Environmental Soil Chemistry
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Lecture – 41
Pollutants - Soil Solution Interactions

Welcome friends to this NPTEL online certification course of environmental soil chemistry and today, we are going to start week 9 or module 9 and in this week, we will be basically talking about pollutants and soil solution interactions.

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CONCEPTS COVERED

Concepts Covered:

- ❑Pollutants in soil solution
- ❑Solubility equilibrium
- ❑Solvents and surfactants interaction
- ❑Acid rain and alkaline soil
- ❑Sewage sludge
- ❑ Complex formation with organic matter
- ❑Solubility of PAH

So, if we just go ahead and see what are the concepts we are going to cover in this so in this, you know in this week we are; we have covered these following concepts. First of all, we will be talking about the pollutants in soil solution, what are the major pollutants and how they interact in the soil solution then we will be talking about solubility equilibrium, some of the solubility equilibrium we have already covered in our previous lectures.

However, we will be covering some more in this week and after that we will be talking about solvents and surfactants interactions and next we will be talking about acid rain formation as well as you know, gypsum dissolution in alkaline soils. Then we are going to cover a most one of the most important aspect that is sewage sludge and its impact on soil pollution and then we will be talking about complex formation with organic matter specifically in terms of heavy metals.

And we will be also talking about solubility of polycyclic aromatic hydrocarbons which is considered as one of the major pollutant in soil, so these are the several important concepts which are basically covered in this week and in this module and we are going to discuss them one by one.

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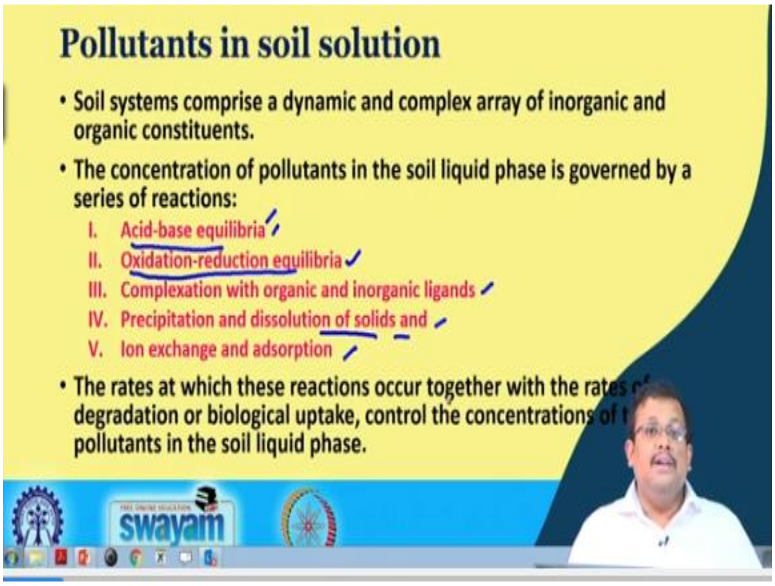

Pollutants in soil solution

- Soil systems comprise a dynamic and complex array of inorganic and organic constituents.
- The concentration of pollutants in the soil liquid phase is governed by a series of reactions:
  - I. Acid-base equilibria
  - II. Oxidation-reduction equilibria
  - III. Complexation with organic and inorganic ligands
  - IV. Precipitation and dissolution of solids and
  - V. Ion exchange and adsorption
- The rates at which these reactions occur together with the rates of degradation or biological uptake, control the concentrations of t pollutants in the soil liquid phase.

So, let us start with the first concept that is pollutants in soil solution, so soil systems comprises a dynamic and complex array of inorganic and organic constituents. The concentration of pollutants in the soil liquid phase is governed by a series of reactions. So, what are those reactions? There are 5 major types of reaction; first of all acid base equilibria reaction, then oxidation reduction equilibria reaction, then complexation with organic and inorganic ligands, precipitation and dissolution of solids and ion exchange and adsorption.

Now, among all these we have already covered in details about oxidation reduction equilibria or redox potential, we have also covered you know in detail discussion about ligands and complexation with organic and inorganic ligands and also we have extensively discussed ion exchange and adsorption in our previous weeks. So, here in this week we will be basically talking about in details about acid base equilibria.

And also briefly we will cover the precipitation and dissolution of solids, so among all these 5 you know, reactions we are going to discuss only this number 2 that is I am sorry, number 1 that is acid base equilibria and number 4 that is precipitation and dissolution of solids. So, remember that the rates at which this reaction occur with the rates of degradation of biological uptake you know, control the concentration of the pollutants in the soil liquid phase. So, basically the rates at which this reaction occurs that means, the reaction rate you know controls the concentration of different pollutants in the soil liquid phases.

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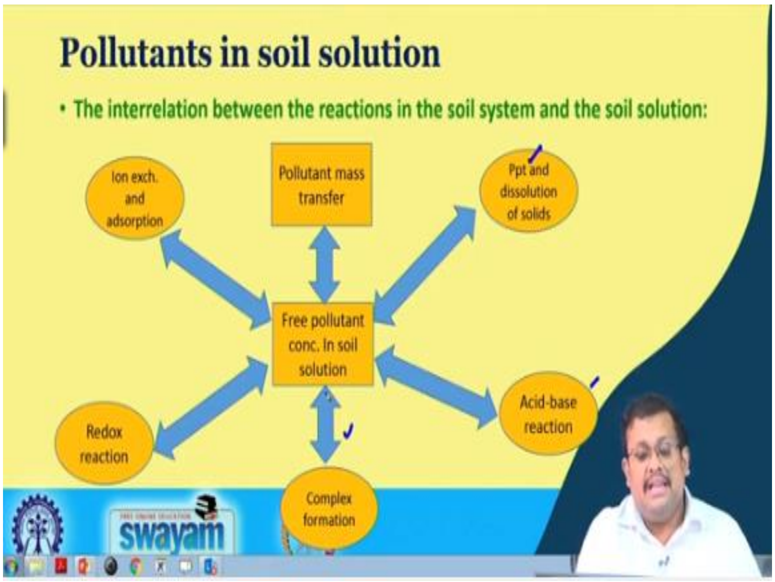

Pollutants in soil solution

- The interrelation between the reactions in the soil system and the soil solution:

Ion exch. and adsorption

Pollutant mass transfer

Ppt and dissolution of solids

Free pollutant conc. In soil solution

Redox reaction

Acid-base reaction

Complex formation

So, if you see the interaction between free pollutant concentration in soil solution and how you know, how they change in the soil solution, how the dynamics change in soil solution these you know diagram will help you to understand it clearly. So, let us consider this is basically the interaction between the reaction and soil system and the soil solution. So, if you can see here, there are free pollutant concentration in the soil solution.

So, let us consider, it can be anything, it can be either you know organic or inorganic, so this free pollutant concentration in soil solution can either go to complex formation and from the complex also, it can go to the free pollutant in soil solution pool. Apart from that it can also take part in acid base reaction and this reaction is basically, both way reactions, so basically from here also, they can go to free pollutant pool in the soil solution.

Further this free pollutant concentration of soil solution can produce the precipitation and also dissolution of the solids and this is also a both way reaction. So, apart from these 3 we can see the pollutant must transfer from this free pollutant concentration in soil solution which is you know, which is also both way reaction. So, all these reaction which you are seeing in this diagram are going in both directions.

Apart from that they can go to the ion exchange and adsorption reaction can show and from the adsorption, when desorption occurs they finally go to the free pollutant concentration in soil solution again and apart from that that also these free pollutant contained in the soil solution can also impact the redox reaction and vice versa. So, these are the, you know snapshot of interrelations between the reactions in the soil system and the soil solution.

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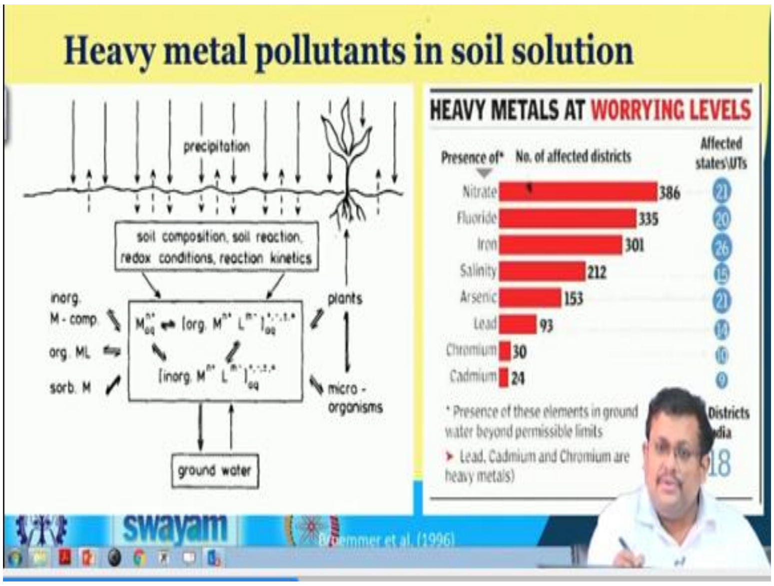

Heavy metal pollutants in soil solution

Brümmer et al. (1996)

So, I hope this is clear to you guys, so let us move ahead and see what is the interaction between the heavy metal pollutants in soil solution, so if we consider there is a you know, precipitation in the soil surface, these water basically moves from the soil surface through the process of infiltration and the soil composition, soil reaction, redox condition and reaction kinetics, all of these can impact the conversion of the metal cations in the aqueous form.

And they can interact with different organic matter and inorganic fractions ultimately, after this reactions are taking place they can ultimately you know converted to new you know, convert to new species and ultimately go to the ground water and also from the ground water also, they can move up into the soil. After different types of you know, different types of fates of these positively charged heavy metal cations, they can be either up taken by the plants or they can be immobilized or they can be uptake by different microorganisms.

So, there is a, you know you can see there is an interaction going on between these microorganisms, heavy metals as well as the plants. So, these way the heavy metals can be up taken by plants and microorganisms, these heavy metals can react with different inorganic components produce the metal you know compound. They can sorbed into the organic matter which we are going to discuss in our coming lectures.

So, they can produce the organic matter metal complexes and also they can sorb to other species, so this is the basically you know, the interaction of heavy metal or dynamics of heavy metals in the soil solution. So, heavy metal pollution as far as the Indian soils and Indian you know heavy metal concentration and you know are in soil and ground water are concerned. This figure shows an important insight of how many districts of India are affected by specific inorganic pollutants.

So, if you see the nitrates, you see that 386 you know districts are affected by this nitrate pollution and the affected states or union territories at a total of 21, in case of fluoride 335 and the number of affected states or union territories are 20, iron contamination can be found in 301 districts and 26 states or union territories, salinity problem is prevalent in 212 affected districts or 15 affected states or union territories.

Arsenic problem is prevalent in 153 you know affect you know districts and 21 states or union territories, lead which is another very important you know heavy metals as far as the potential you know contaminants are concerned. So, lead showing the you know they affect you know 93 number of districts and 14 you know states or union territories as far as the chromium is concerned, this chromium is affecting 30 districts and as well as 10 you know states or union territories.

Cadmium, cadmium pollution can be found in 24 districts and 9 states or union territories, so you can see you know as far as the total number of districts are concerned which are showing different types of heavy metal pollutions or inorganic pollutions are a total of 718 and remember that among all these different elements inorganic elements, this lead, cadmium and chromium are basically considered as very, very potential delete you know hazardous heavy metals.

And these you know, we have seen that these are the elements which are basically present in the ground water beyond the permissible limits. So, this is the data from 2018 you know, we assume that this number of effective districts have increased and it is possible due to the increased amount of industrialization as well as pesticides and other in you know other anthropogenic activities which increases this concentration in the soil solution, we will see in details.

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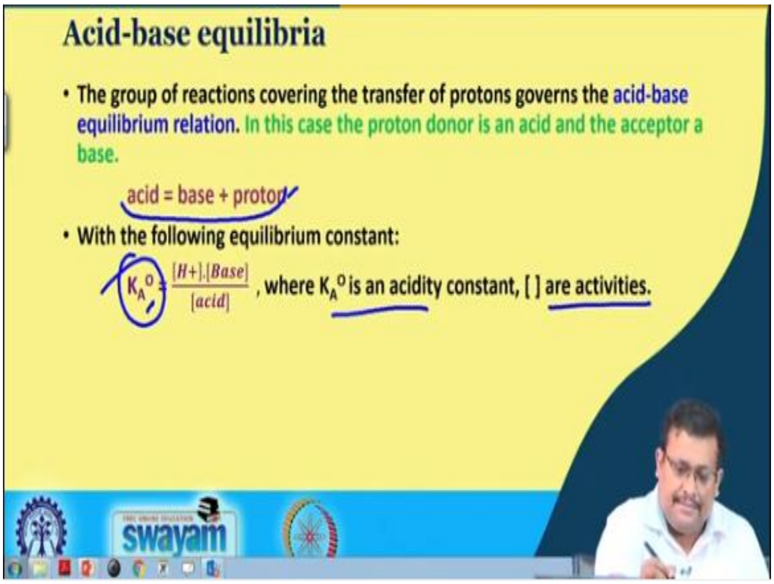

Acid-base equilibria

- The group of reactions covering the transfer of protons governs the acid-base equilibrium relation. In this case the proton donor is an acid and the acceptor a base.

acid = base + proton

- With the following equilibrium constant:

$K_A^0 = \frac{[H+].[Base]}{[acid]}$, where K_A^0 is an acidity constant, [ ] are activities.

So, let us consider this acid base equilibrium, now this the group of reactions covering the transfer of protons governs the acid base equilibrium reaction. Now, in this case the proton donor is an acid and the acceptor is a base, so basically acid is we can write that acid equal to base plus proton. So, with the following equilibrium constant, so these reaction comes with the following equilibrium constant, this equilibrium constant is KA 0, which is denoted by this, you know denoted by this ratio, where this K is acidity constant. So, this is the acidity constant and these parentheses are basically denoting the activities, so this is basically the representation of acid base equilibria.

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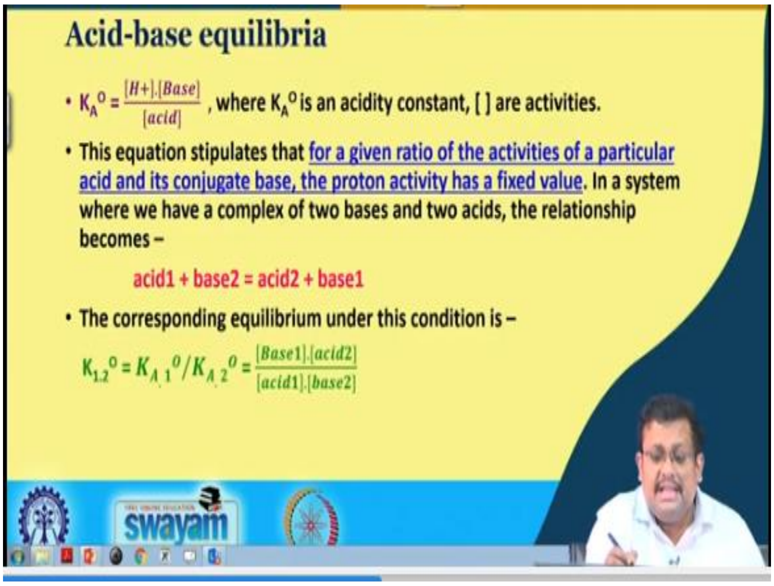

Acid-base equilibria

- $K_A^0 = \frac{[H+].[Base]}{[acid]}$, where K_A^0 is an acidity constant, [ ] are activities.
- This equation stipulates that for a given ratio of the activities of a particular acid and its conjugate base, the proton activity has a fixed value. In a system where we have a complex of two bases and two acids, the relationship becomes –

acid1 + base2 = acid2 + base1

- The corresponding equilibrium under this condition is –

$K_{1,2}^0 = K_{A1}^0/K_{A2}^0 = \frac{[Base1].[acid2]}{[acid1].[base2]}$

Now, given this acid base equilibria you know relationship, where KA 0 is an acidity constant and these brackets are activities, this equation stipulates that for a given ratio of the activities of a particular acid and its conjugate base, the proton activity has a fixed value. So, if we consider that the ratio of an activities of particular acid and conjugate base is a constant, then the proton activity has a fixed value.

So, this is basically the interpretation from there, so in a system where we have a complex of 2 bases and 2 acids the relationship becomes this, when acid 1 plus base 2 equal to acid 2 plus base 1 and the corresponding equilibrium under this condition can be represented by this K120 with the help of this ratio. So, ultimately we are getting the you know activities of base 1 multiplied by activity of acid 2 over you know activity of acid 1 multiplied by activity of base 2.

So, this is for a single acid and single base however, this is for complex of 2 bases and 2 acids, so these are the equilibrium relationship between when these acids and bases are reacting together. So, this is in nutshell the acid base equilibria.

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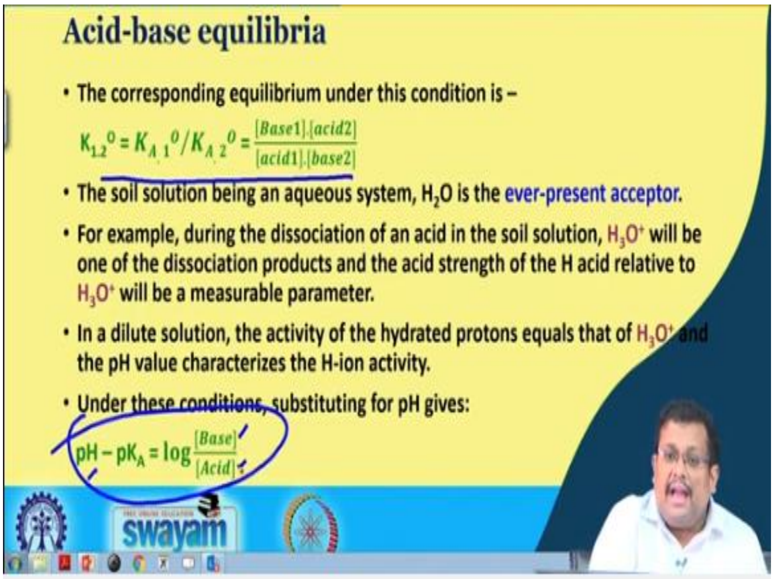

Acid-base equilibria

- The corresponding equilibrium under this condition is –

$$K_{1,2}{}^0 = K_{A\,1}{}^0/K_{A\,2}{}^0 = \frac{[Base1].[acid2]}{[acid1].[base2]}$$

- The soil solution being an aqueous system, H_2O is the ever-present acceptor.
- For example, during the dissociation of an acid in the soil solution, H_3O^+ will be one of the dissociation products and the acid strength of the H acid relative to H_3O^+ will be a measurable parameter.
- In a dilute solution, the activity of the hydrated protons equals that of H_3O^+ and the pH value characterizes the H-ion activity.
- Under these conditions, substituting for pH gives:

$$pH - pK_A = \log\frac{[Base]}{[Acid]}$$

Now, we have seen that for a complex of 2 acids and 2 bases, the corresponding equilibrium is this one in our previous slide, so we have already seen this is basically the ratio for this complex reaction. Now, remember that the soil solution being an aqueous system H2O or water is the ever present acceptor. Now, for example during the dissociation of an acid in the solution, these H3O plus or hydronium will be one of the dissociation products.

And the acid strengths of this H acid relative to this hydronium ion will be a measurable parameter, so in a dilute solution the activity of this hydrated proton equal to this H3O plus and the pH value characterizes the hydrogen ion activity. Now, under these all conditions, if we consider this condition, so if you want to establish a relationship between pKA and pH then we can establish this relationship that pH minus pKA equal to log of activity of base over activity of acid. So, this is a universal relationship okay, pH minus pKA equal to log of base activity by acidic activity.

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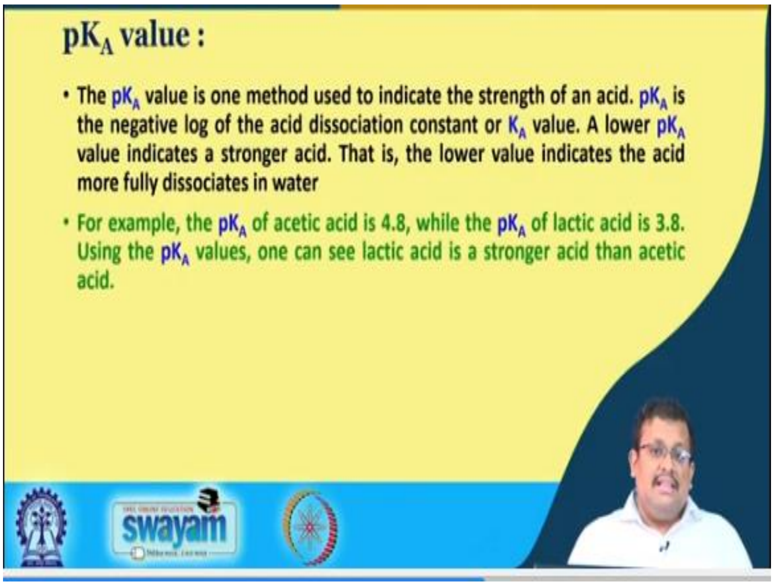

pK_A value :

- The pK_A value is one method used to indicate the strength of an acid. pK_A is the negative log of the acid dissociation constant or K_A value. A lower pK_A value indicates a stronger acid. That is, the lower value indicates the acid more fully dissociates in water
- For example, the pK_A of acetic acid is 4.8, while the pK_A of lactic acid is 3.8. Using the pK_A values, one can see lactic acid is a stronger acid than acetic acid.

Now, you may ask okay sir, what is the pKA value, now what to define a pKA value, this is a, this you know pKA value is one method which is used to indicate the strength of an acid. Remember that this pKA is the negative log of the acid dissociation constant or KA value, so if you consider the acid dissociation constant KA, then the negative logarithm of this acid dissociation constant or KA is basically the pKA value.

Now, a lower pKA value indicates a stronger acid that is a lower value indicates the acid is more fully dissociates in water, again this KA stands for the dissociation constant of an acid and pKA is basically the negative logarithm of this KA value. So, obviously a lower pKA value means a stronger acid that means, more dissociation that is the lower value indicates the acid is fully dissociates in water.

For example, the pKA of acetic acid is 4.8, well the pKA of lactic acid is 3.8, so using the pKA values one can see that lactic acid is stronger acid than that of acetic acid, since the pKA value of lactic acid is less than that pKA value of acetic acid that means, lactic acid is more strongly dissociates in water as compared to the acetic acid and that is why lactic acid is stronger acid than that of acetic acid.

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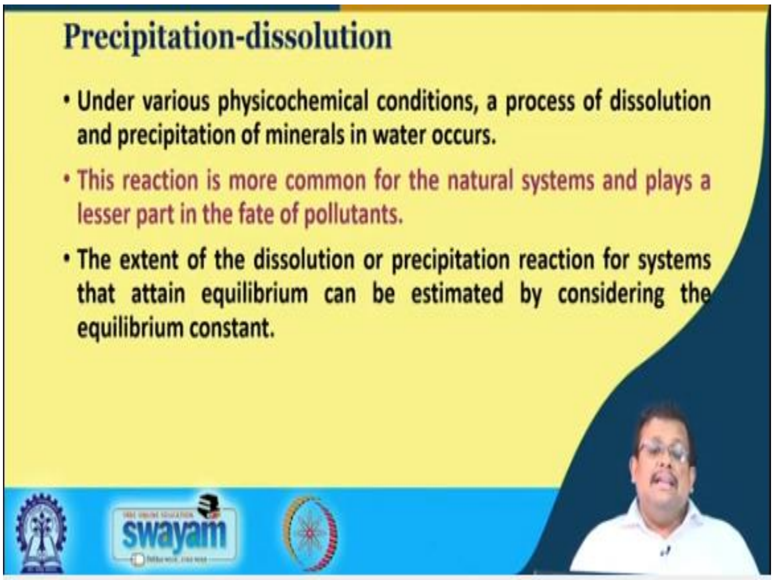

Precipitation-dissolution

- Under various physicochemical conditions, a process of dissolution and precipitation of minerals in water occurs.
- This reaction is more common for the natural systems and plays a lesser part in the fate of pollutants.
- The extent of the dissolution or precipitation reaction for systems that attain equilibrium can be estimated by considering the equilibrium constant.

So, we have covered the acid base equilibrium; next let us talk about the precipitation dissolution mechanism. Now, under various physiochemical condition, a process of dissolution and precipitation of minerals in water occurs, it is a complex interplay between different physiochemical conditions. Now, this reaction is more common for the natural systems and plays a lesser part in the fate of the pollutants.

So, although this precipitation dissolution is more common in natural system however, it plays a lesser part in the fate of the pollutants now, the extent of the dissolution or precipitation reaction for system that at an equilibrium can be estimated by considering the equilibrium constant. So, we have already seen, what is the equilibrium constant.

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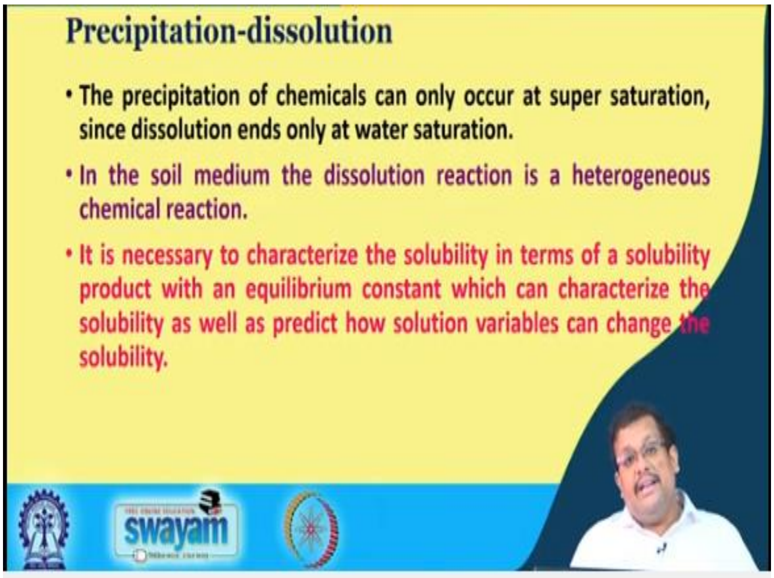

Precipitation-dissolution

- The precipitation of chemicals can only occur at super saturation, since dissolution ends only at water saturation.
- In the soil medium the dissolution reaction is a heterogeneous chemical reaction.
- It is necessary to characterize the solubility in terms of a solubility product with an equilibrium constant which can characterize the solubility as well as predict how solution variables can change the solubility.

Now, remember that the precipitation of chemical can only occur at super saturation, since dissolution ends only at water saturation. So, when there is a super saturation only in that condition there will be precipitation. Now, in the soil medium the dissolution reaction is a heterogeneous chemical reaction, so it is necessary to characterize the solubility in terms of a solubility product with an equilibrium constant which can characterize the solubility as well as predict how solution variables can change the solubility.

So, that is why there is a solubility product you know relationship or we have already discussed the solubility product relationship in our previous lecture, so I am not going to further you know discuss that in details.

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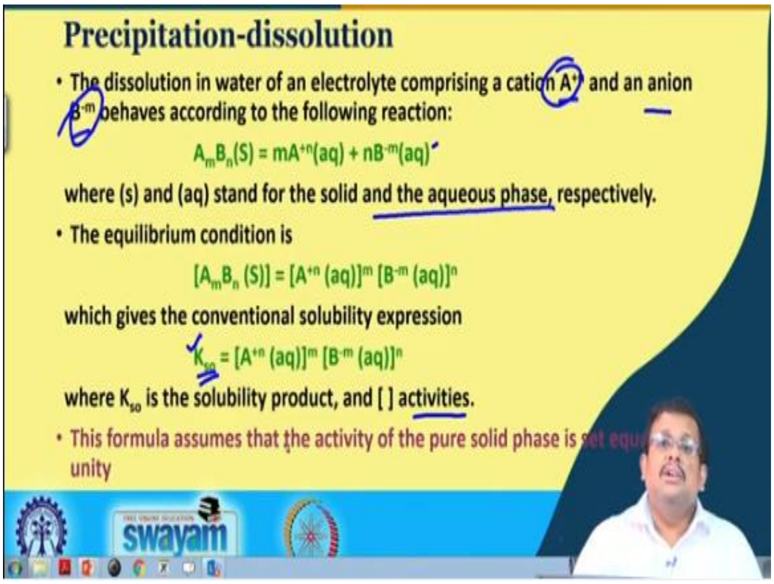

Precipitation-dissolution

- The dissolution in water of an electrolyte comprising a cation A^{+} and an anion B^{-m} behaves according to the following reaction:

$$A_mB_n(S) = mA^{+n}(aq) + nB^{-m}(aq)$$

where (s) and (aq) stand for the solid and the aqueous phase, respectively.

- The equilibrium condition is

$$[A_mB_n(S)] = [A^{+n}(aq)]^m [B^{-m}(aq)]^n$$

which gives the conventional solubility expression

$$K_{so} = [A^{+n}(aq)]^m [B^{-m}(aq)]^n$$

where K_{so} is the solubility product, and [ ] activities.

- This formula assumes that the activity of the pure solid phase is set equ unity

However, let us just consider the you know, when you know this condition, so when the dissolution in water of an electrolyte comprises a cation An+ and the anion Bm-, so this is basically the cation and this is basically the anion which behaves according to the following reaction. So, they behave according to the following reaction, where these Am Bn, S stands for the solid, then mA in aqueous form and nB in also aqueous form, where S and aq stands for the solid and aqueous phase respectively, we have already know that.

Now, the equilibrium condition is in this reaction the equilibrium condition is Am Bn S equal to the so the activity of these solid will be the multiplication of the activity of this a, you know A in aqueous phase multiplied by this activity of B in aqueous phase which gives the conventional solubility expression that is Kso which is basically the solubility product and these brackets basically shows the activities.

So, you can see the aqueous in the aqueous media, the activity of the cation when we multiply the activity of anion in the aqueous condition will get, will give us the solubility product constant. So, this formula assume that the activity of the pure solid phase is set equal to unity okay, so this is the you know expression of solubility product you know, when we are considering the you know electrolyte within cation A+, An + and anion Bm- and their dissolution in the aqueous phase.

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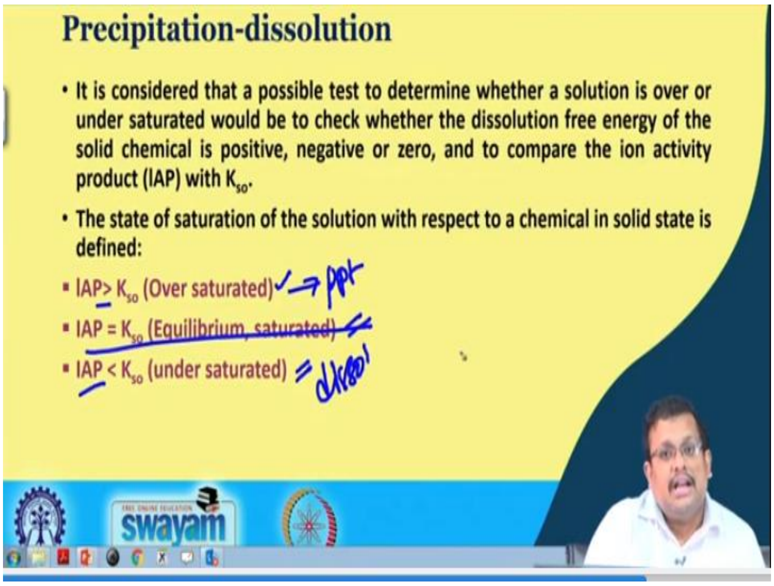

Precipitation-dissolution

- It is considered that a possible test to determine whether a solution is over or under saturated would be to check whether the dissolution free energy of the solid chemical is positive, negative or zero, and to compare the ion activity product (IAP) with K_{so}.
- The state of saturation of the solution with respect to a chemical in solid state is defined:
  - IAP> K_{so} (Over saturated) ✓ → ppt
  - IAP = K_{so} (Equilibrium, saturated)
  - IAP < K_{so} (under saturated) ⇒ dissol

So, it is considered that a possible test to determine whether a solution is over and under saturated, I told you that there will be precipitation only when there is over saturated or super saturation. So, how to you know predict where there will be super saturation or when there will be precipitation or not, so it is considered that a possible test to determine whether a solution is over or under saturated would be to check whether the dissolution free energy of the solid chemical is positive, negative or zero and to compare that ion activity product.

Now, we have already discussed this ion activity product although but I am going to repeat it here, so we have to basically consider these dissolution free energy of the solid chemical whether it is positive, negative or zero as compared to the ion activity product okay. So, we have to consider this, compare this ion activity product or IAP with this solubility product constant.

So, the state of saturation of the solution with respect to the chemical in solid state is defined when these ion activity product is greater than the solubility coefficient then or solubility product coefficient, then we consider it is an over saturated and when there is an oversaturated there will be precipitation okay and when the IAP will be equal to the solubility product constant, then it will be in equilibrium or saturated condition.

And when the IAP will be less than Kso, then that there is under saturated and then there is a possibility of dissolution, so you can see here the condition for precipitation and dissolution. In case of precipitation the you know, ionic activity product has to be greater than Kso and in case of dissolution, this IAP has to be less than Kso and when the IAP is equal to Kso, then we consider this is an equilibrium or in saturated condition. So, I hope that now it is clear.

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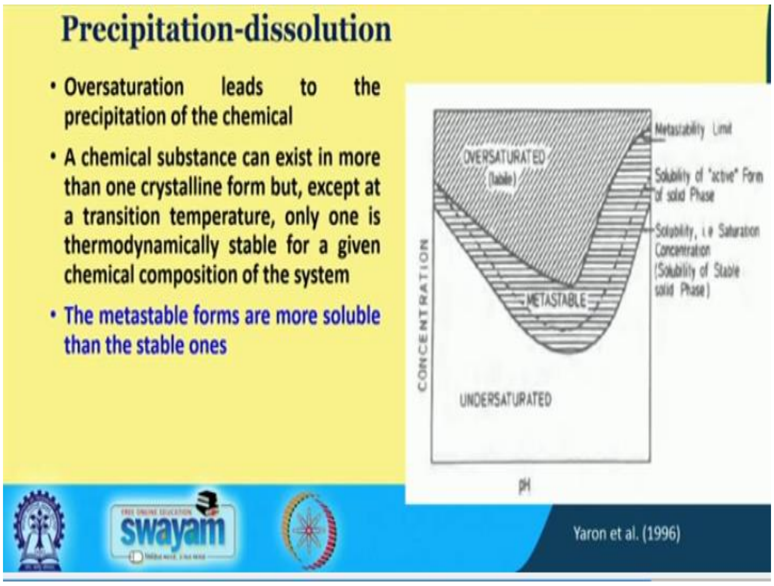

Precipitation-dissolution

- Oversaturation leads to the precipitation of the chemical
- A chemical substance can exist in more than one crystalline form but, except at a transition temperature, only one is thermodynamically stable for a given chemical composition of the system
- The metastable forms are more soluble than the stable ones

Yaron et al. (1996)

So, remember that over saturation leads to the precipitation of the chemical and a chemical substance can exist in more than one crystalline form but except at a transition temperature, only one you know thermodynamic stable for a given chemical composition of the system is possible. Remember that the metastable forms are more soluble than that of stable ones; again the chemical substance can exist in more than one crystalline form.

But at a transition temperature, only one is thermodynamically stable for a given chemical composition of the system okay and these metastable forms are more soluble than that of the stable forms. So, if you see the relationship between the concentration and pH as given Yaron et al. (1996). This relationship will be we can see this is the relationship between pH, concentration and which condition it will be over saturated or under saturated.

And in between these over saturated, under saturated, we can see the meta stability limit and metastable conditions okay, so this diagram basically shows that which the relationship between pH and the concentration and how they can you know manifest themselves in an oversaturated condition as well as how they can be under saturated and what is the metastable limit inside.

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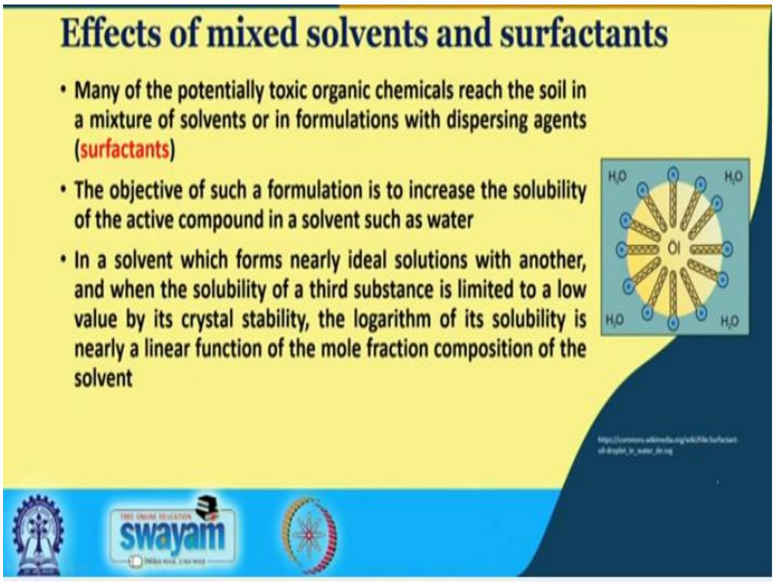

Effects of mixed solvents and surfactants

- Many of the potentially toxic organic chemicals reach the soil in a mixture of solvents or in formulations with dispersing agents (surfactants)
- The objective of such a formulation is to increase the solubility of the active compound in a solvent such as water
- In a solvent which forms nearly ideal solutions with another, and when the solubility of a third substance is limited to a low value by its crystal stability, the logarithm of its solubility is nearly a linear function of the mole fraction composition of the solvent

So, we have already covered the surfactants in our previous weeks, you know about the surfactants, now it is very important to understand the effects of mixed solvents and surfactants. Now, remember that many of the potentially toxic organic chemicals reach the soil in a mixture of solvents or in formulation with dispersing agents; in this case the dispersing agents are surfactants.

And this is a surfactant molecule as you can see it has both hydrophobic tail, hydrophobic side as well as hydrophilic sides. The hydrophobic tail is basically oriented, so that they can be directly in you know in contact with organic you know immiscible form, it may be liquid form, it may be solid form, so it is basically immiscible with water, hydrophobic phase and the hydrophilic ends are arranged towards the aqueous space.

So, there is a, you know specific you know, orientation which helps them to acts as a dispersing agent okay. Now, the objective of such formulation is to increase the solubility of an active compound in a solvent such as water and remember that in a solvent which forms nearly ideal solution with another and when the solubility of a third substance is limited to a low value by its crystal stability, the logarithm of its solubility is nearly a linear function of the mole fraction composition of the solvent.

Again, I am telling it is complex to understand, so in a solvent which forms nearly ideal solution with another, so let us consider there are 2 solvent which can form an ideal solution with another and when the solubility of a third substance is limited to a low value by its crystal stability, the logarithm of its solubility, if you plot the logarithm of its solubility is nearly, we will see a nearly linear function of the mole fraction composition of the solvent.

So, mole fraction composition of the mixture of the solvent, so we will discuss this in more details in our next class, I hope that in our, in this lecture we have gathered some information about the complex interaction between these heavy metals and their dynamics in the soil solution, you have gained some knowledge about acid base equilibria and we have briefly covered the precipitation dissolution and their preconditions also. So, we will talk in more details about these effects of mixed solvents and surfactants in our next lectures of week 9 or module 9, thank you very much.