Environmental Engineering Chemical Processes
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Lecture - 43
Equilibrium of Precipitation - II

Hello everyone. Again welcome back to a latest lecture session. So in the previous sessions we have been discussing precipitation and mostly we have been discussing the relevant aspects about kinetics and then we moved onto equilibrium and that we have a new equation in this particular case as in precipitation we have the solubility product or the solubility constant and then we started looking at the relevant aspects of how to solve for our equilibrium, right.

As into be able to calculate how much solid will precipitate out and so on and so forth. So obviously for that we need to develop our equilibrium model, right.

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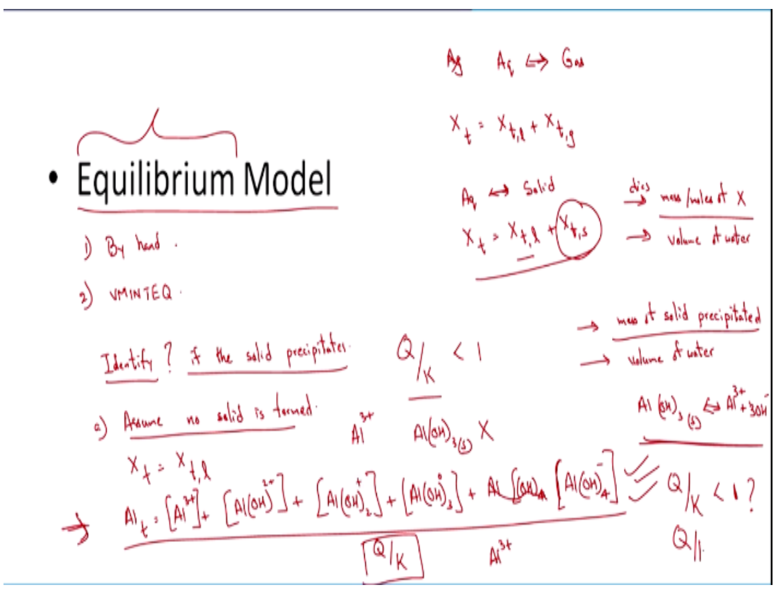

And in that context we are talking about how earlier we had phase equilibrium with when the aqueous and gaseous phase, right and how we describe x total right which is our component total component balance right as x total into aqueous phase or liquid phase and x total in the gaseous phase. So similar now we have aqueous space in what do we say in equilibrium with the solid phase, right. So obviously now I am going to have x total = x total the liquid phase + x total in the solid phase, right.

So it is just that we need to add new term here and what is that about, we need to have the relevant component that gives us an idea about the solid, the solid that precipitated out. So there in lies key though. So whenever we come up with concentrations, right so what is that we look at? Concentration is let us say, mass or moles let us say of a particular component let us say of x, right per volume of that particular solution, right which in this most of our cases is volume of water in which x is dissolved, right.

So in general we look at mass of x per volume of the water that it is dissolved in. But here you know how do I come with express in x total as solid because this solid is no more in the aqueous phase, right so it as a solid right. So this phase is different, but unlike the gaseous phase where we had partial pressure to approximate that particular activity or such right, here we usually look at mole fractions right, here as in the solid.

So mole fraction obviously right, if it is a pure solid you know, number of moles of that solid per total moles will be equal to 1 so that is why the activity is going to be equal to 1, why is that again? Mole fraction is equal to 1, right. So how do I go about it here? So here I guess we need to tweak it a little as in we are going to express x total or you know the precipitate let say the amount of solid that has precipitated out the solution. So how are we going to express that?

Let us say for a solid case we are going to express it as, mass of solid that has precipitated out of the unit volume of water it has precipitated from, so again this is not activity or such; we are just trying to understand let us say I have one litre and 1 gram precipitated out of this particular 1 litre of water let us say.

So the concentration terms you know, these are not strictly concentration, right why is that we look at concentration or activities in terms of mole fractions for our solid phases, keep in mind this is a different phase as in the numerator here is in the solid phase, the denominator here is in the you know obviously aqueous here. Here it is a dissolved phase, right and here it is obviously the relevant solvent here so that make sense, but here the phases are different.

But what are we trying to express then as -- we are then-- the numerator is the amount of solid that has precipitated out from the given volume of water, right that is one aspect we are going to consider here. So obviously, here how do I, how do you go about it? So here we first look at two aspects, one is By hand and the other is By VMINTEQ, right. So first we are going to discuss the aspect related to how to solve this by hand let us say, right.

And I guess we are going to look at a few examples later on, right or few practical examples and look at how to go about it. So first by hand let us say how do I set this up now; so this is the key here as in first I need to identify and yes I should make the people think, so here again we are looking at precipitation. And keep in mind this is an equilibrium model, right this is an equilibrium model, right. So before we go further what do we need to look for now, right.

Just take a few seconds to think about that please. So here we are-- so I guess what I am trying to hit at is we looked at the few conditions that need to be satisfied for equilibrium and what is th? So first you need to know, right a solid can be formed or not formed, right. So here you need to make an assumption, right and then go ahead with that assumption and see if that assumption is satisfied, okay. Let us say if I am going to assume that solid is formed.

I am going to make the relevant calculations then calculate Q and K, let us say and let us say obviously if I make the solid Q/K right and only then will it make sense let us say or if the solid term comes out to be negative what does that mean that $Q/K < 1$. Again, what we try to explain that here? So what we going to identify, I need to identify if the solid is formed or precipitates, if the solid precipitates, right. So how can I do this now?

So first I can assume that one assumption one way is assume no solid is formed, right. Assume no solid is formed, yes. So as I am going to assume that there is no solid phase right so just that x total = x total in the liquid phase. For example, let us say, for the case of Al 3+ right I am assuming that no solid is formed as an A1 OH thrice solid is not formed, so I am just going to solve for it as an Al total will be equal to what now?

Al 3+ + the concentration right + what else now? This is just the component balance + Al OH right and the charge would be 2+. I am just listing the complexes here, right. Al OH twice + + Al OH thrice 0 charge, this is still a complex + Al OH 4—pardon me, negative charge the concentration here. So I am going to solve for this the usual way, this is more or less just your aqueous complexes, right.

So once I get the relevant what do we say concentration of Al 3+ then I can calculate Q/K let us say for that particular equation as an Al OH thrice, solid in equilibrium with Al 3+ and 3OH-, right. So once I can from this particular case assuming that no solid is formed I am going to solve and calculate Al 3+ and H+ let us say, right and then I am going to calculate Q/K for this relevant equation, right.

So what does Q/K if it turns out to be <1, what is that mean? That means the solution is under saturated, right. So thus your assumption having no solid you know being precipitated out is valid and you can say this is the final solution and I am done with it. But if you calculate that Q/K is >1 what is that mean? So that means that obviously, the solution here is saturated and most probably let us say your solid can be formed or will be formed and then going to have solve for different case.

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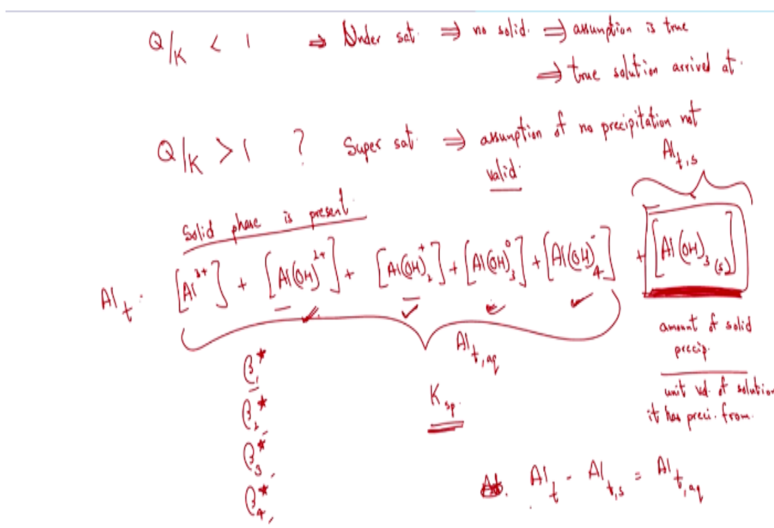

So again let us list them out here. So after solving it from previous in the previous manner and Q/K is <1 what is that mean? So under saturated, under saturated meaning no solid is formed, right meaning assumption is true; meaning true solution has been calculated, right. But what if after calculating the relevant variables and calculating the ratio of Q/K and that turns out to be >1, what does that mean? So it is super saturated, right or over saturated let us say.

And now assumption is not valid, assumption of no precipitation is not valid, right. So thus, I now have to resolve for it. And how am I going to resolve for it now? Now I am going to assume, so now I know that solid phase is present—is present, right. So for example now how will that Al total change now?

So Al total earlier was Al 3+ concentration + all the 4 complexes usually form what is the Al OH right and 2+ concentration + Al OH twice + 1 charge Al OH thrice, this is still the complex, 0 charge + Al OH 4 times a negative charge. But now I know that solid phase is present so that needs to be plugged in. And what is that here? Let us say depending upon the type of solid assume that Al thrice solid is formed.

So here we are going to have new term here, right. And why is that because Q/K is > 1 from based on your assumption earlier, right and that means your previous case is not valid anymore right. So now you are assuming, not assuming you know that the solid will be formed, right and thus you have a new term for your concentration of solid. And what are the units of this particular solid now, right.

Let us say in a mass of this solid precipitated out or amount of solid precipitated, amount of solid, so obviously they need to be in conjunction with the units here as in if you are using moles and so on right, amount of solid precipitated per the unit volume of solution it has precipitated from, anyway it is still be the same here but you need to be understand that you know, it is no more in the Aqueous phase, right this is a different phase.

So thinking of it in terms of concentration does not make much sense. So maybe you can think of it as maybe you know total suspended solid but not milligram per litre maybe mole per litre in—

to make the unit similar to what we have here I guess, amount of solid precipitated out, per unit volume it has precipitated from right, that is one particular case and you are going to go ahead and solve for that, right.

So once you solve for this you will get the relevant variables. So earlier though you know you can use beta 1*, beta 2*, beta 3* and beta 4* right to be able to solve for you know, or express these four complexes in terms of Al 3+, all these complexes is using the constant beta 1, 2, 3 * which are more or less from your equilibrium constants for your direct and I believe protonated addition right of your particular complex formation.

So for that you can use these coefficients to express these variables as in this four complexes in terms of Al 3+. But how can you express this Al OH thrice solid though? For that you are going to need an additional equation, so that is going to be an unknown. But obviously, if you have additional unknown you need an additional equation, right. So how can you get this additional equation? So you can use the additional equation as in from your solubility product, right Ksp I guess, right.

So again this will be your unknown, yes. So instead of earlier Al 3+ and H+ being your unknowns. Let us say you now have an additional unknown, right. So for an additional unknown you need an additional equation so for that you will use your equation with respect to your solubility product and then solve for your Al OH thrice solid, right and get the relevant value. So once you get this particular value, what can I calculate further?

Let us say Al total – Al total in the solid form well what be that obviously? Al total in the Aqueous form, and what is that, more or less that is your-- this is your Al total in the Aqueous form and obviously this is your Al total in the solid form, right. So again what is that we have been discussing here, right. So with that we can go ahead and solve for it. So again let us say there is another method too as in—

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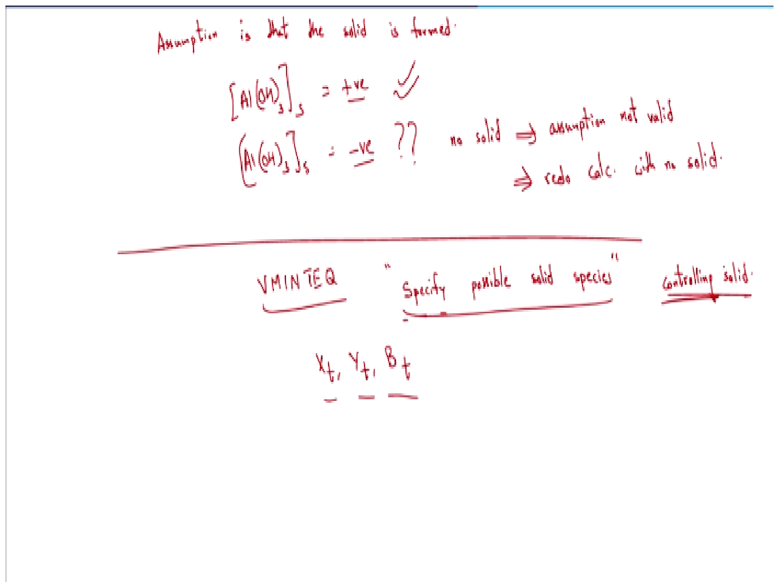

The assumption is going to be that instead of assuming that the solid is not present you can assume that assumption is that assume, assume assumption is that the solid is formed, solid is formed, right. And then you can go ahead with your relevant calculations and I am going to continue with the earlier example and let us say then I calculate this value of Al OH thrice the solid to be a positive value, right. Okay that means a two solutions has been arrived at.

But if I end up with a negative value for Al OH thrice the solid, but what does the negative value mean though, right. Right means no solid is formed, that means no solid is formed right, so that means assumption is not valid, right. And what is that more or less translate to that you need to redo your calculations with no solid, right.

So you can either start with you know either of these assumptions as in one assumption would be assuming that there is no solid and solve for it and then check the Q/K values and then redo the calculation if necessary when $Q/K > 1$ indicating that the solid is formed, or you can also choose or go with the assumptions that the solid is going to form or precipitation occur and solve for the concentration of the solid that has precipitated out, right.

And then if it is a positive value that means okay the precipitation has occurred, but if it is a negative value what are you going to understand I guess you need to understand that you know there is no precipitation and so you need to redo the calculations, remove your particular solid term and just solving for your aqueous phase species, right. So that is how you can go about it I guess. So in VMINTEQ-- how do I go about it in VMINTEQ?

I believe in the initial class itself those people have been paying attention closely might have seen that there was an option as I specified I believe solid possible solid species, right, specify I believe possible solid species in VMINTEQ, right. So VMINTEQ obviously cuts down on your time. So what do you need, obviously you need to give the X total, Y total and B total let us say, right and then specify solid species or possible solid species.

So obviously if you have no clue and select everything what it is going to look for the true equilibrium so it will usually look at you know the most stable form or the most insoluble form. But as you know let us say you are looking at coagulation, flocculation your most stable form of Al OH thrice is not going to form that takes way too much time. So in general in your coagulation, flocculation let us say in your where you look at swap fluctuation with respect to aluminium let us say, right.

Aluminium hydroxide complexes it is usually the amorphous form which is the most soluble form that is going to be form first. So you need to have that understanding about which solid is the controlling solid here, right. So specify solid species, so you need to look at or try to have an understanding about the controlling solid, right; and this is something we discussed in the previous classes too, yes. So I just plug this in; specify the possible solid species and then go ahead with the solution, right.

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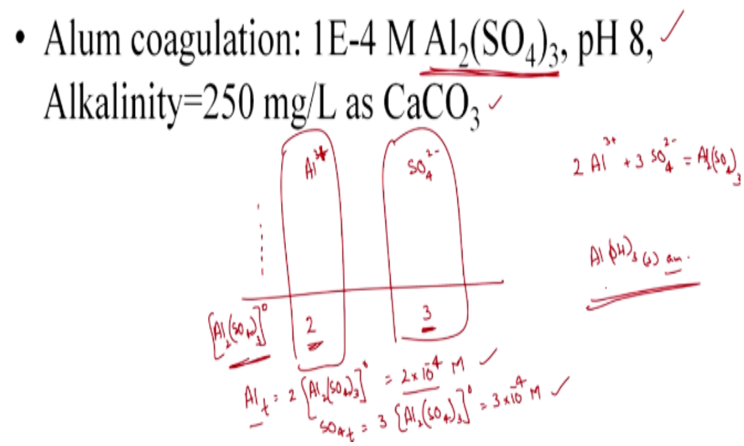

So I believe I have one or two examples here, first we will work it out with just the VMINTEQ and then look at how to setup the equation to also solve it by hand. So here I have Alum coagulation right so 10 power -4 (()) (18:21) Al2 4 thrice and the relevant variables are given. So here obviously I have two components they are 3+ and SO 4 2-. So here I am going to solve it by VMINTEQ so that means I am not going to list all the species, right.

I do not need to list these species but I need to know the total component concentrations, so the Recipe is nothing but Al 2 SO 4 whole thrice, right that is my initial concentration or Recipe species, so Al 3+. So what is the equal to, that is going to be equal to 2 here, right two times Al 2 SO 4 thrice that is what you see here, and why is that obviously if I look at the formation equation that is two times Al 3+ + 3 times SO 4 2- right, will be equal to Al SO 4 thrice.

And this is the formation equation the people should be comfortable with it, without having to write it down, so 3. So obviously what is this mean here? So Al total and SO 4 total, Al total = 2 times Al 2 SO 4 thrice, not that =2*10 power -4 molar, right. And what is SO 4 total? That is equal to three times the initial Al 2 SO 4 thrice that you are adding to the solution, right. So that is going to be equal to 3*10 power -4.

And with that I am ready to plug-in the relevant values to VMINTEQ, so obviously again I am reiterating what we have been doing until now. So I just calculated the total component that I need to plug into VMINTEQ. So here obviously it is Al total and 2* that is equal to 2 times the initial Al 2 SO 4 thrice that does not, right. Again why is that? It is two times, so if you look at the total components you need two components of Al 3+ to form your 2 SO 4 thrice

So again you know we have done this multiple times and I believe I might have skipped it or have been skipping the relevant calculation because I presume that you are now what do we say, confident enough to get this done without having to go through these right upsides here, right. So let us plug them in, I need to plug-in Al total, need to plug-in SO 4 total, looks like the fix pH at 8 and Alkalinity is given.

And let us say I am going to look at some particular solid let us say, so here if it is not given it is a safe assumption to say that Al OH thrice the solid in the amorphous form, right. Usually, this is the most soluble form which is going to be form first, so I am going to assume that this is the first solid that is going to be form.

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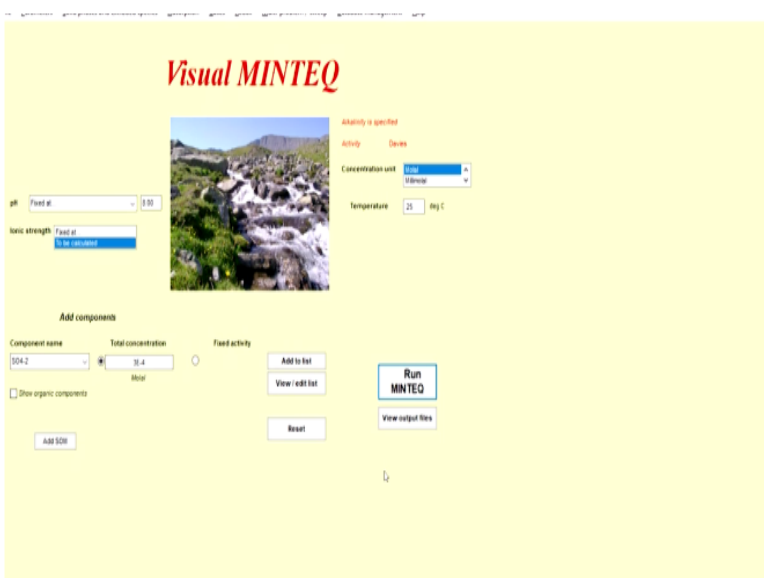

So let us go to VMINTEQ I guess, right, okay so I am going to fix the pH at 8 okay and I need to add 3+ 2e-4 right 2*10 power -4 add to the list and what else please, I think SO 4 2- yeah I believe it was 3*10 power -4 and that is something I am going to add to the list but I believe the solution also says Alkalinity, so I believe was what is the Alkalinity here please 250 milligram power litre as CaCo3 so it is 250 here and I am going to say OK.

And again move back to VMINTEQ hopefully. And here am I done with it? Not yet, because let us say I need to specify the possible solid phases, right. So here, so limit to those species otherwise if I do not give this particular option as we have talked about we are going to have all the possible solids for all the different types of components. Well, that is an exhaustive list. So I am going to ask VMINTEQ to limit the choice to those solid that would be present based on the relevant what we visit now, components we chose.

So obvious we have different kinds solids that can be form, but we are going to choose the solid that is going to form initially which is the most soluble form which is the amorphous form, right so I am going to choose that and add that and back to main menu, right. So let us view our “Add to list” to be on safer side okay this is from your Alkalinity addition more or less, right and I am going to go back to the main menu and run MINTEQ. Okay, so now still pH 8 fixed.

So let us first look at this species distribution, so CO3- obviously at pH 8, right. Now let us understand it holistically. So pH 8 right acid-base relevant chemistry so you need to know the pK, pK is 6.3 and 10.3 so pH 8 is > pK 1, so which form will be predominate now? The—what is it now? H CO3-, H2 CO3 would predominate when pH is < pK 1, right.

So let us just to refresh our memories get that down to, so here your species diagram and this for H CO3-and this is for let us say CO32-, so H2 CO3, H CO3- and this is for CO32-. So we know that the pK 1 is 6.3 and the current pH is at 8, so I am going to write this as 8, so obviously what predominating here, the concentration species, so obviously what is predominating you know that H CO3- is going to predominate and I believe that is what you are going to look at here.

So you see that 97% is present as H CO3- and that is what you would expect to based on your knowledge of the relevant acid and base chemistry. The SO4 2- you are saying it is going to be present as SO4 2- there is nothing surprising in that knowing the relevant pK of H2 SO4 and H SO4, right. And here 3+ looks like you know it is mostly going to present as in the aqueous phase, keep in mind this is for the aqueous phase, right.

So within the Aqueous phase it is mostly going to be present as 98% as the Al OH 4 (()) (24:48) complex, right. But here we know that we are also going to look at the relevant solid, right. So how do I look for that now. So here I have amount of finite solids. So the amount of finite solid that is going to precipitate out and is going to be in equilibrium is going to be 1.32*10 power -4 moles per litre. So, you know that is one particular case, I guess, right.

And if I look at the Equilibrated mass distribution so it tells me that if I am looking at Al 3+ right 1.3 2*10 power -4 has precipitated and only 6.8 3*10 power -5 is in the dissolved phase. So what is that mean 65% of Al 3+ has precipitated out, right and only 35% of the Al 3+ that you put into the solution initially is in the dissolved phase, and within this 35% what is the form that is predominating, that was Al OH4-, right. So that is where we see here.

So all these three corresponding to only 35% of Al total and which is present as 98% is present as Al OH 4-. And amount of finite solid obviously 1.36*10 power -4, mass distribution right 34% or 35% as dissolved and 65% precipitated. So those is something that is obviously remarkably useful to you right. And obviously, now if you need to do this by now, that is going to be an exhaustive process, yes.

So we are going to do one particular or try to setup the equation such that we can solve one particular problem by hand but we will do that in the next session. I believe I have one more what do we say example here that we can look at.

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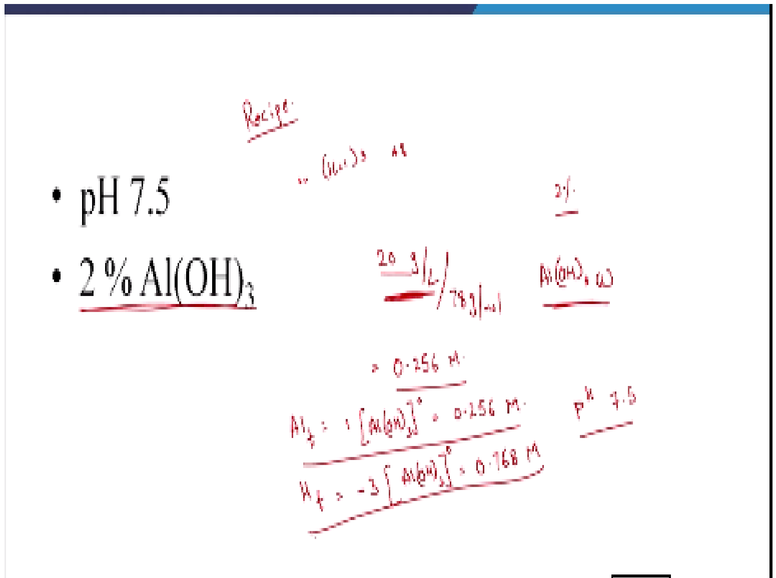

So here I guess you know 2% Al OH thrice, right and pH is 7.5. Let us also plug this in and see what it transforms into. So 2% right let us say per kg let us say how much that be present, so 1000 grams right, so 1% would be 10 grams and 2% would be 20 grams, so 20 grams per litre that is 2% Al OH thrice. So here gain I guess I am getting ahead of myself. So let us say the recipe, it is a recipe problem as I know that it is that I am putting into the solution.

So I am adding Al OH thrice or Aluminium Hydroxide, right which is at 2% concentration, 2% right. So 2% per kg it is going to be more or less be 20 gram or 20 gram per litre right. So that is what we have here and I guess the molecular weight of Al OH thrice is going to be, okay maybe I can units of grams per litre in my particular case there. So I am going to plug this in and again I am going to assume that the amorphous form is the possible solid. I am going to specify this.

And Al 3+ but because I have to guess specific Al total I need the relevant molecular, I guess it 78 gram per mole, right and with that I go end up with I need to calculate 20/78, let me calculate that is equal to 20/78* so it is 0.56 moles so the solution is nothing but it is 0.256 moles, right. So obviously, Al total is going to be equal to initial, what is it now 1times Al OH thrice that I am plugging in and that is equal to 0.256 molar.

And H total is going to be -3 times right, why that is -? Because it is 3 OH – that means it is -3H, so -3 times Al OH thrice naught that = 0.25 times 3 0.75 right and 6 would be 18 right 0.768

molar right and that should be right anyway minor mistake at this, H total and Al total I have that and I know that the pH is 7.5 but if I am plugging this and I guess I do not need to put in H total here, right.

So I am going to plug this value and also show that it is or assume that the solid is Al OH thrice solid. So I am going to VMINTEQ back to input menu right and view Edit list and delete Alkalinity, I need to delete Alkalinity, back to main menu parameters, specific Alkalinity and No, right. Sometimes I might need to restart with VMINTEQ otherwise you know, it is going to mess up the relevant equation-- and SO 4.

What is this going to be equal to please? This was 0.256 molar I guess right, so let me change that here, motel I guess I do not need to specify that but let check that because the pH is fix that 7.5, right. And let me see if that itself can give me the answer, so this specify solid phases right and again I need to choose Al OH thrice the amorphous form, right and add that; back to main menu and run MINTEQ, okay. And now I am going to look at species distribution.

So Al 3+ again, I guess because the pH is similar to 8, the pH value is going to be equal to 95% is present as Al OH 4-complex. But how much of it is in the first case present in the dissolved form, right. So here you see that when you are adding Al OH thrice right at pH 7.5 right most of it is in the precipitated form, right Al 3+ most of it or almost 99.99% or 100% has precipitated out and < 0.1% is in the dissolved phase, right.

So obviously, what is the concentration of your particular precipitated solid, so that is more or less equal to what you plugged earlier which was 0.256 molar Al 3+ so that is more or less equal to 0.256 molar Al 3+, right. So I guess with that I can be done. Let me just look at what we have been up to. So I need to fix the pH and give the relevant components and more importantly specify the relevant solids species, right.

So list of possible species we say that it was Al OH thrice amorphous, right. And why did we choose amorphous, I mean if no one using the relevant information let us say we will assume that the least or the most soluble form of the solid which is form first is the controlling solid and in most cases it is the amorphous form, right. So with that I guess I will end the class for today. And we are going to look at a few more examples or applications, right.

Hopefully real life examples, and then solve them by VMINTEQ and also see how to setup the equation by hand, right. So with that I am going to be done for today and thank you.