Environmental Engineering: Chemical Processes
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Lecture – 41
Applications of Precipitation & Dissolution

Hello everyone. So again welcome back to latest lecture session and obviously we are going to continue from where we left off, that is with respect to the applications of precipitation and dissolution in which I tried to illustrate, I guess, with respect to at least coagulation and flocculation, the different roles that Fe3+ can play and Fe2+ can play, right and we discussed, I think, charge neutralization and the relevant effects as in why Fe2+ would be more effective there, right.

Because it is mostly in the soluble form and stays as Fe2+. So the net positive charge would be greater when you add Fe2+. So if charge neutralization is the relevant aspect that your mechanism for coagulation that you are looking for, so choosing Fe2+ might be a greater, better way to go about your coagulation or more efficient way obviously, but if you are looking with forming sweep floc or co-precipitation.

So obviously choosing Fe3+ is the much better option. Why is that? Because you know that at pH 7 obviously as you noticed that Fe2+ does not precipitate out, right which is essential for, I think, the sweep floc or the co-precipitation. So again what are some of the other aspects that you might look at?

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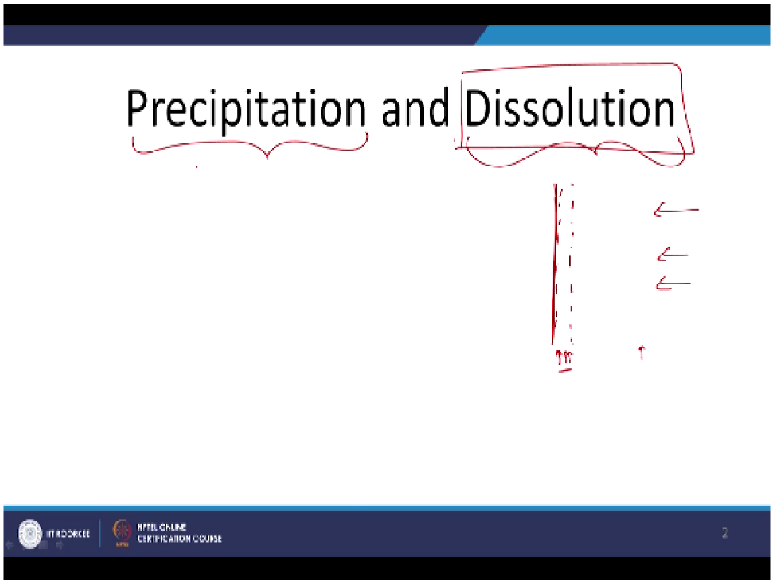

Precipitation and Dissolution

So one case we looked at until now were with respect to application of precipitation. So where do you think you might need to look at dissolution, let us say. So I guess the aspects would be that, let us say, you know, we have contaminated soil with some precipitate of the relevant heavy metal on it, right. Let us say the heavy metal precipitates out and it is contaminating the soil now, right.

It is not in the soluble phase. So in that case you want to either change the pH or effect the ligand concentration, right so that you make the compound more soluble and then you can either by washing or, you know, relevant techniques, you can remove that particular heavy metal from the soil, right, that is one particular case and obviously when you have what we say evaporative cooling towers, right, you have scaling formation.

And, let us say, you want to remove them, again that is one particular case where you would want to look at dissolution again, right. Overtime you have scales formed on this particular evaporative cooling towers that people look at in the thermal power plants, right. And again, let us say, in membranes, let us say, right, so you have scaling, not reversible, I guess. There are reasons why people call them irreversible or reversible scaling.

Irreversible as in under most chemical conditions, you cannot remove that particular scale or the solid as in what does that means? So that particular solid is remarkably insoluble. So, you know, even with change in the conditions with respect to pH or any other compounds that you add, you cannot make it soluble but reversible scaling, let us say, right, you can change the relevant parameters or chemical water quality parameters, let us say, or add different compounds to, you know, make the compound more soluble, right.

So again, membranes overtime, let us say, membranes we use them in, what do we say, physical process based removal of contaminants, right or particles, let us say. It is obviously depends upon the principle of size exclusion, right. Again, so thus at the surface of your particular membrane where concentration of the relevant compounds are very high, you can obviously, you will obviously have, what is it now?

Conditions that favour the precipitation. Let me just try to plug this in. Let us say, this is my membranes here, let us say. Anyway I will just use this and let us say, now this is the flow of the water, let us say, right. So obviously near this particular membrane, right, the concentration of the relevant compounds will be remarkably high compared to what they would be in the bulk solution, right.

So obviously if you have remarkably high concentration of the relevant, let us say, electron poor and electron rich compounds, you have favourable conditions for forming a precipitate, right. So but obviously that will lead to, what do we say, decrease in the efficiency of your filtration or, you know, the life of your membrane. So you need to remove that particular scaling from this particular surface of your membrane now, right.

So there you did look at the applications of dissolution, right. So again, so let us, we are done with, let us say, applications of precipitation and dissolution. I guess they are a good present, right. Let us move on from that. So now we are going to look on, look at the other aspect as in kinetics, I guess, right.

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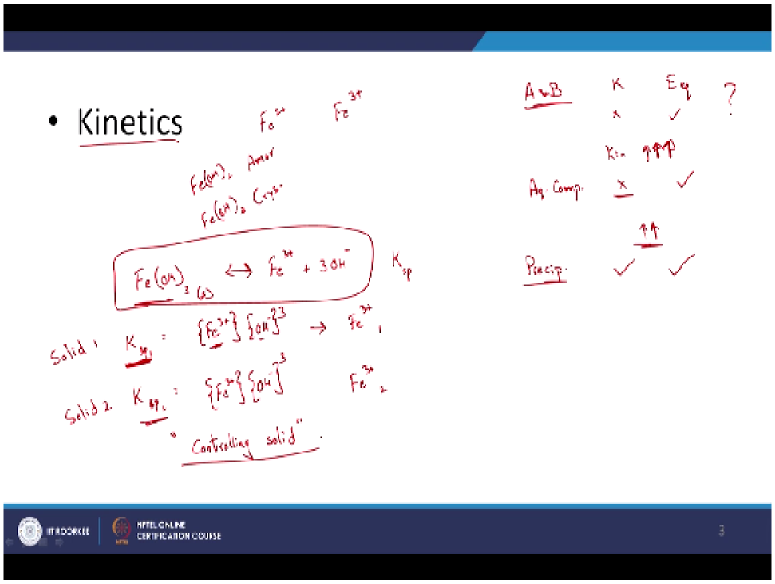

- Kinetics

Fe^{2+} Fe^{3+}

$Fe(OH)_3$ Amor

$Fe(OH)_3$ Cryst.

$\boxed{Fe(OH)_{3(s)} \leftrightarrow Fe^{3+} + 3OH^-}$ K_{sp}

Solid 1 $K_{sp_1} = \{Fe^{3+}\}\{OH^-\}^3 \rightarrow Fe^{3+}_1$

Solid 2 $K_{sp_2} = \{Fe^{3+}\}\{OH^-\}^3$ Fe^{3+}_2

"Controlling solid".

A+B K Eq ?

× ✓

Ki. ???

Aq. Comp. × ✓

↑↑

Precip. ✓ ✓

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So what have you been discussing with respect to each and every case thus far acids and bases? We discussed only equilibrium, right, and not kinetics. Why is that? Because the kinetics are very very fast in acids and bases and in aqueous complexes too, we mostly only consider, not mostly, we only consider equilibrium because again why is that? The kinetics are relatively fast, may be not as fast as the acid and base reactions but still they are fast enough.

The aqueous complex base relevant reactions such that most conditions in your practical scenarios, you end up reaching equilibrium, right. But with respect to precipitation though, right, that is not the case. The kinetics, they are slow or pretty slow depending on the type of compound that you look at and the type of solid that you are considering. So kinetics play remarkably important role in our particular precipitation related aspects.

So obviously we need to consider the relevant rates of this formation of the precipitate or the formation of the solid and so on. So we are going to spend some time with respect to kinetics in this particular precipitation related aspects and then look at obviously once equilibrium is reached, what are we going to look at. So obviously in precipitation we are going to discuss both precipitation and, kinetics and equilibrium.

Why is that? Again, kinetics are, is relatively slow with respect to the precipitation relevant reactions, right. Say again, now let us say, kinetics again, why is this important now right in this case? So first there are different stages before, you know, or not before, let us say, during the formation of the solid. So, let us say, if you want to promote precipitation, you know, you need to consider the rate at which all these stages proceed.

So that is something we are going to consider but that is later though. More importantly though, you need to also look at the type of solid that is being formed, let us say. If you remember that when we looked at the example in VMINTEQ let us see, with Fe2+ or Fe3+, right and we had to choose the type of solid phase that was feasible, we came across for Fe2+, I think, 2 forms, amorphous, right, I think of FeOH2 and also of the same molecular formula, crystalline, right and let us just to refresh our memory, let us go back there and look at VMINTEQ, I guess.

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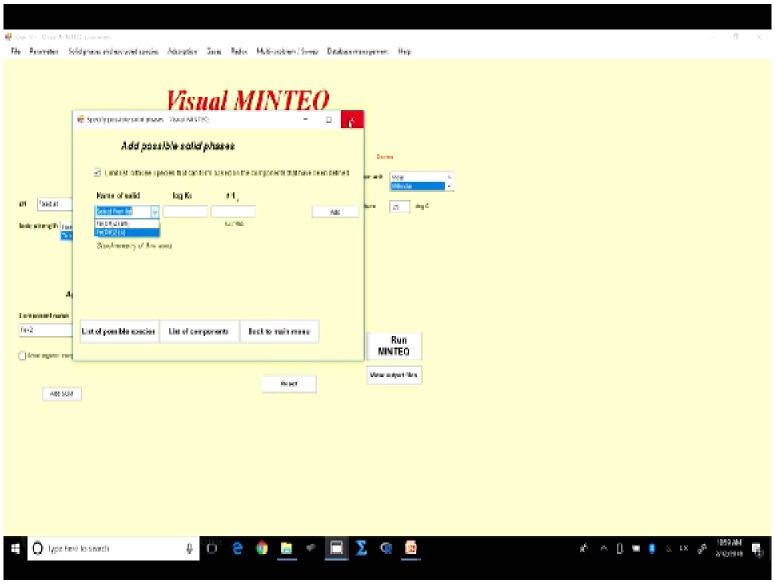

So let us say I choose Fe2+2, B C D F, add to the list and I am going to remove or delete Fe3+, right, back to main menu and I am just trying to point out to you what are the different salt phases possible and so I am limiting it to those species that can be formed only if Fe2+ is present. So here you see that 2 forms are feasible. What is that now? Amorphous and crystalline, right. So that is one particular aspect.

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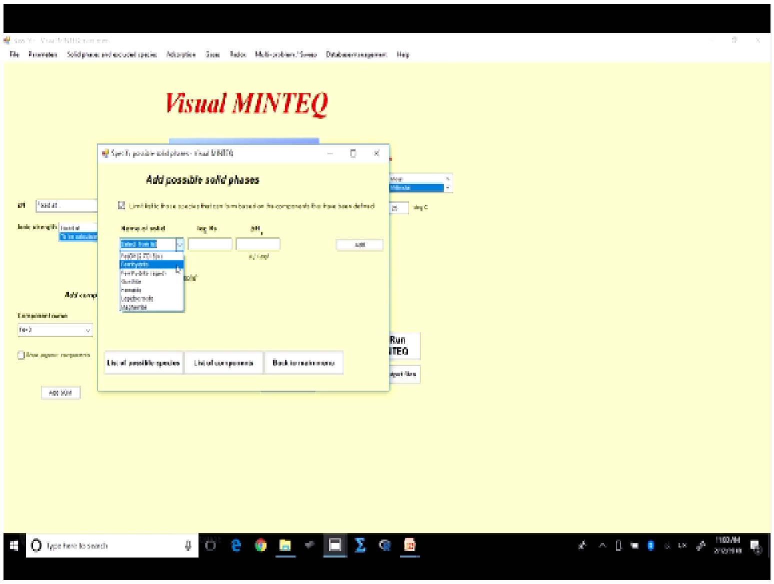

So keep that in mind please and now let us say if Fe3+ is considered. Fe3+, let us say, add to the list and I am going to delete Fe2+ now. Again what are we trying to do? We are trying to demonstrate what are the different possible solid phases. For Fe3+ though, we have different kinds of, types of solids present. Ferrihydrite, hydrite, again, there is something certainly with respect to amorphous and crystalline form and so on, right.

So why do I need to know what kind of solid is prevalent or predominant in my particular solution now? Because if you look at the relevant equation, right, what is the relevant equation here? So let us say I have FeOH3, right, as solid and the relevant Fe3+ and 3OH-, right. So again, the key is with the same molecular formula or slight variations, we can have different types of solid, right.

So the key is why do I need to look at this particular aspect now, right? Because for each different type of solid, I will have a different equilibrium constant. Now, let us say, K1 for 1 type of solid, K2 for solid type 2 and so on. So what is K1, or you know it is the solubility product here. So the precipitation dissolution reactions usually we write it in the form of the solvent, solid dissolving into the relevant cations and anions, keep that in mind and the relevant equilibrium constant, we call that the solubility product.

So Ksp1 and Ksp2, let us say, for solid 1 and solid 2, right. So here obviously, let us say, what is this going to be equal to? Activity of Fe3+ and activity of OH- cube by activity of the solid which is as you know activity of solid is 1, right and again, here again in the second case, Fe3+ and again OH- cube/activity of FeOH3, the relevant solid but again as we know activity of the pure solid, it is 1, right, the reference state, right.

So again, why is this important now? As you see, the relevant concentration of the metal or the ligand, right, that is going to be present in your solution is dependent upon the type of solid as in because Ksp1 is different from Ksp2. In this case, I will have 1 concentration of Fe3+ and here, I have a different concentration of Fe3+ right. So I need to know or identify what is the solid that is going to be present in my solution at this time that I am looking at it, right.

Because that will obviously control my particular metal concentration. So obviously what is it we try to need to identify? We always need to identify the controlling solid, right. So whenever we are looking at precipitations, so you need to ask the relevant, you know, person, so what is the possible solid or what is the solid that you expect would be the controlling solid. As in, there are many forms of solid, but only one would be the controlling solid and why is that?

Because based on knowledge from that controlling solid, you can get the knowledge with respect to the concentration of the relevant dissolved metals or ligands, right. So obviously you need to identify that particular controlling solid. So again, before we go further, how can we identify controlling solid? Now in general, let us say, as we know from our particular background with respect to your Gibbs energy or free Gibbs energy and such, right.

So in general, what is it that the system would drive towards or tend to move towards when the Gibbs energy of the mixture is minimum, right. Yes or if you are trying to look at it from delta G0 point of view when even delta G0 is relatively less, right. So we are going to, the system is going to move in such a way that the Gibbs energy of the mixture is going to be minimum. So in which case will that be minimum, right? So let us look at that.

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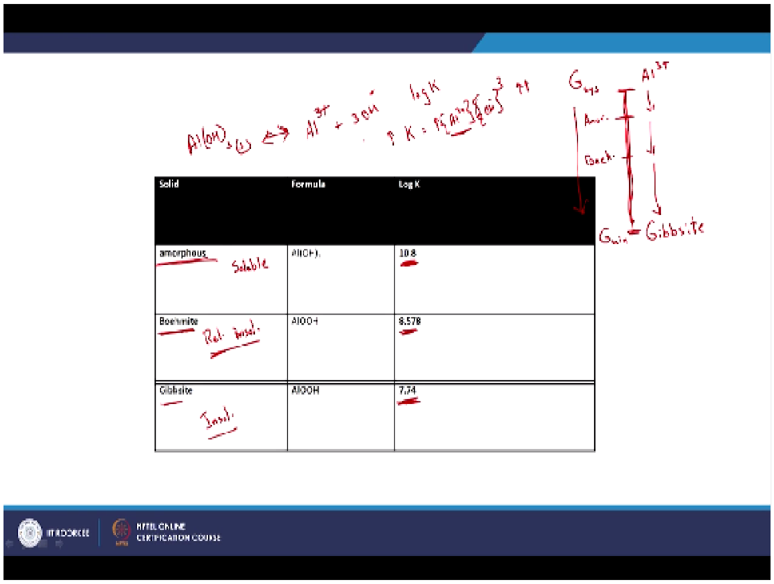

$Al(OH)_{3(s)} \leftrightarrow Al^{3+} + 3OH^-$ log K

↑ $K = [Al^{3+}][OH^-]^3$ ↑↑

Solid	Formula	Log K
amorphous Soluble	Al(OH)₃	10.8
Boehmite Rel. Insol.	AlOOH	8.578
Gibbsite Insol.	AlOOH	7.74

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So here I have an example, I guess, again with respect to the based on Al3+ precipitation out. So here we have different forms of Al3+, right. These are all solids, keep in mind. Okay, amorphous, Boehmite, Gibbsite of Al3+. So keep in mind that now again log K values are given here 10.8, 8.6 and 7.7, right. I think these are from VMINTEQ, yes. So what is it that this tells you about the system now?

So let us say if I add aluminium to a particular solution form looking at or observing and analysing the relevant K values or log K values, you can understand which is the solid that is going to precipitate out first. Obviously as we say now, let us see, initially let us say, Gibbs energy of the system when I added Al3+ is say relatively high, right and it wants to travel down the ladder, right.

It wants to reach equilibrium, right as in Gibbs energy of the system needs to keep falling now, right. So, let us say, this is the minimum Gibbs energy that is, of the system that is possible now, right. You know, this is just for your nomenclature. Initially we are here and this is the minimum feasible for that particular mixture. So where does the system want to travel? From here to here. But obviously there are different stages here.

So the first stage will be when in this case, obviously because we look at the log K value, that is higher, right. So initially you will come across the amorphous form, right and then you will come across the Boehmite form, right and then you will reach the Gibbsite form where looks like you are going to have the minimum Gibbs energy of your system, right. So initially, let us say, what is it that I am trying to help you visualize or understand?

Here I am putting in Al3+, let us say, right where we say in general the Gibbs energy of the system is relatively high. As in why does the compound want to precipitate out? Because, you know, every reaction, you know, wants to, you know, lead to such a system where the Gibbs energy of the mixture is relatively less, right. So obviously here, as you see, we are trying to move towards a more stable system.

So initially the system is not stable and as we are representing in this particular manner, right. So next it will move to the next feasible stable form which initially would be amorphous, right and then it would move on to the Boehmite and then to the Gibbsite, right and obviously you can look at that or understand that from the log K values. The log K is highest for your particular amorphous form.

What does that mean now? So in AlOH3 solid, and whenever we write log K values, this is, this is the equation we are talking about as in the solid precipitate dissolving into the relevant cations and anions, right, 3OH-, right. So what does this mean now, log K is relatively higher for this particular equation as in what does that mean? So as you know K=the activity of Al3+*the activity of OH- cube.

So the greater the K, what does that mean in effect for certain pH or, you know, fixed pH? It means the greater the concentration of Al3+, right. So from this again, you can understand that the amorphous form is soluble but this is relatively insoluble or relatively, okay insoluble, I will call that insoluble compared to amorphous, the Boehmite form, why is that? Log K value is less. So if log K value is less, what does that mean?

The Al3+ concentration in solution at equilibrium is also going to be relatively less compared to the amorphous form, right. I will try to do straight that in a better manner again. So compared to amorphous form, the Boehmite is relatively insoluble, again obviously with respect to Al3+ and again Gibbsite is the insoluble form or the most insoluble form and you can understand that from the lowest possible value for this particular aluminium relevant, what do we say, precipitates which is 7.7, right.

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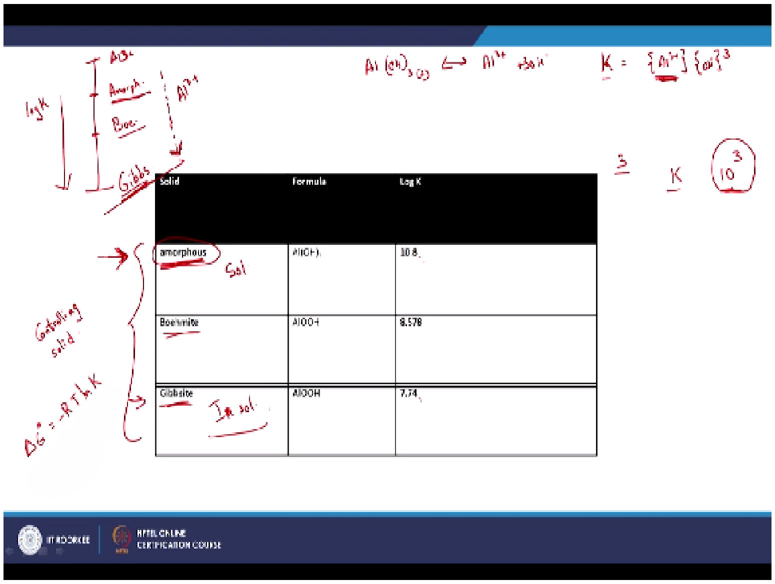

Solid	Formula	Log K
amorphous	Al(OH)3	10.8
Boehmite	AlOOH	8.578
Gibbsite	AlOOH	7.74

So again, let us try to plug this in somewhere here. So, let us say, you know, the relevant form for AlOH3 write solid and that can go to Al3+ +OH-, write 3OH-. So the log or K value=the activity of Al3+*OH- cube, right. So a higher K as in an amorphous form, what does that mean? It translates to a higher value of Al3+ that will be in solution with the solid, not solution pardon me, in equilibrium with the solid as in keep in mind.

Obviously you are also going to have some metal in the form of the dissolved phase and that is going to be in equilibrium with your solid here, right. So again what was the example we looked at? We came down the ladder, initially let us say, Al3+, right. The next possible form was the first solid that we formed, amorphous form that was the, amorphous form is formed first and next will form the relatively insoluble form of Al3+, that is Boehmite, right.

And next we will see the Gibbsite and obviously as you see, what is happening with respect to log K value too. That is decreasing, right. So again, as K keeps decreasing, you see that Al3+ concentration too keeps decreasing, yes. So what does that mean? That means when Gibbsite is the predominant or controlling solid, the Al3+ concentration would be the minimum compared to the other 2 cases, right.

So again, that is what we are trying to understand here and that is why you need to know the controlling solid. As in why is that? Let us say, you know, people think that Gibbsite is the controlling solid when actually amorphous form is the controlling solid. What will it lead to? See that the difference in log K values is 3 orders of magnitude, right or 3, I guess, 10.8 and 7.7 or 7.8.

So the difference in log K is 3, right. So as in K would be differing by 10 power 3, yes. So your aluminium concentration would be lower by 10 power 3 if you choose Gibbsite compared to if you choose amorphous, right. So if you incorrectly identified Gibbsite as your controlling solid, you would assume or from your calculations that, you know, the aluminium concentration is 10 power 3 times lower than what is actually present if, let us say, amorphous form is the controlling solid, right.

So that is what we can understand here. And obviously as you go down from this particular ladder, the Al3+ that is present in equilibrium with the solid, the solid in this case is amorphous, in this case Boehmite and Gibbsite, the Al3+ concentration too will obviously keep decreasing, right. So that is one particular case. So what is it that you can understand from here? The most soluble form of the solid will be formed first and the least soluble form of the solid will be formed last, right.

So the thermodynamically what is favoured now as in G of the mixture should be minimum or delta G should be also relatively less, right? Delta G0 anyway, not delta G, pardon me. As you remember delta G0, how can you get that equal to -RT natural log of the (()) (19:33) K. Again, so when is that particular aspect be favoured obviously again? Only when, what is this now? Log K values are lower, yes.

And that is what we observe here. So again what is it that we are trying to say again? Let us summarize here. So the controlling solid is important because that drives the concentration of the metal or the ligand that is going to be present in your solution, that is one aspect and secondly when we are looking at which forms first, the most soluble form would be formed first, right as in first amorphous form will be formed first.

Al3+ cannot directly jump to Boehmite. First it will form the amorphous, then it transforms into Boehmite and then it transforms into Gibbsite. So last would be the form that would be the most insoluble, right. So this is the most insoluble and this is the relatively more soluble, right. So first amorphous is formed and last Gibbsite is formed.

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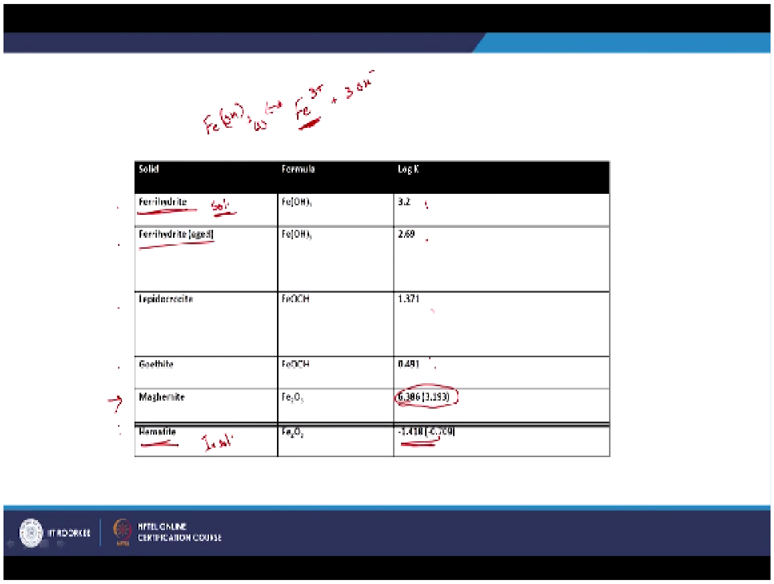

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+} + 3OH^-$

Solid	Formula	Log K
Ferrihydrite Sol	$Fe(OH)_3$	3.2
Ferrihydrite (aged)	$Fe(OH)_3$	2.69
Lepidocrocite	FeOOH	1.371
Goethite	FeOOH	0.491
Maghemite	Fe_2O_3	6.386 (3.193)
Hematite Insol	Fe_2O_3	-1.418 (-0.709)

Let us just try to understand that here. So, I guess, with respect to Fe3+, right and we have different forms, one is ferrihydrite, ferrihydrite aged and Goethite and ending up with Hematite, right. So here from our background, what is it, which form will be formed first now? I need to look at the log K values, right. So this is, okay, again 6.386 is and 3.193, I guess the different conditions.

So -4 if I neglect this, let us say for now. So I see that it is in a decreasing order, right. The log K is in decreasing order. So what is it that we know? Ferrihydrite is the more soluble form of the solid. Why do I call that the more soluble form? Because FeOH3 the solid is in equilibrium with Fe3+ and 3OH-, right. The greater the log K value, the greater the Fe3+ concentration that is in equilibrium with the particular solid, right.

And the lower the log K value, obviously the Fe3+ concentration in equilibrium with the solid is going to be lower and lower. So that is why I call ferrihydrite the relatively more soluble form and hematite the most insoluble form, right. Why is that again? As you see the log K value is remarkably low, right. So obviously what can you understand now? First ferrihydrite will be formed and then ferrihydrite the aged form is going to be formed and then Lepidocrocite I guess, Goethite and then Hematite, right.

So it is going to go in those stages and obviously again I need to identify which particular solid is the controlling solid. Why is that again? Only from that can I know what is the log K value and depending on that, I can understand what the particular Fe3+ concentration is, right. So that is something that we can look at here, let us see, okay.

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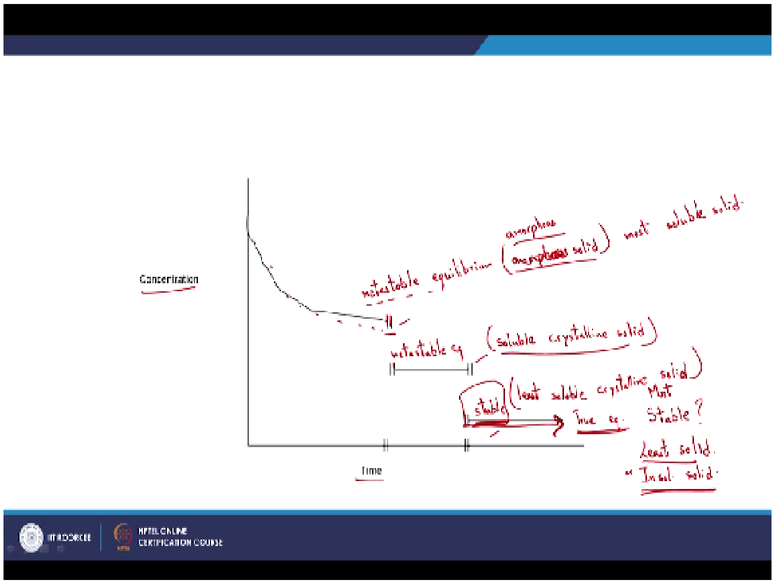

So let us look at what it is that we are trying to represent here. Here we have a graph with concentration and time. So this is the concentration of, let us say, your particular, what do we say, metal, let us say and so that is keeping on decreasing, right. So, let us say, this is the true equilibrium, right. This is the true equilibrium and at the true equilibrium, what is going to be formed?

The most stable form, the most stable form and what is the most stable form? It is the least soluble or the insoluble solid, right, insoluble solid. So at the, when the true equilibrium is reached, what is it that we have? We have the most insoluble or the least soluble form, solid, pardon me. This is the solid, right. So here it is truly stable and as in one example is that, it will be the least soluble crystalline solid, right.

So what will be formed first here? We have 2 different kinds of equilibriums here. One would be the metastable equilibrium, I guess, right. So for practical cases, it might look like we reached equilibrium but that is not the true equilibrium. The changes are so infinitesimal or relatively small that it appears as if you reached equilibrium. So I am going to call that the metastable equilibrium, equilibrium.

So first stage, what am I going to form? As we looked at earlier, we are going to form the amorphous form of the solid, right, where the solid has p h o u s, right, amorphous form of the solid, right. So this obviously is the most soluble solid, right and next stage, what would that be again? This is again metastable equilibrium and here I am going to have a crystalline solid but it is going to be a soluble form of the crystalline solid.

So obviously initially we have the amorphous type of the solid being formed, right. As in the structure, there is no particular structure, right and later on, you are going to have the most stable forms, right. More stable form, obviously are the crystalline forms, right where, I believe, you can have or, you know, the x-ray diffraction patterns are visible. So anyway, crystalline forms, you have what do we say, I guess, repeatable structure or a certain kind of structure, right.

So amorphous, you do not see that there though. So initially you will have the amorphous form which is the more soluble, right but is it the most stable form? No, not really. So the next stage would be the soluble crystalline form and the last stage would be the most insoluble or least soluble crystalline form and that is what we are looking at here, right. So obviously the concentration of the relevant metal keeps on decreasing, right and initially, the metastable equilibrium with respect to the amorphous solid and then again, the next stage.

So this is with respect to lapse in time, right. This is what the nomenclature means. So after again considerable amount of time, after passage of considerable time, you are going to have the next stage of metastable equilibrium which is the soluble crystalline form but at time equal to not infinity, I guess, considerable time that is when you are going to have the true or truly stable form or the equilibrium form, right.

Or true equilibrium being reached and that is where it will be truly stable, right. So obviously you need to identify where you are at as in in the amorphous stage or soluble crystalline stage or such, right and why is that? Because you need to know the log K values, right. So let us move on to see where we are at.

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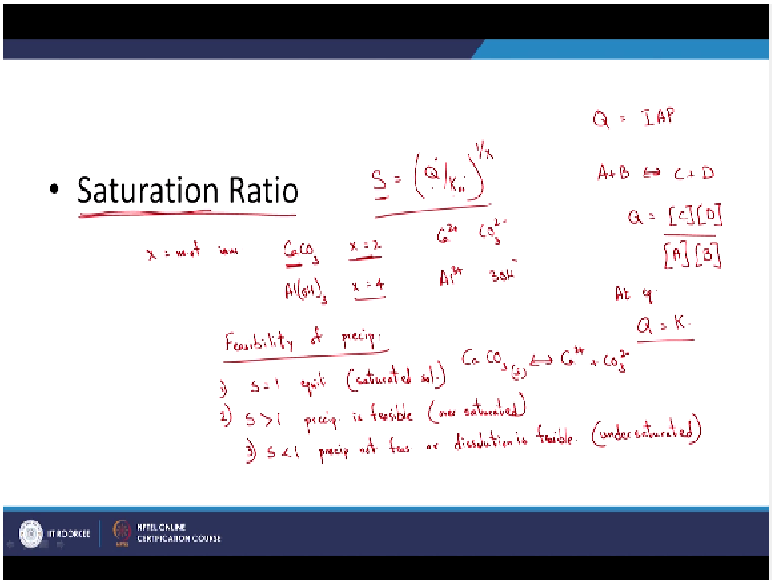

- Saturation Ratio

$S = \left(Q/K_{s}\right)^{1/x}$

x = no. of ions

$CaCO_3$ x = 2 Ca^{2+} CO_3^{2-}

$Al(OH)_3$ x = 4 Al^{3+} $3OH^-$

Feasibility of precip.

1) S = 1 equil. (saturated sol.) $CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-}$

2) S > 1 precip. is feasible (over saturated)

3) S < 1 precip not feas or dissolution is feasible. (undersaturated)

Q = IAP

$A + B \leftrightarrow C + D$

$Q = \frac{[C][D]}{[A][B]}$

At eq.

Q = K.

So obviously here I want to know when is the equilibrium, not equilibrium, pardon me, the precipitation going to go through and if it is going to go through, at what rate is it going to go through. So obviously in that case, we are going to look at or consider this particular variable called the saturation ratio. So I am going to call that S=Q/K solubility constant or solubility product, let us say, to the power of 1/x, right.

And Q, what is Q? You know that it is your ion activity product, right and that is something we discussed in great detail in your, in your, what is it now, equilibrium related aspects, right. Again, if A+B are in equilibrium with C+D, what is Q? Q is nothing but the concentration or in this case, I am approximating concentration to be equal to activity concentration of the products raise to the stoichiometric coefficient by the same case with respect to the reactants.

But obviously this is not at equilibrium. So if the system is at equilibrium, obviously what will that be equal to, Q will be equal to the equilibrium constant, right, anyway. Q is the activity product which we discussed earlier. I am just trying to refresh your memory because it has been quite some time. Anyway, so you can get these values too. But what is x? x is the number of ions, let us say.

As in for example CaCO3, right, the x=2 and for AlOH3, x=4 again, why is that? Ca2+ and CO3 2-, so 2 ions and Al3+ and 3OH-, so that is why 4 ions, so x=4 in this case and x=2 in this case. So you have different, what do we say, levels of S. So more or less what we are trying to do? We are trying to compare Q. Q is, it gives you an idea about or snapshot about the current picture with Kso, which is the picture at equilibrium, right.

So Q is the current picture, Kso is the picture at equilibrium and you are obviously trying to compare those aspects. So how can, how will that help me, I guess? It is going to define feasibility of my precipitation, right and how can I look at that in general, in vague terms. So when S=1, what does that mean? It is at equilibrium, right. When S=1, when is that? When Q=Kso, so that is when it is at equilibrium.

So for example for this particular case, when is the system at equilibrium? Let us say, CaCO3 solid, Ca2+ +CO3 2-, right. So when is it at equilibrium? When the solution is saturated, right. And the second case, when S>1, right. This is the case when precipitation is feasible, right. Consider this when Q>Kso, right and what is Q>Kso mean? It is oversaturated, right. And obviously the next case, when S<1 and the precipitation is not feasible or dissolution is feasible, I guess.

What does that mean? That Q<Kso, right and Q<Kso, what does that mean now? So Ca2+ and CO3 2- can, can dissolve as in the solid can transform into or dissolve into Ca2+ and CO3 2- and what does that mean? It means it is undersaturated, right. So again, you can have the saturation ratios depending upon calculating the Q value or the ion activity product, right.

So once you calculate that, you can know is it undersaturated or oversaturated and obviously if it is undersaturated, the solid moving to the or dissolving would be feasible and if it is oversaturated, obviously what is it now? The precipitation is going to be feasible, right. So let us look at what we are going to discuss next.

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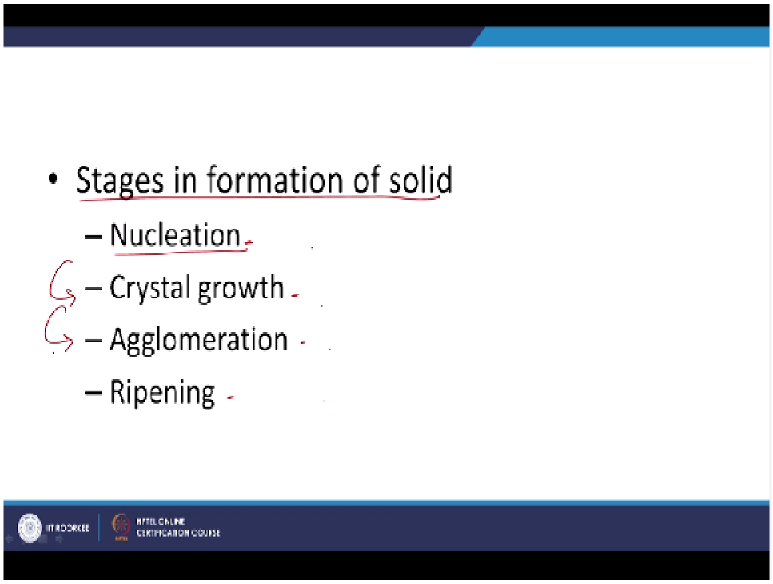

- Stages in formation of solid
  - Nucleation
  - Crystal growth
  - Agglomeration
  - Ripening

So earlier we talked about some aspects as in stages in formation of a solid, right. So a solid as in, you know, is not going to start with, let us say, just dump or increase the concentration of your relevant compounds. It does not mean you are going to immediately have or end up with particles of, you know, considerable size, let us say., As when I say considerable, it is all relative, right.

Initially it is not the size of the particle that are formed initially or not feasible probably to the naked eye unless they start agglomerating together again. We see those aspects here. So let us just briefly look at what are these aspects here. We have nucleation, right. So this is the process in which solid is formed from initially formed from only the soluble species, right. So again the process in which the solid initially formed from only the soluble species that is nucleation, right.

Crystal growth again that is self-explanatory. Agglomeration is in general when you have, what do we say, increase in particle size, right. Ripening is in when you have change in the type of solid to more insoluble phases, right, either due to the change in structure or due to the change in your particular, what is it now? Size of your particle. Again, we are going to discuss all these aspects in detail.

So initially for precipitation, you are going to have nucleation. The next step would be crystal growth, right. Growth of the crystal and then increase in particle size with agglomeration. You have agglomeration and then you have ripening, right. Ripening of your fruit again here guess it is not good colouring here, right but again ripening here, right. So let us look at each of these process in greater detail. I guess we only have time for nucleation.

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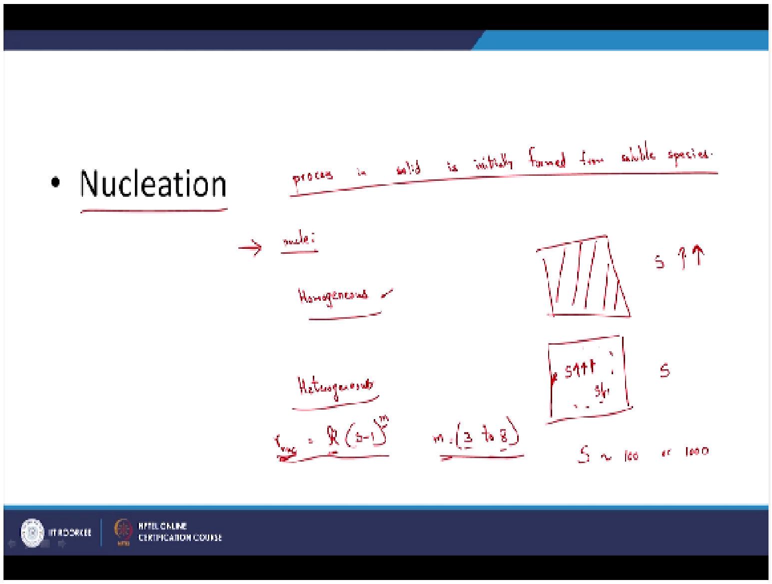

- Nucleation

process in solid is initially formed from soluble species.

→ nuclei

Homogeneous

Heterogeneous

$r_{nuc} = k(S-1)^{m}$ $m = (3 \text{ to } 8)$

S ↑↑

S

$S \sim 100$ or 1000

So let us just discuss that for now. And we are going to say, what is nucleation now? It is a process in which solid is initially formed, anyway obviously nucleation, it is the first step in your precipitation, right. So for the precipitation to go through, you first need to have nucleation, right. So obviously these nuclei as we are calling of the smallest possible forms of the solid, right.

Anyway, process in which the solid is initially formed from soluble species, right. Again as it says this is the initial step or the trigger that is required for precipitation to go through. Obviously what are the relevant conditions that are required now. You need oversaturation. So we are going to look at how do we quantify that or why we need oversaturation, I guess, we look at that again in a few moments, right.

Again, we initially need to have formation of this, the initial, the tiniest possible solids that we can call them before we call them as solid and they are called, let us say, nuclei in this case, right. So we call that step the nucleation, I guess and we need to form nuclei initially or we need to promote conditions such that you form these nuclei, I guess. So obviously what are the different kinds, I guess.

So here we have homogenous and we also have heterogeneous. So again think of this as in homogenous as in you have nucleation. Let us say, I have a beaker or let us say any control volume, let us say and I have the nucleation occurring throughout the particular, what is it now? Control volume at the same rates, let us say, right. So that usually does not occur. Why is that now?

Because for nucleation to occur, you need very high levels of saturation, right. So for your particular solution to be oversaturated over the entire control volume, you need to have a very high concentrations of your relevant, what do we say, cations and your anions, right. So that is usually not the case where it occurs. So in general, heterogeneous and that is what you see in nature, I guess.

Where is it that your particular precipitation occurs first, let us see? So you have heterogeneous systems, right and then you might have noticed it when you are boiling water or such, overtime where is it that you obviously observe more and more precipitation? On the sides specially or on the surface, where is that? Because that is where you end up having, let us say, your initial nuclei being formed.

Why is that again? Because you need a surface, right. For nuclei to be formed initially, we are going to look at that again, Gibbs energy change required or a delta G required for formation of the surface, let us say. Again, at the surface or those heterogeneous layers or zones where you have high saturated concentrations? As in let us say, this is my control volume. So for precipitation to occur throughout.

So throughout the control volume, I need S to be very high, right. But that is not always feasible. But, let us say, I have particular zones, let us say, let us say, cracks or such, right, where the S is high, let us say, right. So the precipitation can start in this particular zone, right where the saturation ratio is relatively high but not in the bulk solution where the saturation ratio is still relatively low, right.

So again difference between homogeneous and heterogeneous, I guess. So that obviously again depends upon how you want to promote precipitation if you want to look at. So the next stage obviously is the rate at which this nucleation occurs, right. Because that is the key again. If it takes too long, way too long, I know it is not feasible for me. So I need to look at, you know, how do I promote nucleation or such.

So I need to know what are the factors it depends upon. So here, I guess, the rate of nucleation is going to be equal to, let us say, a weight constant and S-1, S-1*m, I believe this is empirical and m can vary from 3 to 8, I believe, right, 3 to 8, yes. So what does this mean for you, let us say, for you or, you know, for a guy who is trying to promote precipitation now? So K, it is a constant, right.

R is the rate of nucleation. So we say that in this particular case for nucleation, the rate is K*S-1 to the power m but keep in mind that m is 3 to 8. So S is the saturation ratio, right. So when do we say precipitation was feasible? When S>1, right that is what I believe we discussed in this case, right. When S>1, precipitation is feasible or when it is oversaturated as in Q in Kso, right. But just because Q>Kso and S, let us say, is 1.5, let us say or 1.1.

So here it says 1.5-1*3 and such, does that lead to considerable rates of nucleation? No. So what it more or less translates too is for nucleation to occur, you initially need to have remarkably high concentrations of or you know remarkably oversaturated solutions, right. As in S needs to be around 100 or 1000, right and that is what you can observe from the equation too. For this particular rate of nucleation to be, to be relevant, I guess, right.

Otherwise, if it is just oversaturated or slightly oversaturated, you know, as you see the rates are going to be relatively less. But because m, right, is from 3 to 8, so it is like a trigger, I guess. Once you have a relevant high concentrations of the relevant compounds or, you know, when your solution is relatively very oversaturated, you know, because m is 3 to 8, you know the order is relatively high.

So once you create those conditions, the rate of nucleation is going to be very fast but to create that particular, what do we say, scenario, you need to obviously have very high concentrations of your relevant compounds for you to create high S values of 100 or 1000 or so on, right. So but once you reach that value, the rate is going to be remarkably fast.

Again, so with that I am going to end today's session and then we are going to talk about crystal growth and the relevant kinetics there and then, I believe, agglomeration and ripening and so on and then move on to the equilibrium models and so with that I am done for this session and thank you.