$
MnS	$1.4x10^{-15}$

You can see here mercury sulphide, copper sulphide and cadmium sulphide have low solubility product and so they are insoluble compared to this zinc sulphide and manganese sulphide. So, what is happening on passing H_2S gas into a solution of salts of these metals? The metal sulphides will precipitate when only when product of $[M^{2+}]$ and $[S^{2-}]$ exceeds the solubility product that is K_{sp}. This we have seen already that the saturated solution, unsaturated solution and super saturated solution when this will reach the K_{sp} value then only they will be precipitated.

H_2S is a weak acid and its dissociation is readily suppressed in presence of H^+ ions:

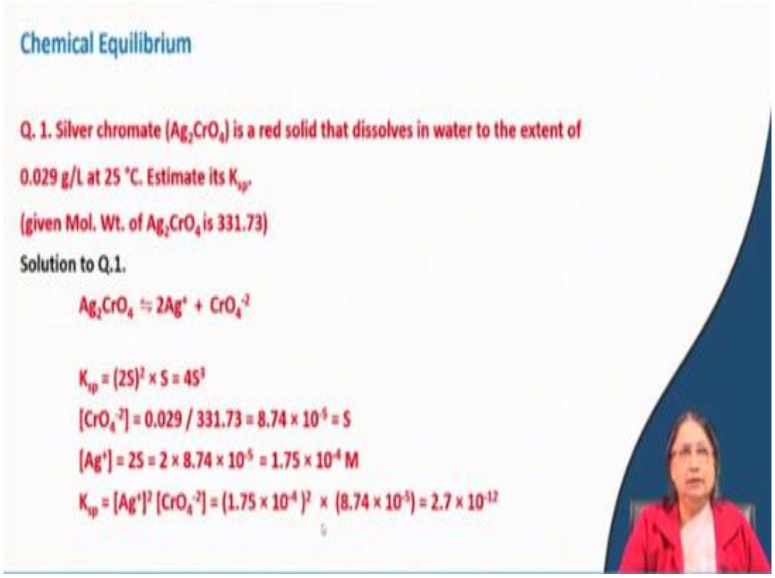
$H_2S \leftrightharpoons 2H^+ + S^{2-}$...........................(10)

Now consider a saturated solution of H_2S of 0.1M at 25^0C and the concentration of sulfide ion it produces is can be written:

$$[S^{2-}]=\frac{1.1\times10^{-23}}{[H^+]^2}\text{....................(11)}$$

Now if we increase the $[H^+]$ by means of adding 0.3M HCl, the concentration of S^{2-} will be so decreased so that solubility product of group II metal (Hg, Cu, Cd) sulfides will be exceeded and they will be precipitated while that of Fe, Zn, Mn will be in solution. This is an elegant demonstration of solubility product and common ion effect which has been used in group separation in analytical chemistry.

(Refer Slide Time: 22:02)



Chemical Equilibrium

Q. 1. Silver chromate (Ag_2CrO_4) is a red solid that dissolves in water to the extent of 0.029 g/L at 25 °C. Estimate its K_{sp}.

(given Mol. Wt. of Ag_2CrO_4 is 331.73)

Solution to Q.1.

$Ag_2CrO_4 \leftrightharpoons 2Ag^+ + CrO_4^{-2}$

$K_{sp} = (2S)^2 \times S = 4S^3$

$[CrO_4^{-2}] = 0.029 / 331.73 = 8.74 \times 10^{-5} = S$

$[Ag^+] = 2S = 2 \times 8.74 \times 10^{-5} = 1.75 \times 10^{-4}$ M

$K_{sp} = [Ag^+]^2 [CrO_4^{-2}] = (1.75 \times 10^{-4})^2 \times (8.74 \times 10^{-5}) = 2.7 \times 10^{-12}$

Now let us solve a simple example:

Q. 1. Silver chromate (Ag_2CrO_4) is a red solid that dissolves in water to the extent of 0.029g/L at 25^0C. Estimate its K_{sp}.

(given Mol. wt. of Ag_2CrO_4 is 331.73)

Solution:

$Ag_2CrO_4 \leftrightharpoons 2Ag^+ + CrO_4^{-2}$

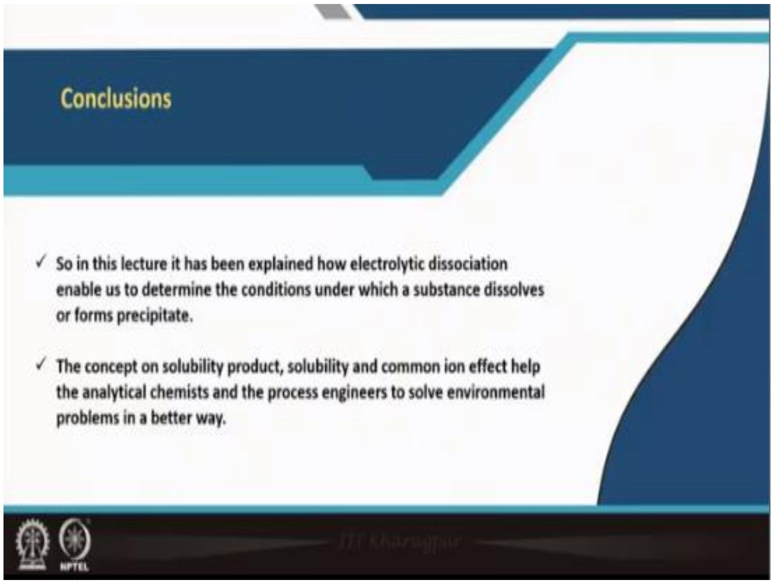
$K_{sp} = (2S)^2 x S = 4S^3$

$$\text{So, } [CrO_4^{-2}] = \frac{0.029}{331.73} = 8.74 \times 10^{-5} = S$$

$$[Ag^+] = 2S = 2 \times 8.74 \times 10^{-5} = 1.75 \times 10^{-4}\,\text{M}$$

$$\text{So, } K_{sp} = [Ag^+]^2 [CrO_4^{-2}] = (1.75 \times 10^{-4})^2 \times (8.74 \times 10^{-5}) = 2.7 \times 10^{-12}$$

(Refer Slide Time: 23:02)



Conclusions

- ✓ So in this lecture it has been explained how electrolytic dissociation enable us to determine the conditions under which a substance dissolves or forms precipitate.
- ✓ The concept on solubility product, solubility and common ion effect help the analytical chemists and the process engineers to solve environmental problems in a better way.

Now as the conclusion we can say that in this lecture it has been explained how electrolytic dissociation enable us to determine the conditions, under which a substance dissolves or forms the precipitate. So, solubility product is the key factor that will tell you whether under which condition it will precipitate but K_{sp} value is constant while you can vary solubility by adding either common ion. Without adding common ion, you can change the solubility where we need to know whether it is in solution phase or it is it has to be precipitated out. So, it is a very important thing to know in chemical equilibrium in process engineering or in environmental engineering or in analytical chemistry the concept of solubility product and solubility and what is the common ion effect. Thank you.