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Lecture – 46 Solubility and Competitive Precipitation

Hello everyone, so again welcome back to our latest lecture session, so until now, I guess we were discussing precipitation and dissolution and I believe in the last couple of sessions, we have been looking at applications, right and I think in the last session, we have been looking at the addition of quadrant in a form of FeCl3, right and how let us say, you know the relevant precipitation and the effects on sweep floc and also charge neutralisation go through, right.

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Let us just quickly have a brief about what we discussed, so we were adding a source of Fe3+ right and we saw that under when there is no alkalinity, right that the pH fell to 3.5, right upon addition of this source of Fe3+ and why is that; obviously, because the ferric hydroxide complexes form thus releasing H+, right so thus obviously would expect a drop in pH and that is why I believe we saw that the pH drop to 3.5, yes.

And I think we saw around 98% precipitation of the Fe3+, right and in the second case, we looked at a case where we had some alkalinity and also initial pH of 8.2 or 8.3 I think, right and then obviously, because you have alkalinity, what is alkalinity now, it is an acid neutralising

capacity, right so again in that particular system we had HCO3-, right and thus obviously, it can neutralise any protons or H+ release into the solution.

Thus, I believe you saw that after addition of this FeCl3, right, you did not see a great drop in the pH, I think the final ph was around 7.1 or something like that right, after addition of FeCl3 and we saw that it was still around 100%, what do we say, a precipitation of Fe3+ yes, right and this is what we understood that right, in general we know that the flocculation or coagulation goes through in 2 two mechanisms, right primarily anyway.

So, one would be charged neutralisation and the other one would be the sweep floc mechanism obviously, for the sweep floc mechanism, you need to have what do we say, the precipitate been form, which in this case the ferric hydroxide, right if you remember that we had the FeOH thrice solid being formed, right and thus will assist in the sweep floc, right but obviously there is no point in adding any further base, right that was a part of the question too.

Because adding for the base, we would only increase the net negative charge, right or decrease in net positive charge on the complexes if any and that obviously would not resistance charge neutralisation in any manner, so obviously you know as it is for this particular scenario of pH 7.1 where we had more or less 99% or 100% precipitation was good enough and we did not need to add any further base that was our particular logical reasoning in the last time, right.

So, let us say for now we are partly done with precipitation and obviously we are going to look at the other relevant aspect, which is solubility, right I guess you know that is self estimatory, right I think the process of the solid dissolving into what do we say, aqueous species that is what I believe we discussed in the initial class, right. So, obviously how am I going to measure solubility to?

It is the amount of solid that will dissolve, at the dissolves per unit volume of solution at specified conditions I guess, right, so again the amount of solid that would dissolve per unit volume of the solution, right or more or less the total amount of your particular what do we say

compound that would be in the solution, right, amount of solid that dissolves would more or less be equivalent to the total amount of your particular compound that will be in the solution, yes.

So, let us look at how to go about this now, so let us say by hand how am I; how are you going to about it, right, so here obviously you are going to start with the assumption that there is solid phase in equilibrium with your water as an let us just take an example let us say, let us say I have some precipitates here and this is my water here, so there is going to be equilibrium between the solid phase and the aqueous phase, right.

Now, I want to find out the concentration of the relevant compound let us say in the water or a aqueous phase that is going to be in equilibrium with my solid as in if the solid was CaCO3, right you know that it is going to be an equilibrium with Ca2+ and CO3 2-, right and so obviously what are we try to find out; we are trying to find out the concentration of this calcium but keep in mind that we, when we talk about what do we say, solubility, we are not just talking about let us say the free metal or such that.

We are talking about the total concentration as in when we talk about a solubility, we are talking about Ca total per unit volume or Ca total, right it is not just Ca2+, why is that because as you know there can be other complexes formed in such but we considered them to also be soluble species for example, in this case we can have calcium hydroxide complexes formed too but still that well add to the total calcium that is present in the aqueous phase, right.

So, whenever we calculate solubility, we do not calculate just let us say Ca2+ or such or the free metal, we calculate the total component, I guess, yes, so let us see how to do that by hand obviously, let us say you know in your component balance equation, you have a x total, right and let us say you have one other or specified variable usually pH right, for example the question; not question I guess.

This scenario would usually be, you have this salt present, let us say CaCO3 and let us say the pH is around 7, right, so what would be the total concentration of calcium present in the solution, so that is nothing but calculating the solubility, so again that is just setting up the balance

equations, so you can set it up x total or let us say in this case Ca total, right, as a function of H+, right, as a function of H+ and then just solve for it.

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Because you know the pH I guess, right so again that is relatively straightforward but I am; thus I am going to skip that but we look at how to get this done by VMINTEQ right, so let us move on to VMINTEQ, right and here I am going to specify the possibles infinite solid, so there are different aspects here as in as you can see you can specify in infinite solid phase or you can specify a finite solid phase, right.

Again, the key is that let us say if you have relatively little or very little solid phase, right, so it obviously will dissolve, right but we do not know if the equilibrium will be reached before the salt has completely dissolved, right or it has not reached equilibrium even after all the solid has dissolved, right. So, obviously let us say, you know we have only one gram per litre or a finite solid.

So that you can specify in the specify finite solid phases but let us say you are looking for an infinite solid as in there is an in exhaustible amount of your particular solid that is going to be in equilibrium with your solution, right, so you are going to use let us say specify infinite solid phases, right, again I am going to try to you know explain this in a better manner hopefully, so

when we talk about specify finite solid phase in which scenario would you look at let us say, when you have a limited amount of solid, right.

And why does that matter let us say, I have 1 gram and it is of relevant solid and that is in equilibrium with let us say 1 litre of a particular solution rather than 1 gram, let us choose 1 milligram, I guess, right, so let us say rather than 1 gram, I have 1 milligram of solid let us say and that will be in equilibrium with let us say 1 litre of water let us say, right. So, here let us say you did not know when the equilibrium will be reached.

Will the equilibrium be reach let us say after 0.25 milligrams as dissolved, right or 0.75 or let us say, when let us say, 1.5 milligram dissolves in the litre of the solution, right, so you do not know when the equilibrium will be reached, right or the amount of solid that needs to dissolve before the equilibrium is reached between the solid and the aqueous phase, right, so thus obviously, when you have limited amounts of solids present, you are going to have to specify that right in your particular VMINTEQ.

And obviously, if you have infinite solid, you are going to choose a relevant option there, so far one example we are going to choose let us say infinite solid phases, right and here I am going to choose calcite, right the source of CaCO3 and was that okay, here it is calcite, I am going to say add, right, back to main menu, second; what are we trying to set up; I am trying to set up the quotient in such a way that I have an infinite amount of calcite, right or source of CaCO3, the solid.

And that is going to be in equilibrium with my particular water, right and what is the final concentration or the total concentration of calcium that is going to be present in the water, so how do I do that obviously, I need to specify some pH, so let us say we will go with at neutral pH, right and let us just run VMINTEQ and obviously, you have you know calcium just the free, what do we say, compound, right, Ca2+ right.

And also the relevant complexes CaOH, right, CaHCO3+ and so on but this is not what I want, what do I need; I need the total component or Ca total and this is what I have 3.84 * 10 power -3,

so for this particular condition right, what is the solubility of this calcium here, it is 3.8×10 power -3, right and keep in mind that it is going to be different from your just Ca2+ the cation, right which is 3.7×10 power -3.

But obviously, considering the relevant complexes or such, the Ca total is going to be relatively higher and this is the solubility, right 3.84 * 10 power -3, so let us just try to increase the pH and see if that is going to cause any particular change here, right, we go with 9, right, okay and equilibrate mass distribution, so I think it decreased right, it actually decreased that is what you see here and that is what you see here too with increase in pH I guess that is what something we should have expected to, right.

So, here you see that the total solubility or the solubility of calcium decreased and it is not 3 * 10 power -4, here right and again obviously, the cation is going to be at relatively lower concentration, why is that, you have the relevant complexes taking of the share of this particular calcium, right, so let us go back to the main output menu, let us give it at lower pH let us say, at around 3.

So, let us find out the relevant solubility here, right and it should be obviously at relatively high concentration and here that is what we see here that the calcium concentration is at relatively high value, what is it now; 10 molar concentration I guess, right, so at pH 4, we had what is it now, we have concentration or pardon me solubility of calcium at 10 molar or 11 molar, right but at pH 7 and i think at pH 9, we saw that it was at 10 power -3 and 10 power -4 concentration ranges, right.

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So, let us just try to understand this for a second I guess, so let us try to understand why we see such a change obviously, so the relevant reaction is CaCO3, this solid that is going to be in equilibrium with Ca2+ and CO3 2-, right, so I think we looked at 3 cases; one was at pH 7, where the concentration was in the order of around 10 power -3 and pH 9, where the concentration was in the order of around 10 power -4 and pH what 4, I guess when the concentration were in the order of 10 power 1 I guess, right.

So, why this particular variation or why this particular increase in solubility, right, so more or less what do you see, as you decrease the pH, right or maybe i should have written this pH 9 here, right so as you decrease the pH, you see that the solubility is increasing, right, as you decrease the pH, you see that the solubility is increasing, right try to understand the system.

So, let us say at higher pH, let us say at pH 9, right, yes, so CO3 2- concentration as you know will be relatively high, right at pH 9 again, where is this from; from our acid base relevant background, right, so this is H2CO3, right and this is going to be HCO3- and this is going to be CO3 2-, right and we know that pK1 is 6.3, pK2 is 10.3, so as we are approaching let us say 9, let us say write somewhere around here, you know that CO3 2- is going to be present, right.

And also HCO3-, yes, so again at; what is it now, pH 9, this CO3 2- concentration is relatively high and at pH 7, right around here, you see that there is going to be no CO3 2- concentration, right, at pH 7 you see that there is no CO3 2- concentration, so I am going to say at pH 7, it is almost = 0 and same case with pH 4, it is = 0, right or you know if not almost you know slightly I guess, right.

But at pH 4, you know that CO3 2- is not going to exist in solution, so why is this important now, as this calcite dissolves and form Ca2+ and CO3 2-, right, yes, so when will the equilibrium be reached now, you are going to look to the saturation values, yes but if this CO3 2- concentration is high, right yes, what is that mean now, right the equilibrium will be reached earlier, right.

But let us say as in think of this now, if I increase this CO3 2- concentration, the reaction to towards the left would be favourable but if I decrease the concentration of CO3 2- which is what I would have observed at pH 7 and pH 4, right which reaction would be favourable now, the reaction going from left to the right or the dissolution reaction, make sense, hopefully right.

As I decrease the CO3 2- concentration right, I remember one of the products, so CaCO3 the calcite would want to dissolve, right or the dissolution reaction would be promoted but obviously, as I keep increasing one of the products as in CO3 2- or let us say Ca2+ but in this case obviously, we are looking at pH and the carbonate system here and that is why CO3 2- concentration.

So, as I keep increasing the product here, it would want to form the reactant here, right or the reverse reaction would be favourable, so that is why the calcium concentrations would be obviously less and that is what we see out here I guess, right, again so this is with respect to the solubility, so by hand to whenever you calculate, you need to calculate x total and not the relevant cation or anion that something that is important.

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Again, why is that you are talking about the solubility, right, the total solid that would dissolve or let us say that is going to be in the dissolved phase, the total solid let us say, right and okay, so we are done with this and we all move on to the next relevant aspects, so it is competitive precipitation aspect. So, until now obviously, we have looked at cases, right when we consider only one particular solid or one form of the solid.

So, with time we know that it can form more stabler forms, right I think, amorphous to crystalline and then remarkably insoluble crystalline phases and so on but more or less with respect to only one type of solid, right, so in general as we know because they are more stable or relatively more insoluble, the most insoluble forms would be form last, right I think we looked at this particular case, as we fall in down the ladder, right.

The most insoluble form will be formed last, the most soluble form would be formed first, usually more soluble forms what are they, the amorphous forms, right and unusually insoluble forms they are the different types of the crystalline structures, I guess, right, crystalline forms, yes and this is the way, it would go through and why would it try to be in the form of the most insoluble or the crystalline form.

Because that is the most stablest form, right and obviously, everything in nature tends to be at what do we say, or reach its more stabler state, yes, so but thus as you can remember, I guess we

looked at only one particular kinds of what do we say, solids, as an AlOH3 solid, then the amorphous crystalline or so on, right but here let us say you know, different what do we say metals can precipitate out in different forms now, right.

So, for example, you know you can have CaCO3 precipitate out and you can also have calcium precipitate out in the form of CaOH twice, right, so the key here is obviously, it is competitive precipitation, right but in general obviously, in the solution only one particular solid will predominate or will precipitate out, so you want to be able to figure out which particular solid will you know predominate or precipitate out under the given conditions, right.

And again, why is that important because depending on the type of solid that precipitates out, the relevant concentration of Ca2+ will be depend upon that; what do we say now, solid, right, again this is more or less similar to the controlling solid, right. So, here though we have different types of solids, so how do we go about it? So, the key here is that you know anytime, the system will try to be relatively more stable, system tries to be stable, right.

And what does that mean? That means it prefers the insoluble solid, so the preference is always for the most insoluble solids as in what is that mean, it means that the energy of the system I guess, this is the way to understand it right, the range of system is relatively less or gives energy, right, G system, this is something we discussed in some of the earlier classes to, this is going to be relatively less, right.

Or the system is going to be more stable, when you have the more insoluble form, so what does this more; having this more insoluble solid form mean I guess, so whichever let us say, you know that CaCO3 solid can be in equilibrium with Ca2+ and CaO3 2- and you know that CaOH twice, the solid will be in equilibrium with Ca2+ and OH-, right, so but obviously, in solution you would not have 2 different concentrations of calcium, right.

You only have one particular concentration of calcium, so you want to know, which one; which solid would precipitate out, right so obviously, we are saying that the more insoluble form will precipitate out, what is it mean? So, more insoluble form means that particular solid which will

give the minimum concentration or the lesser concentration now, let us say in this case calcium will predominate, right.

So, what is that we are trying to say as in if the calcium Ca2+ that is in equilibrium with CaCO3 solid let us say, if that is going to be less than the calcium that is going to be in equilibrium with the CaOH twice solid, right, so what is this mean now, right that CaCO3 in this particular scenario is more insoluble that is why CaCO3 will precipitate out but obviously, let us say, if this Ca2+ that is going to be in equilibrium with CaOH twice solid is lesser in concentration to the Ca2+ that will be in equilibrium with CaCO3 solid, right.

What is that mean, CaOH twice will precipitate out in this particular condition, right, so whichever particular solid is more insoluble meaning, whichever particular solid will lead to the metal concentration or the relevant anion being at or in general, cation let us say, right being at lower concentration that is what the system will favour and that is what we are trying to see, right.

So, let us try to take this further I guess, let us try to see you know set up one particular equation for this, so one case I am going to look at now, which we are going to use later use, so obviously there will be one particular scenario, when the concentration of calcium in equilibrium with what is it now, CaCO3, will also be equal to the concentration of calcium in equilibrium with CaOH twice solid, right, so let us try to plug that you know I guess.

What am I trying to do here, I am trying to plug in Ca2+, CaCO3 solid right, it is going to be in equilibrium with Ca2+, in equilibrium with CaOH twice solid, right so this Ca2+ concentration that at a particular scenario right, the calcium that would be in equilibrium with CaCO3 is going to be equal to the calcium concentration that would be in equilibrium with CaOH twice, right.

At that point you will have both the solids precipitating out, right so when those 3 concentrations are same, what is that mean obviously, both the solids will precipitate out, so let us try to write down the relevant or you know equation I guess, right, so here what is the equation here, you we

know that K, solubility product for CaCO3 is going to be equal to concentration of Ca2+ into concentration of CO3 2-, right.

And here, K solubility product of CaOH twice is going to be equal to concentration of Ca2+ times OH- square, right, so obviously here the concentration of calcium, Ca2+ in equilibrium with CaCO3, right, what is that going to be = K CaCO3/ CO3 2-, I mean you do not need to mug this up but let us just try to understand where we are going to end up I guess, right, so this is one relationship for this Ca2+, CaCO3, right.

And the other one here, and how can I express this, Ca2+ at CaOH, twice, right, is going to be = K CaOH twice/ OH – square, right and again, what are these equilibrium coefficients; it is nothing but the solubility constants or the solubility products, right, so here let us say but in the second case to have it expressed in terms of H+, if I multiply it by what now or OH-, if I express that as Kw/ H+ and then transform it.

And Kw, let us say I considered that to a constant, so I have call this new this thing, K star let us say, CaOH twice K star * H+ square and obviously, what is this K star CaOH twice that is nothing but K COH twice/ Kw square in this particular case, right, I am just trying to express OH- as Kw/H+ and the relevant transformation. So, here I have the other relationship and now I am going to equate these 2 as I see, fit here right.

So, what do I have? Solubility constant; CaCO3/ concentration of CO3 2-, right, it is going to be equal to K star CaOH twice * H+ square, right, so again what is it that we are trying to develop, right, we are trying to develop or understand the system when both these solids can precipitate out that is why we have the concentration of calcium that would be in equilibrium with each of the solids to be equal only then, we have both the solids precipitating out.

So, right, you do not need to obviously mug up these derivations or such but obviously, you need to understand how to get it them or understand the basics, so again let us get this further, so we are going to have K CaCO3 = K star CaOH twice * H+ square and what is CaO3 2-, right, it is

nothing but alpha 2 * CO3 total, right. So, for a total alpha 2, right I think let me just write that down for the sake of; so what is alpha 2 now?

Alpha 2 is nothing but CO3 2-/ H2CO3 + HCO3- + CO3 2-, which is nothing but CO3 total, so the concentration of CO3 2- is alpha 2 times, the second or the third ionisation fraction times the CO3 total and that is what we have here, so when this particular relationship is met, right you will have both the solids precipitating out, right. So, before we go further let us just try to understand when or visualise I guess, when is at that your calcium hydroxide is going to precipitate out.

And when is it that the calcium carbonate is going to precipitate out, so obviously for this let us look at an log c pH graph that I have in next slide, so obviously the key here is that to understand which solid will precipitate out, you need to see that the calcium concentration that is in equilibrium with that particular solid will be lower, right. Why is that because the system wants to be at relatively more stable state?





So, here; what do we have here; so we have log c here and obviously it should be pH here on the x axis, right, so log c I guess. So, what do you see here, so let us just try to understand the system here, you know let us just look at the solid line for here now, so this is the Ca2+ that would be in

equilibrium with calcium carbonate and this is the calcium concentration that will be in equilibrium with calcium hydroxide, right.

So, what do you see here; you see that Ca2+ CaCO3 you know, this is the trend for this particular case, right. For, CaOH twice or calcium, this is the trend, right, so obviously in all these region here, right until here let us say, until this point which particular, what do we say, a solid will predominate obviously, that particular solid which will give the lowest concentration of calcium.

So, obviously as you see that in this region, the Ca2+ at CaCO3 is < the Ca2+ at CaOH twice, so obviously until this pH, right that were you see this intersection here, this is from theoretical log c pH graph, right, you can get this from vminteq or such, so again you see that CaCO3 will thus predominate in this particular region, again why is that because in this region, as you can see Ca2+ in equilibrium with CaCO3 is going to be less compared to the Ca2+ that is going to be in equilibrium with CaOH twice, right.

But obviously, as you see in this particular region here or in this particular region here, right and now where is the CaCO3 concentration here; it is out here, Ca2+ in equilibrium with CaCO3, right, the red line but the green line is the Ca2+ that is in concentration with your, what is this now, CaOH twice, so as you see in this particular region, this Ca2+ in equilibrium with CaOH twice is < the Ca2+ that is in equilibrium with CaCO3.

And thus obviously, in this particular region, CaOH twice is going to predominate, right, so again, let us try to understand this, so at remarkably high pH, CaOH twice, this solid is going to be precipitating out, so again why is that? If you want to look at it, it is nothing but CaOH twice right, is going to be in equilibrium with Ca2+ and 2OH-, right, yes, so it remarkably high pH, what is happening here?

So, at very high pH, OH- concentration is going to be very high, right, so as in then, which particular, what do we say, the forward or the backward would be favourable, you would see that the backward reaction would be favourable, right, so that would obviously lead to what now, more precipitation of CaOH twice and leading to lesser concentrations of Ca2+, right, so that is

why you see that with increasing pH, the calcium concentration that would be in equilibrium, the CaOH twice keeps decreasing, right.

Again, why is that because as you keep increasing the pH, the OH- concentration keeps increasing and now the backward reaction would be relatively more favourable, right and thus you would have more precipitation in the form of CaOH twice lead into further decrease in the calcium concentration that would be in equilibrium with the CaOH twice, the solid and that is why you see that at high; remarkably high pH, the CaOH twice predominates or will precipitate out, pardon me.

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And at a minute, it is not low pH, relatively lower pH, CaCO3 would control, right so that is the particular aspect here, so in another aspect that I want to point out here is; right, so let us look at now, let us say if you increase the concentration of CO3 total, so this particular solid line was at one particular CO3 total, right and here let us say, here we have CO3 total one and here we have CO3 total 2, right, which is greater than CO3 total one and that is what we say here.

So, before we go further, let us just try to understand what this means for the system now, right, you know that CaCO3 this solid can be in equilibrium with Ca2+ plus and CaO3 2-, right, so for a given particular case of CO3 total one, we looked at the earlier case for this solid line, right.

So, let us say though but I end up increasing the CO3 total, how is the system going to change? So, here if I increase the CO3 total, what does that mean?

I am increasing this particular variable here, so leading to which reaction being favourable now; the backward reaction compared to the previous case, right, so I am increasing the CO3 total that in effect means I am also increasing the CO3 2- concentration yes, so if I increase this CO3 2- concentration, what is going to happen now, the backward reaction is going to be more favourable compared to the previous particular equilibrium, right.

And so, you are going to have more of the solid precipitating out, what is that lead to; that will lead to a decrease in Ca2+ concentration, so that is why you would see that at greater total CO3, this Ca2+ in equilibrium with CaCO3 is going to be lesser, right and obviously that is the expression we looked at here, yes, so in that is why obviously, the equilibrium would slightly shift out here though, right, yes at a particular CO3 total, this is the case where CaCO3 predominates.

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Predominance area diagrams

But when you increase the CO3 total, you see that you know there is a much higher range to which at which CaCO3 would precipitate out, again this is for our particular understanding, right. So, let us move on to the other particular aspect, so here I guess, we have predominance area diagrams, yes.

And so, we knew we are running out of time, so I will just briefly look at what it is that we need to understand or try to understand from this predominance area diagrams and we are going to continue this in the next session. So, the name is self-explanatory, right its predominance area diagrams, so for example let us say you are trying to understand system and you did not have let us say the time or the patience to go to that in relevant detail or look at VMINTEQ let us say.

So, these obviously predominance area diagrams will give a snapshot, right you know overview of those particular regions, right at which a particular compound is going to predominates, so that is obviously nothing but the predominance area diagrams, right. So, I guess with that I will end today's session and we will continue discussing this precipitation and dissolution relevant aspects and hopefully, you know get it done by the next session I guess and thank you.