Environmental Engineering: Chemical Processes
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Lecture – 42
Different stages in Precipitation, Equilibrium of precipitation - I

Hello everyone. So welcome back to our latest lecture session. So we were discussing, I believe, precipitation and dissolution and in the first session or relevant session, we looked at the applications initially and then, I believe, we moved on to looking at, I guess, why kinetics play an important role in this particular aspect of precipitation, right and then we moved on to looking at the 4 major aspects or stages, pardon me, that are involved with precipitation.

And again, there are, there is a particular reason why we are going to reach stage because later on, let us say, when you want to either promote precipitation or, let us say you know, hinder precipitation, you need to tinker with some of these stages, right. So again that is the reason we are going through these stages and the stages, I believe, we looked at were nucleation and what is it now the next step.

Obviously would be crystal growth and then agglomeration, more or less accumulation, right or coming together and then ripening, I guess. So we are done with or, you know, we started discussing about nucleation. So nucleation, nucleation, I guess, you have the solid being, what do we say, formed and more or less, they are at the nanoscale.

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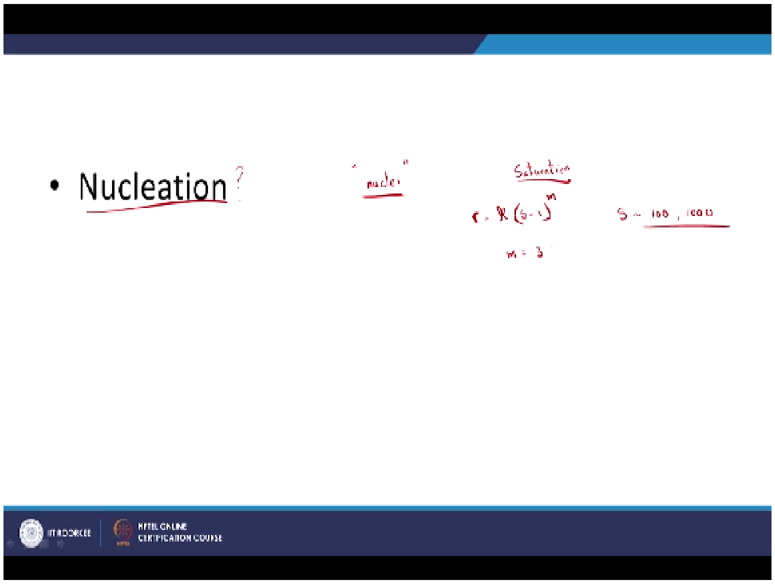

- Nucleation ?

"nuclei"

Saturation

$r = k(s-1)^m$

$m = 3$

$s \sim 100, 1000$

So I guess the smallest particle that you can call to be a solid and, I think, the term we are using in this context is nuclei, right. So the nuclei are formed obviously, right and then this is the terminology again, more or less nanoscale, right and then what is the aspect that we need to consider here, I guess, right. So just saturation is good enough? Saturation good enough for your nucleation to go through?

No. Again, why is that? I think that is because the rate of your nucleation=k*s-1 to the power of m, right. So just say if s is 2 or so, right, you know, even though it is saturated, you see the rates are going to be relatively less, right, are not good enough for your particular nucleation to go through now. Again, nucleation as in we are considering that there are no other solid phases present in the solution or suspended in the solution, right. So here it is from scratch and so obviously for that, what do you need?

You need supersaturated solutions so when s> around 100 or 1000 or so, right and again, I think, we talked about the order of m, I think 328 or 329, I guess right. So as you see, you know, once you have the supercritical saturation as well as in the order of around, you know, s is in the region of about 100 or 1000 let us say, then you are going to have more or less, what do we say, rapid nucleation going through, right. Again that is because m is relatively high. So I believe we have a relevant figure here.

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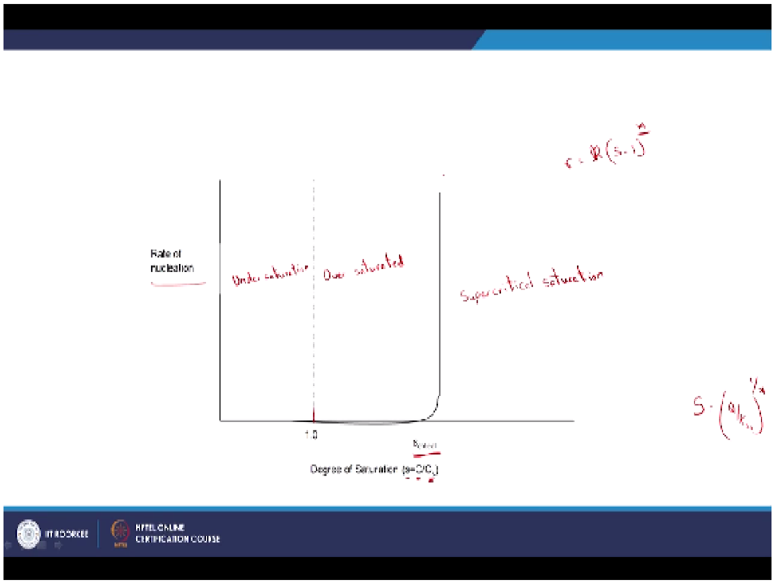

So here we have rate of nucleation, right and here is, what do we say, degree of saturation. C is the concentration of the relevant ions in solution and Cs is the saturated concentration of those particular ions let us say. So s here we are saying is the degree of saturation, right and also keep in mind, we looked at saturation ratio too earlier, right. I think that was equal to Q/kso, right, to the power of 1/x, right.

Again degree of saturation here, so obviously when is less than 1, what does it mean now? C is less than Cs, right. The current concentration of the relevant ions is less than their saturated values, right, you know. So it does, is going to be undersaturation. Yes, thus obviously will be solution is undersaturated. There is going to be no nucleation as such that is going to go through. So that is what you see here, you know, in this region.

You see that there is no nucleation here. So this particular dotted line is just to, for our particular understanding of where the s=1 lies, right. So you see that even when s>1 in this region where we say it is oversaturated, right, s>1 or C>Cs, right, then s>1, C>Cs but you still see that, you know, the solution does not favour or promote nucleation, you know. Again this is from particular graph I guess, right.

Still you see no nucleation here. But only when you are within the supercritical saturation zones or when you reach the supercritical, write s critical, let us say right and you see a rapid increase, more or less like a switch turning on or off, that is what we, you know, we are trying to understand, why is that again? Because the order rate or the R=ks-1 to the power m, the order is relatively high, so once the conditions are favourable, you know, it takes off, as in nucleation takes off, right.

So that is something that we looked at, yes. So obviously the next step would be, what do we say, now you have just these, what we are seeing, independent, what do we say, nanoscale solid particles, the smallest particle that we could call as what do we say now as solid, right. So next step obviously is the crystal growth, right. And let us look at that, right.

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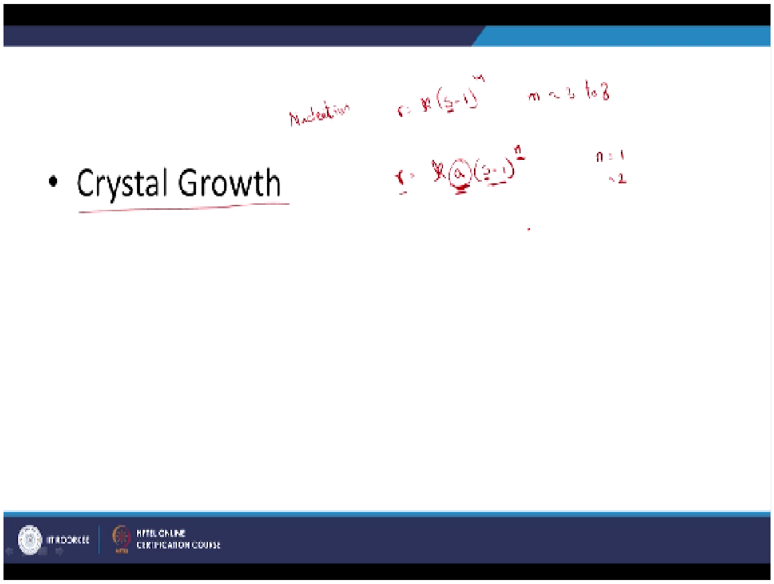

- Crystal Growth

Nucleation $r = k(s-1)^m$ $m \sim 3$ to 8

$r = k\,a\,(s-1)^n$ $n = 1$, ~ 2

So crystal growth, I guess, yes. So here let us say there are aspects involved. So obviously first, let us look at what is the rate of this particular crystal growth. r=k*a is the concentration of your surface area, let us say right, *s-1 to the power of n. n is usually 1 and sometimes also equal to 2, right. So here, you know, let us understand, you know, which aspects play an important role here, right.

So earlier if you remember that, you know, s, you know, with respect to nucleation, what was the equation r=k*s-1 to the power of m, m is around, let us say, 3-8, right. This is for nucleation. So here s plays an important role, right and why is that? Because the order of the relevant set of variables is relatively high. But here, the order is only either 1 or 2, right. So actually what plays a much more important role is the size of your particular particles here.

Here a is the surface area concentration needed, right. a is the surface area of concentration here and that is why as you see here again, the saturation ratio does have an affect but here we have an important new variable that is the surface area concentration here, right. So the greater the area available for your, of your particular solid, right, that would mean the greater will be rate of your crystal growth, right.

So if you want to promote precipitation at this stage, what can you do? You can either add a lot of your particular, what is it now compound or the solid? To increase, yes, but the effect will be relatively less because the order is 1 or 2, right or you know, obviously you can also try to add smaller size particles, right, which will have a greater surface area, yes or obviously even adding more solids will have net effect, you know, have net increase in the surface area.

So it is better off that you try to, what do we say, tinker with a rather than s but more or less, depending on relevant size of the particles, they obviously are interrelated, right. Again so if you want to promote crystal growth, you know, the surface area concentration, right, is an important aspect here, right. So again that is one aspect that we need to consider. So let us move on to the next aspect, I guess.

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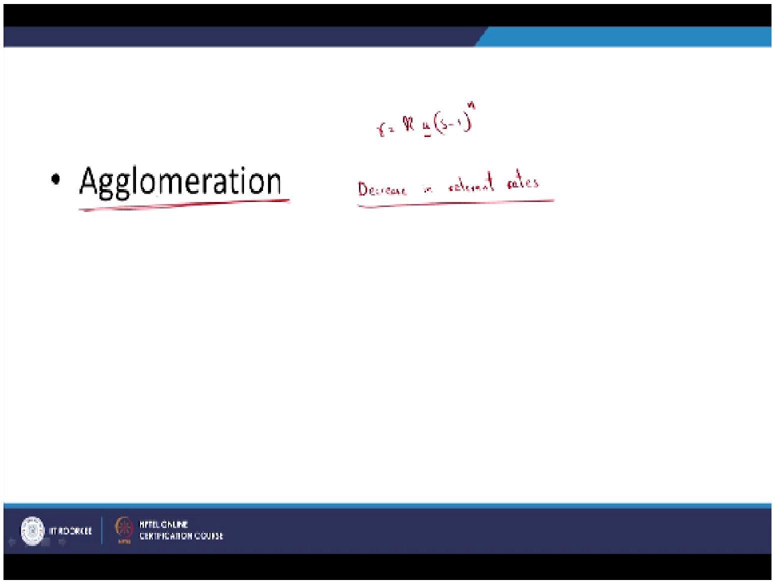

$r = k\,\underline{a}\,(s-1)^n$

- Agglomeration

Decrease in relevant rates

And then here the next stage in your particular precipitation after nucleation and then crystal growth is now going to be agglomeration as you know accumulation or, you know, the solids come in together now, right. So here what is it that meets now, how? What is it, how is it going to affect your particular precipitation? So keep in mind that the relevant equation is still the same, you know.

What is it now? r=, r=kas-1 to the power of n, right and now let us say as the size of the particles keep increasing, right, a keeps decreasing, right. The surface area concentration keeps decreasing now. So in effect what does agglomeration or the stage of agglomeration leads to? It leads to a decrease in the relevant rates, right. Because the size of the particles increases and as you see size increases, right, the surface area concentration decreases in your particular solution, yes. So obviously that is one particular affect of agglomeration, yes. So let us move on to the last stage.

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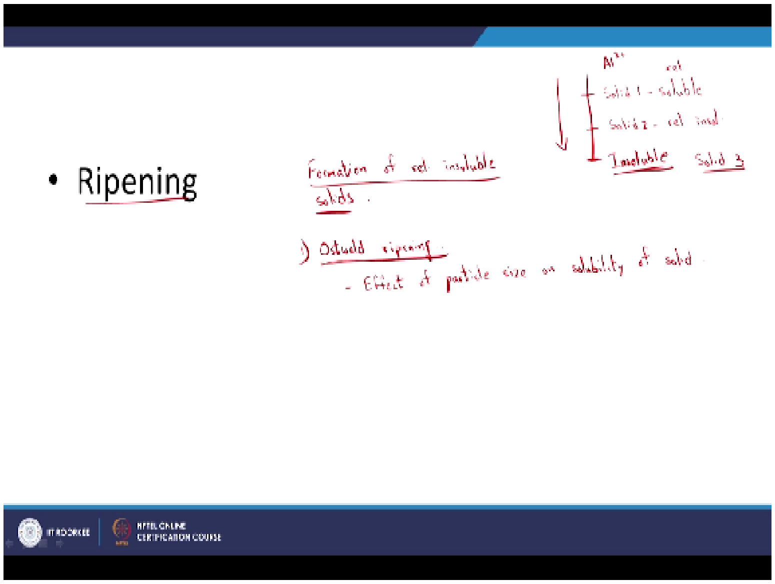

- Ripening

Formation of rel. insoluble solids.

Al^{3+}

Solid 1 - soluble

Solid 2 - rel insol.

Insoluble Solid 3

1) Ostwald ripening

- Effect of particle size on solubility of solid.

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It is ripening, I guess, you know, you do have the natural colouring of fruit turning ripe, right. So in the same case, I guess, that is what, that is how I tend to understand this particular stage anyway. So ripening here, it more or less means you have formation of, and just keep in mind is the last stage, right and if you remember, I think, the example for Al3+ or something like that, right.

It falls down the ladder different solids. So the last stage would be the most insoluble form of your solid, right. So we know that, you know, this is how the precipitation or the kind of solid changes. So the last form, let us say, this is solid form 1 which will be relatively soluble, right, relatively soluble and solid 2, let us say, which is relatively insoluble and then solid 3, I mean assuming that there are 3 solid phases that Al3+ can precipitate in the form of, right.

So here solid 1 is more soluble and that is why it is going to be formed first then solid 2 which is relatively insoluble and then solid 3, you know, which is the most insoluble of the 3 solids, right. So again, keep in mind that this is the order in general obviously that it proceeds, right. So your most soluble solid obviously will be formed first, right. So that is what it means here. The most soluble solid would form first, right.

Again, so here what is it now? We have the formation of relatively insoluble, relatively insoluble, what do we say? Solid species I guess or solids, right. Formation of relatively insoluble solids, right. Transformation of the relevant solid into more insoluble forms that might be a better understanding guys. So transformation of the solids into relatively more insoluble forms, right.

So that is what we have here. There are 2 cases here. I think one is the Ostwald ripening, right as when your solid becomes more insoluble, more or less due to the increasing area or surface area or increase in the particle size, you know. So the effect of particle size here. That is more or less one particular case, right. We are going to look at the other case too.

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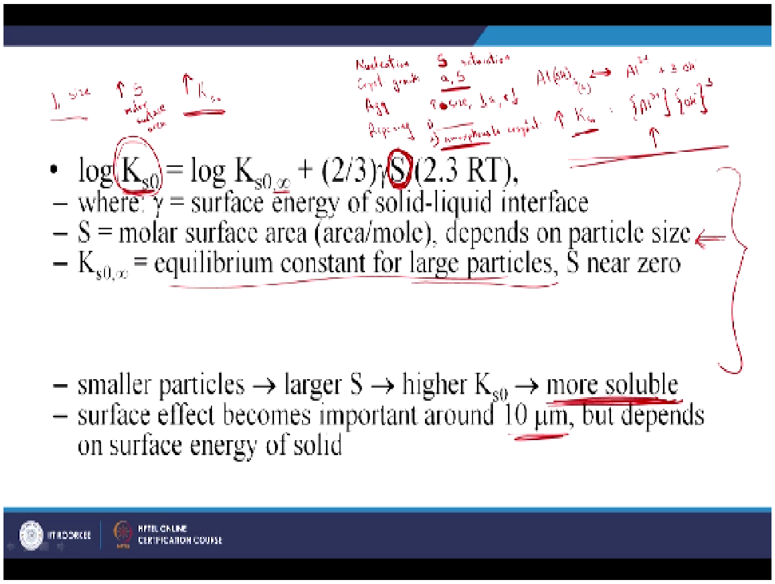

- $\log K_{s0} = \log K_{s0,\infty} + (2/3)\gamma S/(2.3\ RT)$,
  - where: γ = surface energy of solid-liquid interface
  - S = molar surface area (area/mole), depends on particle size
  - $K_{s0,\infty}$ = equilibrium constant for large particles, S near zero
  - smaller particles → larger S → higher K_{s0} → more soluble
  - surface effect becomes important around 10 µm, but depends on surface energy of solid

But before we move on, we have relevant equation here. So here we have the solubility constant of, let us say, the smaller particle, you know, kso, right. Let us just try to, we have a relevant equation here. Let us just try to understand this particular system here. So log kso, right and what is kso obviously? The solubility constant which I sometimes call the solubility product of the relevant smaller particles.

kso at infinity time at infinity means it is for large particles, right. So that is what it means kso at infinity the equilibrium constant for the larger particles, right. S is the molar surface area, area per mole, right. Again, here I have a new term here. This is not the saturation ratio keep that in mind please, you know, we have this as relevant variables. So molar surface area or area per mole, right.

So obviously that depends on the particle size, right. So the lesser the particle size, the greater will be s, right and that is what we need to understand here. So obviously here what can I understand here, right. What are the effects of s on kso now? So the smaller the particle size, right, the greater the value of s, right, the area per more. The smaller the particle size, the greater the available of the solid per more, right.

So here obviously the smaller the particle, the greater the s that more or less translates to a higher value of kso, right. So the smaller the particle size, the greater the value of this area per mole or molar surface area, right, molar surface area, right, so that more or less means, a higher value of kso, right. And what does higher value of kso more or less translate into now? So obviously kso, let us say, you know, let us say, for one particular example AlOH3 solid in equilibrium with Al3+ and 3OH-, right.

So obviously kso for this particular case, what is that now? Activity of Al3+*activity of OH- to the power of 3/activity of AlOH3 solid but as we know activity of a pure solid is 1, so that is why we are not going to have that here. So obviously here, let us just understand what we are up to? So the smaller the size of the particle, the greater the value of kso. So if kso is higher, right, what does that means?

The greater the concentration of the relevant, what do we say, cations or anions, right or in this case the metal Al3+. So again what does that means? Smaller size particles are relatively more soluble, right. So that is our particular understanding from here. I think we have a descent aspect here or graphic here. Smaller particles, larger s, right. That means higher kso which as we looked at in this particular example means it is more soluble, right.

Again small statistic as and when the surface area affect or, you know, the concentration becomes apparent, it becomes apparent, it seems around 10 micrometers, right. So that is one particular aspect that, you know, you can keep in mind, I guess. So let us move on. Okay, let us just summarize, I guess, before moving on to the other aspects. So we looked at nucleation, right and we saw that this greatly depends on, what is this now?

This is the saturation ratio, saturation ratio s here, that is different from the s here in this particular equation and then we looked at, what is it please? Crystal growth, right. Crystal growth. So that depends both on, what is it now? The surface area concentration or more or less, let us say, I can even call it molar surface area in a way and also the saturation ratio, right, crystal growth and what happens in agglomeration now?

Due to increase in these, what is it now? Increase in particle size, a decreases, thus rate also decreases, that is what you see in agglomeration, right. And obviously the last aspect was ripening where we, I believe, I missed the second aspect which I am going to discuss now. One aspect is as the size increases, just what we saw now, I guess, right. So do we see now? The size increases, right, the solubility decreases, right know in this particular equation as such, what did we see?

When the size is lesser, the solubility is greater, right. So more or less what does that mean now? When the size increases, you know, you have more insoluble forms of the salt, right. So that is the Ostwald ripening. So the second case, when you have change in structure or the way your particular atoms or molecules are arranged, right. So in general, here I guess, let us say, an example will be transformation from amorphous to crystal growth, let us say.

So in general amorphous is more soluble and crystal growth is less soluble, right. So obviously crystal structures relatively more stable than compared to the amorphous, what do we say arrangement, let us say, right. So obviously what does that mean now? The less stable one is formed first as in amorphous form is formed first.

And later given enough time, it will transform into the crystal structure, right. So that is the second case of, what is it now? Ripening. One is due to the effect of particle size, the other is due to the transformation in the arrangement of your particular atoms or molecules here, right. And let us, with that let us move on.

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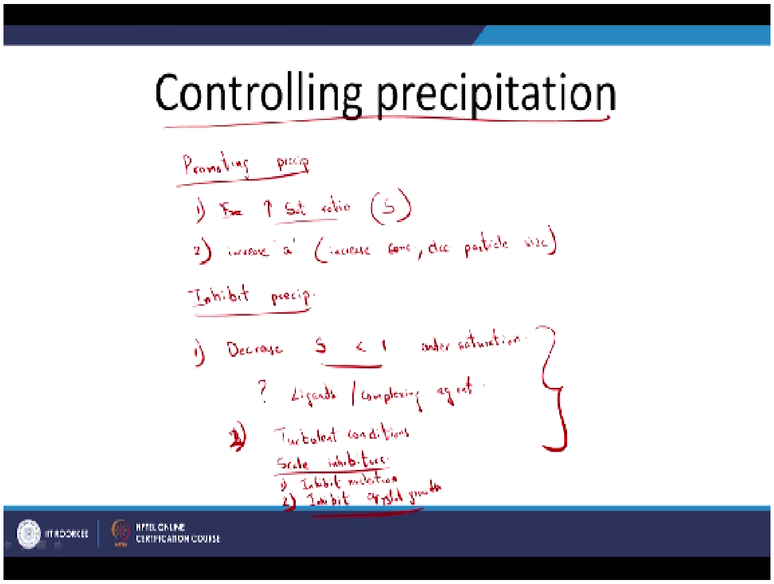

Controlling precipitation

Promoting precip

1) ~~Inc~~ ↑ Sat ratio (S)

2) increase 'a' (increase conc, dec particle size)

Inhibit precip.

1) Decrease $S < 1$ under saturation

? Ligands / complexing agent

2) Turbulent conditions

Scale inhibitors

1) Inhibit nucleation

2) Inhibit crystal growth

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So here one aspect is, how can I control the precipitation, right? How can I control the precipitation now? So obviously that is the reason I just listed the various aspects here. So here we have different aspects. Let us say we are talking about promoting, what do we say, precipitation let us see. Which is the case when you want to remove heavy metals or such and so on, let us say.

So how can you do that now? As we listed it in case of nucleation, what can you do? You need to increase, increase the value of the saturation ratio, right. So you can increase the effect of, what is this particular s, right, saturation ratio, increase in that. As we see in that nucleation, when s is in terms of 100 or 1000, you know, that is one particular case or even in your particular crystal growth, s-1 to the power of n.

So increasing saturation ratio is one aspect. So obviously another aspect is increase in a, right. What is this now? Surface area concentration, right and how can we look at this particular aspect? How can we improve this now? We can improve that by just increasing the concentration of your solids to, we will end up increasing the area available per mole, let us say, right or, or what else can you do?

By decreasing the particle size. Because as you know the smaller the size of the particle, you know, the greater the area available per unit volume, let us say, right. So that is one particular aspect. So how do you want to, you know, inhibit or decrease or slow down precipitation now, right? So let us say you have scaling and it will evaporate to cool intervals or in your on the surface or your membranes, right, or at the membranes and so on.

So how do you do that now? Again one aspect, right, how is, how can I go about that now? I can decrease s<1. What does this means? So only I can create undersaturation conditions, right. So how can I do that now? How can I, you know, make the, what is it now, or bring down the value of s, right? So for example keep in mind that let us say for our example, let us say, you know, we had Al3+ and OH-.

So how can you bring down the free metal concentration, right? So you can bring down a free metal concentration by how now? Adding a complexing agent, a ligand, right. So if you add a ligand, you know that the free metal concentration is going to be relatively less, right and then obviously the saturation ratio is going to be less than or, you know, decreasing. So depending upon how much of your complexing agent or ligand you add, the free metal concentration can decrease to less than 1 and that is 1 particular way.

So we can add, what do we say? Ligands or the relevant ligands anyway, right or the complexing agent, right, complexing agent and what else now? So the second aspect that you can look at is, obviously you need to have or we can create turbulent conditions, right. So at that particular case when you create turbulent conditions too, let us say at the surface of your membrane let us say, nanofiltration or ultrafiltration membranes, you can create turbulence, right.

So at that case through you are going to be able to decrease the value of the saturation ratio. So that is one particular aspect, right and that is with decreasing the saturation or, you know, creating undersaturation conditions to inhibit the precipitation and one particular case where we look at or, you know, we just looked at was scaling on the membranes. Obviously the second aspect is the scale inhibitor, I guess, right.

As when we can try to limit the 2 stages, let us say what is it now? We can try to inhibit nucleation, right, the initial step or trigger that is required or we can inhibit crystal growth, let us say, by adsorbing on to the surface or such, right. So again, there are different ways to either promote or what is it now, inhibit precipitation. So that is one particular reason why we looked at the force is to have a better or deeper understanding, right. So let us move on.

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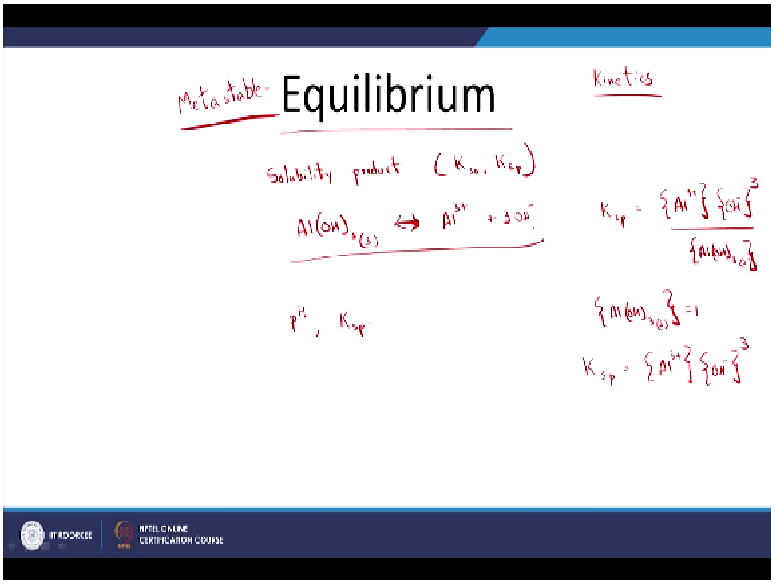

Metastable Equilibrium

Kinetics

Solubility product (K_{so}, K_{sp})

$Al(OH)_{3(s)} \leftrightarrow Al^{3+} + 3OH^-$

pH, K_{sp}

$K_{sp} = \frac{\{Al^{3+}\}\{OH^-\}^3}{\{Al(OH)_{3(s)}\}}$

$\{Al(OH)_{3(s)}\} = 1$

$K_{sp} = \{Al^{3+}\}\{OH^-\}^3$

So here, let us say, until now we have talked about the relevance of kinetics and precipitation and dissolution and we say that at least in precipitation, right, the relevant reactions are relatively slow. So in general first the most soluble form of the solid is formed first and then it is usually very slow process to reach the true equilibrium then the most insoluble form of the solid is formed, right.

Again, kinetics, we looked at the different stages and the relevant role of the kinetics as in the different rates at different stages, right. So now obviously let us say if the system reaches equilibrium or even the metastable equilibrium, right, either true equilibrium or the metastable equilibrium as in even when you have one controlling solid, how do I find the relevant concentrations of the relevant, what is it now, metals or such, let us see, right.

So how do I go about that now? So obviously, you know, I think, we talked about this solubility constant or which as I call it the solubility product. So we have this kso or ksp, right depending on, depending upon the type of source you look at, either kso or ksp. So what is it we talked about here? Let us say, you know, I have a solid here AlOH3 solid. So it is solubility product, right.

So it is more or less the dissolution reaction that we always write then we refer to kso or ksp. So that is going to be Al3+ +3OH-. So obviously ksp or kso will be equal to, what is it now? Al3+*OH- to the power of 3/the activity of AlOH3 the solid, right but activity of the solid is equal to 1, right. So that is why we end up with ksp=the activity of the products raise to their stoichiometric coefficients, right, again, you know, ksp, I guess, so that is what we have here.

So this is what, how would you go about, you know, understanding or solving for a system at equilibrium. You obviously need to have the knowledge about the relevant solubility constant or the solubility product, right. So again, let us say, given a particular system, let us say, aluminium or in this case, aluminium, let us say. Can you directly use this particular equation. For example, let us say, assume you have the pH, right.

Consider this case where we have the pH of the solution, let us say, right and let us say, you know the k solubility product for this particular equation now. So if someone asks you can you solve for Al3+, right, the free metal concentration, do you think, you are ready to solve for it? Not really, why is that? Because from our background, we know that the relevant reactions as an acid-base, may be not acid-base in this case, so aluminium will form complexes, right.

So all the complexation reactions are also obviously going to occur simultaneously and they are also going to reach equilibrium within or before the solid is formed, right. So at this equilibrium or the metastable equilibrium for a particular solid that we are considering, not only will you have the precipitation or the relevant dissolution, you will certainly have the complexation reactions too.

So you cannot directly just apply, okay I know the pH, so I know the OH-, I know the ksp and I can calculate Al3+, right. That is not how it is going to work? Why is that? Because Al3+ is also going to be in equilibrium with not just the solid, it is also going to be in equilibrium with the different complexes as in. So the Al3+, let us say, is not only going to be in equilibrium with your solid but at the same time, it is also going to be in equilibrium with your complexes, right.

So obviously you cannot just ignore, you know, one such of your particular, what do we say, species and just go ahead with the particular solution for the solid, right. So here try to understand what we have been doing until now? Initially we talked about acids and bases which more or less is, let us say, a foundation for our class other than the fundamentals obviously and then the next logical step was complexes.

And the next logical step is now solid or precipitation, right. So again all the 3 aspects, you know, occur in conjunction. So that is something you need to consider. Okay, so with equilibrium too, what are the conditions that I need to keep in mind, let us say, when I solve for precipitation, let us say.

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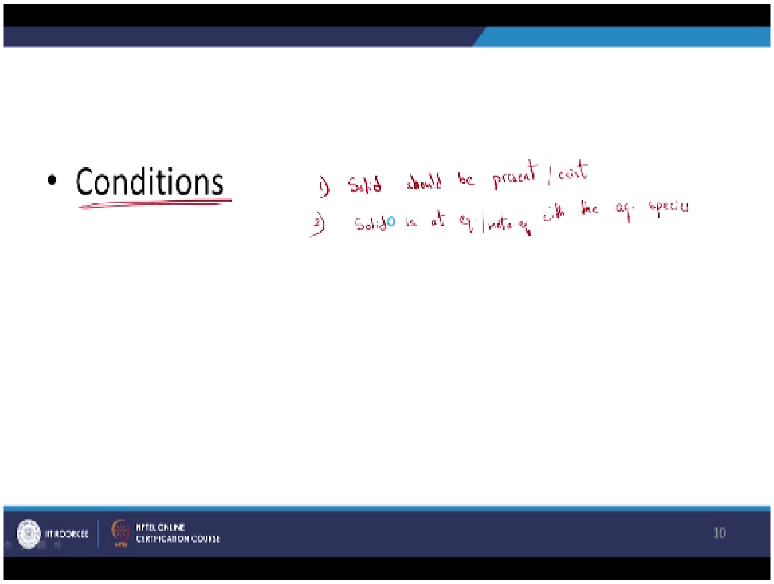

- Conditions

1) Solid should be present / exist

2) Solid is at eq. / inter eq with the aq. species

So obviously we are talking about precipitation. So what does that means? First aspect is that a solid needs to be present, right or it should be present or exist in the solution. So that is obviously one, what do we say, underlying phenomenon that you need to look for, right. When you are solving for equilibrium, you need to first check whether you have a solid that is precipitated out or not, right.

Otherwise, it makes no sense. So we are going to look at this particular aspect later on again and we will look at that, look at why it is important and obviously just having a solid is not good enough. So you should also be the case that the solid is at equilibrium, equilibrium, either equilibrium or metastable equilibrium, right with the aqueous species, right.

So first obviously one condition is that, what is it now? The solid should be present and then the solid should also be at equilibrium with your relevant species that are dissolved in the water, right. So those, these are 2 aspects that we should certainly consider now, right. So let us move on, I guess.

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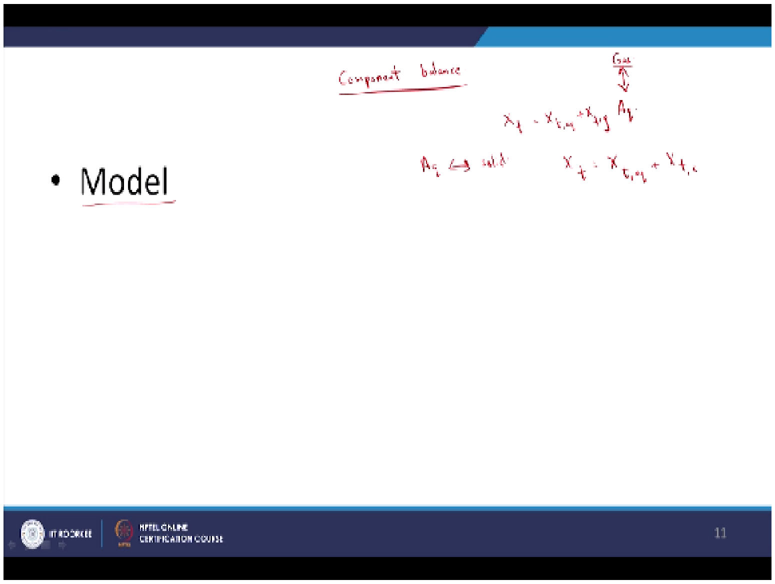

- Model

Component balance

Gas

$\updownarrow$

Aq.

$X_t = X_{t,aq} + X_{t,g}$

Aq $\leftrightarrow$ solid

$X_t = X_{t,aq} + X_{t,s}$

So Model, I guess. So in general until now, how have you solved for systems at equilibrium now? We came up with this conservative quantity. What is a conservative quantity, right, you know, that we looked at? That is the component. So we defined components and we solved for the relevant aspects, right. So in this case too, we are going to follow the same approach. What is that now?

The component balance approach, right. Yes. But here what is the key, I guess? Similar to when we had the gaseous phase and the liquid phase. So earlier if you keep in mind, you know, we had the aqueous phase and it was, you know, we solved for cases when it was in equilibrium with the gaseous phase, right. So we identified some components, right, X total, I think,=X total in the aqueous phase+X total in the gaseous phase, right.

So similarly here too we are going to have case where aqueous phase and the solid phase, they are at equilibrium, right. So the X total is now going to be X total in the aqueous phase+X total in the solid phase, right. So we are going to take this further but I guess it needs some more time which we are short of right now.

So we are going to go through with, you know, understanding how to solve for your particular system first by hand, you know, first you are going to understand the basics, right and then obviously we are going to look at the applications with respect to VMINTEQ, right and so I guess, with that I will be done for today's session and thank you.