Environmental Engineering: Chemical Processes
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Lecture – 38
Aqueous Complexes of Aluminium (Al)

Hello everyone, so welcome back to latest lecture session, I guess we have been discussing you know aqueous complexes in the last couple of sessions, so we will continue that discussion for 2 more sessions and then move on to precipitation and dissolutions based reactions, yes, so let us just recap what it is that we have been discussing about the aqueous complexes, so in general, let us say, as an environment let us say, you know in which scenarios would to be concerned with aqueous complexes, now right.

In general, when you have metals right, we looked; we saw that in the presence of an electron rich compound, which we are saying is a ligand, let right, you know, we are going to have formation of aqueous complexes, so the metal is the electron pore, right compound and the ligand is an electron rich component and it has a binding site and depending on the number of binding site, I guess we you know, had different terminologies, right I think, multi dentate or mono dentate and so on, yes.

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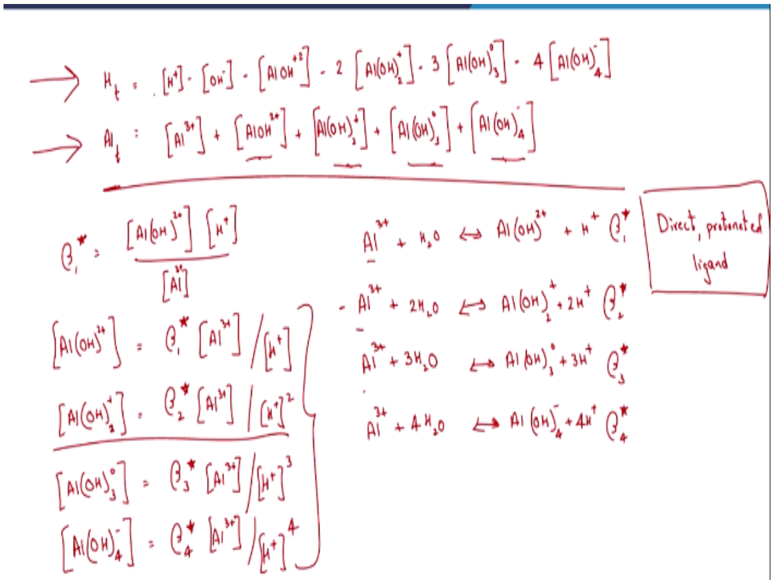

$$\rightarrow H_t = [H^+] - [OH^-] - [AlOH^{+2}] - 2[Al(OH)_2^+] - 3[Al(OH)_3^0] - 4[Al(OH)_4^-]$$

$$\rightarrow Al_t : [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-]$$

$$\beta_1^* = \frac{[Al(OH)^{2+}][H^+]}{[Al^{3+}]}$$

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \quad \beta_1^*$$

$$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+ \quad \beta_2^*$$

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3^0 + 3H^+ \quad \beta_3^*$$

$$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+ \quad \beta_4^*$$

Direct, protonated ligand

$$[Al(OH)^{2+}] = \beta_1^*[Al^{3+}]/[H^+]$$

$$[Al(OH)_2^+] = \beta_2^*[Al^{3+}]/[H^+]^2$$

$$[Al(OH)_3^0] = \beta_3^*[Al^{3+}]/[H^+]^3$$

$$[Al(OH)_4^-] = \beta_4^*[Al^{3+}]/[H^+]^4$$

So, anyway, so what are the applications I guess right, so let us just quickly recap that so, one is that let say if it is a toxic metal as in if the free metal is a toxic, is toxic, right, so by addition of let us say an appropriate ligand, you can from complexes, again here the assumption or the scenario is that, the free metal is toxic, right, so if you a ligand you know the concentration of the free metal is going to decrease based on obviously, appropriate choice of the ligand, right and (()) (01:59).

So, let us initially when there is no ligand let us say and let us say x is my metal and x total is only in the form of the free metal let us say, you know the x + z let us say, you know it is a random example here but let us say if you know, I am adding ligand here, let us say, x totally still going to be the same, right but here I am going to have a lesser concentration of my particular free metal.

And then I am going to have the relevant complexes here, right, so thus as you see you know the x1 concentration is going to be less than x, right without the complexes, right or the scenario when we have no complexes and thus you see that or you can observe that you know the toxicity of the particular system you know can be decreased let us see, again, keep in mind that as you remove the metal again it is the equilibrium, so the equilibrium is going to shift towards the left and so on.

But those examples we are going to come back to later on and obviously another aspect I believe we discuss was it can also have a solubility of the metal and in general, as we discussed earlier aqueous complex are relatively more soluble right and let us say if you have metal whose concentration is or you know who or which would precipitate out at low concentrations, let us say buy you want to have a higher total metal concentration in your particular solution.

So, what is one solution; adding a ligand, right so that even though the free metal concentration might be less, the total metal concentration in the form of both the free metal and the aqueous complex is going to be higher, right, so again you can affect solubilty in such a case or in such cases and I think we also discuss sorbability, so in those cases where you are looking at adsorption or sorption let us say, right.

And you can depending on the relative sorbabality of your complex, relative to or compared to just the metal you can either decrease or increase the sorbabality, right, again this is something that is no brainer, so we would not spend more time on that and I believe we moved on to looking at you know developing some intuition based or intuition about the strength of the complexes, so in this case obviously, right and we talked about strength of the complexes.

And so obviously, multi dentate will be stronger than the mono dentate, again multi and mono dentate, what are they about? So, multi means, you have complex or you know ligand with multiple binding sites and mono dentate is one with only one binding site, right and thus obviously, I guess the multi dentate would in general be multi dentate complex, would in general be stronger than mono dentate complex.

And a second one; obviously, stronger the greater the charge of both metal and ligand let us say, so the greater the charge on your metal or ligand, the stronger in general the strength of the complex is, again that is a no brainer again and the third aspect is; I believe we talked about briefly about hydrated ion radius, right and obviously, you know that with respect to the concentration of the charge with a smaller radius let us say, right.

So, the greater the hydrated ion radius, the greater the strength of the complex, greater as an obviously the concentration will be greater, concentration of charge when we have a small hydrated radius, right, as an within a smaller what do we say, radius, I mean this is the Lehmann’s description I guess, within a smaller hydrated radius, you have more concentrated charge and thus you would have greater strength of the complexes.

And so, we then talked about individual metal ligand interactions, right as an we classified metals as A metals, or B metals and then we listed the preference; order of the preference, right with respect to the strength of complex for these 2 kinds of metals, right, anyway one would form the ionic bonds, at least the A metals I believe, right, again and then we started moving onto an example.

And I believe the example, we looked at was when we add aluminium to water let us say, right and the relevant complexes that need to be formed and such or are formed and how to go about understanding what are the concentrations of the relevant compounds at equilibrium, right, so in that context, we what we do; we first listed the species, right, here 3+, H+, OH- and the Al and different OH based complexes, right.

Keep in mind that in this particular example or scenario we looked at, we only had aluminium hydroxide complexes, right so and then we chose the components; components for what is it now; H+ and Al 3+ and then we wrote down the relevant formation equations, got down to the tableau and then I believe we moved on to right in the total component balance equations, right, so the total component balance equation we got that from the tableau from the last class, right.

So, H total = H+ - OH- and so on with respect to the different species of aluminium hydroxide complexes and Al total, again we have that here, Al 3+ +Al OH2 + and the other aluminium hydroxide complexes, right. So, again obviously you can use; ones who have H total and Al total, you can plug in the relevant values in VMINTEQ and it will obviously give the relevant concentrations of either the free metal which is Al 3+ or the relevant concentrations of the different aluminium hydroxide complexes, right.

But obviously, we need to also understand the fundamentals or the basics here, right, so let us just have a brief look about how to solve this by hand, right. So, obviously here we have multiple unknown here, let us say how many unknowns here; 1, 2, 3, 4, 5, 6 and 7 I guess, right unless I missed out something else but looks like we have 7 unknowns, so how I can I solve for them obviously you know we need to look at the relevant, equilibrium coefficient or equilibrium equations I guess.

And in this context, we talk about or when we discuss the coefficients; equilibrium coefficients, we discuss that different; the different nomenclatures out there as in one for stepwise with the protonated or deprotonated, pardon me, and one for direct; direct addition of your ligand, right again with respect to protonated and deprotonated right, I think K and K star and beta and beta star, right, so in general as I believe we briefly mentioned or briefly discuss in the last lecture session.

Looking and beta star, let us say which is the direct addition, I believe, right of the protonated form of the ligand would in general, be easier for your calculations, so let us just try to write down some of the variables in terms of this particular beta star and where would you have these particular relevant coefficients obviously, in the relevant books I guess, these are standard values more or less, right.

Again let us try to plug them in here, so let us say I am trying to form various complexes here, right, so what would be relevant direct term, Al 3+ +H2O would be in equilibrium with Al and let us say OH and the charge would be 2+ and it would release 1H+ obviously, and I am also having to form the other complexes which I will list you, right, Al OH, right these are the 4, let us say complexes that I am trying to form based on my direct and protonated ligand, right.

Direct addition of the ligand in the form of the protonated ligand, right and obviously, we will then have beta 1 star, beta 2 star, beta 3 star, beta 4 star, right, again you know if you are not sure which complexes or how many complexes let us say particular metal can form the particular ligand, you know I would suggest, you know before you develop intuition let us say looking at the relevant tables, right, where you have the coefficients.

And depending upon the number of coefficients listed, you can then estimate the number of; a number of or the kind of complexes that can be found, right, so again here obviously, what else are we left with, so it is going to be Al 3+ + 2H2O would be in equilibrium with Al OH 2+ and 2H+, right, again this is direct addition, right and obviously, here it is release of 3H+, so it is going to be Al 3+ + 4H2O, right + 4H+.

So, obviously what is you know let me just, so let us say if I am looking at Al total H, right, Al 3+ is what let us say, I need to solve for initially assuming that I know the Al total, so I need to express all these other 4 variables in terms of Al 3+, right. So, how do I do that let us see, so I know that the beta one star, what is it going to be now; the concentration of Al OH 2+ into the concentration of H+ by the concentration of Al 3+.

Meaning, what is this now; so the Al OH 2+ concentration can now be written as beta one star into the concentration of Al 3+ / H+, right, in the same manner, I can list the other, what do we say 3 complex system, you know in the form of Al 3+ and the relevant coefficient which is beta 2 star, beta 3 star and beta 4 star, let us just list them out here, so that we get some practice here I guess, Al; and the next one would be Al OH twice, right and +1 charge that is going to be obviously going to be = beta 2 star into Al 3+/ H+ square, right.

Again, that is from this particular equation and what is beta again, a different type of equilibrium coefficient, right or different form of expressing equilibrium coefficient based on the type of reaction, so it is going to be = the product of the activities of your products, right, so it is going to be Al OH twice + charge to the coefficient, which is 1 * H+ to the concentration of h+ to the power of 2/ Al 3+, so that is why we end up with this particular equation here.

And next term would be Al OH thrice 0 charge, would be = beta 3 star * Al 3+ divided by H+ cube, right and again similarly, Al OH4 with one negative charge is going to be = beta 4 star * Al 3+ concentration/ H+ concentration to the power of 4, right, so again here we can now have; we can now express this particular equation in terms of just Al 3+, right by substituting the relevant equations here, which we just developed, right.

We can replace these 4 variables here, this Al OH, all the concentrations or the complexes here, in forms of Al 3+ beta one star and H+, right, so again similarly, we can do so here, right and then you will end up with 2 equations and 2 unknowns, right, so one would be H+, one would be Al 3+ and you have 2 equations and you can then solve for H+ and Al 3+ and once you have that you can obviously, calculate the species, already know the concentration of the different species at equilibrium, right.

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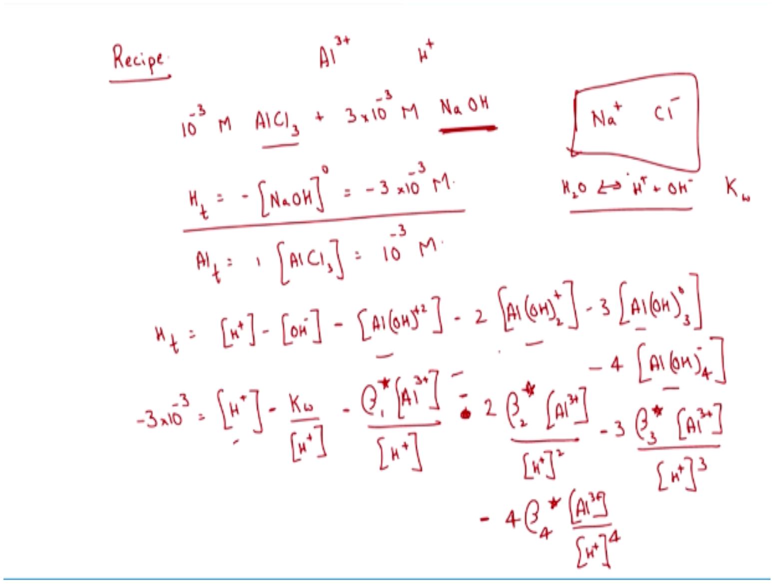

Recipe: Al^{3+} H^+

$10^{-3}\ M\ AlCl_3 + 3\times10^{-3}\ M\ NaOH$

$\boxed{Na^+ \quad Cl^-}$

$H_2O \rightleftharpoons H^+ + OH^- \quad K_w$

$$H_t = -[NaOH]^0 = -3\times10^{-3}\ M.$$

$$Al_t = 1\,[AlCl_3] = 10^{-3}\ M.$$

$$H_t = [H^+] - [OH^-] - [Al(OH)^{+2}] - 2[Al(OH)_2^+] - 3[Al(OH)_3^0] - 4[Al(OH)_4^-]$$

$$-3\times10^{-3} = [H^+] - \frac{K_w}{[H^+]} - \frac{\beta_1^*[Al^{3+}]}{[H^+]} - 2\frac{\beta_2^*[Al^{3+}]}{[H^+]^2} - 3\frac{\beta_3^*[Al^{3+}]}{[H^+]^3} - 4\frac{\beta_4^*[Al^{3+}]}{[H^+]^4}$$

So that is one way to go about that so, let us look at one other aspect here, let us say and I believe you are going to look at a recipe problems, right and what is a recipe problem as in right, you know what it is that you are putting initially, right, have a solution and I know what it is that I am adding to the solution initially and thus or then I want to be able to estimate the concentration of the species at equilibrium, right.

So, let us see, let us look at the example that I am going to have let us see, I believe again it is going to be based on Al 3+ complexes and H+, right but let me see what it is that we have for example, we have 10 to the power of -3 molar, let us say AlCl3 + 3 * 10 power -3 molar NaOH, right, so let us say here the example that I have here is we are adding 10 to the power -3 molar AlCl3 and 3 * 10 to the power -3 molar or 3 millimolar concentration of I mean, NaOH, right.

So, here again based on some intuition or such let us say or some experience as you go by you will see that Na+ and Cl-, they are relatively non-reactive in solution, right that the respective sorts, so we can neglect there or any further role in this particular scenario anyway, so based on that let us see how to go about that so, what is H total going to be = now; what is the only source of H total here, any H here?

Not really, any H here, yes, in the form of OH, right, so it is going to be negative concentration of NaOH initially, so that is = -3 * 10 power -3 molar concentration, right so with that you know and the relevant equation similar to earlier I guess and what about Al total; Al total would be =; what are the sources of Al total here, anything in NaOH, no, right, any in NaOH, not really, any in AlCl3, yes, so it is one times AlCl3, right and that is going to be = 10 power -3 molar, right.

So, based on the equation that we already had earlier, right, what can we express H total; H total =; as we know H+ - OH- right, I mean just listing the equation, this equation I guess, right and we are assuming obviously that Na+ and Cl- can be ignored now, I am ignoring them and which is not bad assumption at least when you are working it out by hand and the equation I guess we have is; Al OH +2, right -2 times Al OH twice + 1 charge -3 times Al OH thrice zero charge -4 times Al OH4 negative charge, right.

And obviously, what is H total here; H total = -3 * 10 power -3 molar that is = H+ and how can I express OH- from our acid base chemistry background, right, what is it now, we know that H2O will dissociate and will be in equilibrium with H+ and OH-, Kw will be equilibrium coefficient for this particular dissociation, water dissociation right, so we now that it is going to be = Kw/ H+, right and how can I express these variables here now, right.

And I can express them in terms of what it is; we calculated it out here, right in terms of the various variables here, yes, and I am going to plug that in here, - beta 1 star * Al 03+, right concentration divided by H+ + 2 times beta 2 star * Al 3+ / H+ square, right/ H+ square – here, right, and -3 times beta 3 star Al 3+/ H+ cube -4 times beat 4 star Al 3+/ H+ to the power of 4, right.

So, here we have an equation with 2 unknowns, right, what are they? H+ and Al 3+, right, so obviously we need another equation and that equation is going to be from this particular equation, right and let us just plus that into.

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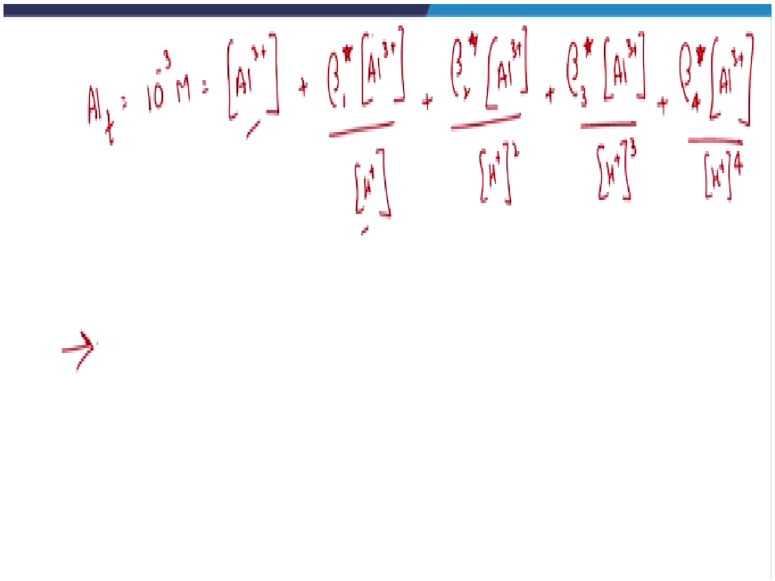

$$Al_t = 10^{-3} M = [Al^{3+}] + \frac{\beta_1^*[Al^{3+}]}{[H^+]} + \frac{\beta_2^*[Al^{3+}]}{[H^+]^2} + \frac{\beta_3^*[Al^{3+}]}{[H^+]^3} + \frac{\beta_4^*[Al^{3+}]}{[H^+]^4}$$

So, we now have Al total and what is Al total in our case now; Al total in our case was 10 power -3 milli molar or 10 power -3 molar, pardon me, right that is = Al 3+ right and what else, + beta 1 star * Al 3+/ H+ + beta 2 star * Al 3+ / H+ square + beta 3 star Al 3+/ H+ cube + beta 4 star * Al3+/ H+ to the power of 4, so again we now have second equation with 2 unknowns, again they are Al3+ and H+ and here we had another equation with H+ and Al3+, so 2 unknowns in 2 equations.

So, now you can end up solving for your particular solution, I guess, right, so by using the relevant coefficients in which in this case for beta start and knowing the initial concentrations which we had in the form of AlCl3 and NaOH, we can now solve for the solution and once we get H+ and Al 3+, from them we can calculate the concentrations of the different complexes again right, so that is something that we can be done with.

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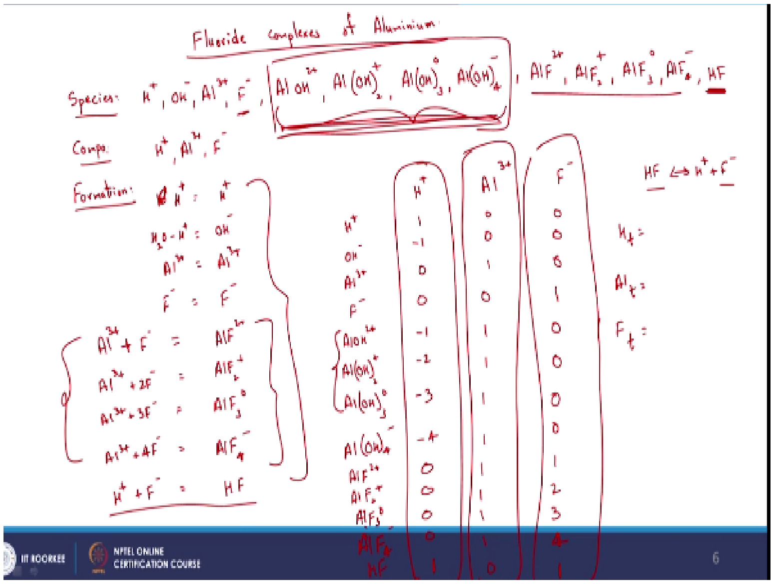

Fluoride complexes of Aluminium.

Species: H^+, OH^-, Al^{3+}, F^-, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, HF

Compo: H^+, Al^{3+}, F^-

Formation:

$H^+ = H^+$

$H_2O - H^+ = OH^-$

$Al^{3+} = Al^{3+}$

$F^- = F^-$

$Al^{3+} + F^- = AlF^{2+}$

$Al^{3+} + 2F^- = AlF_2^+$

$Al^{3+} + 3F^- = AlF_3^0$

$Al^{3+} + 4F^- = AlF_4^-$

$H^+ + F^- = HF$

	H^+	Al^{3+}	F^-
H^+	1	0	0
OH^-	-1	0	0
Al^{3+}	0	1	0
F^-	0	0	1
$AlOH^{2+}$	-1	1	0
$Al(OH)_2^+$	-2	1	0
$Al(OH)_3^0$	-3	1	0
$Al(OH)_4^-$	-4	1	0
AlF^{2+}	0	1	1
AlF_2^+	0	1	2
AlF_3^0	0	1	3
AlF_4	0	1	4
HF	1	0	1

$HF \leftrightarrow H^+ + F^-$

$H_t =$

$Al_t =$

$F_t =$

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So, let us say we can move on to the next example that I have here, so let us say I have an example related to fluoride complexes, so instead of just aluminium hydroxide or in aluminium hydroxide based complexes, we are now going to have fluoride complexes, I guess, so let us see how the situation is going to differ now, aluminium, right. So, obviously, here we need to first identify again the species.

And then move on to the components, write the formation equations, the tableau and then the total component balance equations, from that you can then express the different variables in terms of the let us say, simple variables that you are looking at which would in this case be H+, Al3+ and F-, so we will just look at that very briefly here, so what are the species going to be? Obviously, you are always going to have H+ and OH- and then the metal, right.

And what else let us say, you will obviously have F- fluoride and then we are going to have the aluminium hydroxide complexes which we discussed earlier, right Al and we know that I guess we have 4 of them, right and then moving on to the complexes of fluoride I guess aluminium fluoride AlF 2+, AlF2+ and AlF30 and AlF4 negative, right and with this am I done, no, or we done; so, here I guess one aspect that we need to look at is; we have listed all the complexes, right with aluminium and hydroxide and aluminium and fluoride, right.

But keep in mind that you know the acid base reactions, the aqueous complex, redox or precipitation or dissolution, they do not occur independently, right, once you have equilibrium let us say, you will have all the other reactions you know happening or you know going through simultaneously, so obviously in this case we do not have any redox reactions and we are not considering precipitation at this stage.

But we do know that you know acid base reactions are going to occur, right, so here let us say you can depending on the pH also have the conjugate acid for F- let us say and that it is going to be HF, right, so that something we need to keep in mind now, so not just F- depending on the pKa value, right of HF dissociating into H+ and F-, right, you will also have the relevant conjugate acid and base, right.

So, there is something that we need to look into, as in as we keep progressing through you know the course let us say, you need to understand that all the relevant reactions are going to occur simultaneously, so depending on the situation you know which is the case here, you will also need to look at the relevant acid base reactions too. So, let us just have the formation reactions, before that obviously, we need to write the components, right.

And the components are going to be H+, Al 3+ and F-, right and with just these 3 components we can form all the other species, yes, so now let us say, I am going to have the formation equations, so once you have a relevant background you can do away with this formation equations but for now, we are going to list them here, so H+; so first I am going to list all my species here let us say.

So, H+, how can I form my species from the components, right, Al3+, F- and for the sake of time let us say I am going to neglect the aluminium hydroxide complexes because we already discussed them in detail in the last class and obviously, we need to list them to but I am going to not list them here, I am only going to list the aluminium and fluoride complexes here, right and AlF3 zero charge and AlF4 negative charge and HF.

And now let us see how I can form my species from my components, so in the left hand side, I am going to have my components H+, one H+ would lead to one H+ and H2O; -H+ will lead to OH-, Al3+ would lead to Al3+, F- will lead to F-, so now here I am going to come up with the relevant aspect here, right. So, how do I go about it? Again, as we mention, we need to look at you know, hopefully expressing beta star, right.

So, it is going to be Al 3+, right +, what is it now here; F- that is it here I guess, right that is going to be = AlF2+ and the another one would be Al3+ +2F-, right and that is going to be = AlF2+ +2 H+, is it not really, so Al3+ + 3F- = AlF3, 0 and Al 3+, right and +4 F- is = AlF4 - and HF is HF+ F-, right, so I am neglecting again these 3 species; not neglecting, I have not listed these 4 aluminium hydroxide species.

Because we already looked at that earlier, now I am going to move on to writing my tableau, so in the tableau, I need to first come up with my components here in the columns, right and F- and here I am going to list all the relevant species here, so H+ OH- Al 3+ F- and assume that we are already writing down this 4 species here, these 4 as in aluminium hydroxide species, right or you know let me list them for the sake of understanding I guess, right and so on I guess, right.

So, again from this particular equations here, we can; from formation equations, we can fill out the tableau, so that is going to be H+ -1, 0 here, 0 here and we know it is going to be -1 here, -2,-3 and -4 here, right, with the Al3+ it is going to be 00101111 and 4 species of the aluminium fluoride complexes, right, Al F3, 0 and AlF4 negative and HF, so it is going to be equal to again 1211, right and 0 here and 00001 and F-, right and obviously 0 here, OH- 0, Al3+, 0, 1 here and 0000 here.

But from here, we need to look at these particular equations here, so it is 1F- for ALF2+ and 2 here, right and 3 for AlF3, 4 for AlF4 and 1 for HF, right and again so, we just looked at a particular you know relevant example where we have not just aluminium hydroxide complexes but aluminium and fluoride complexes, so just to be able to understand what goes on right, I listed the relevant formation equations and then the tableau in great detail.

So, from here obviously what can we do; we can apply the H total, H total and then again Al3+ total, right and F total, right, so from here we can just get that and relatively easily, which I am not going to go through again in detail, right F total but obviously we need to be able to come up with the relevant coefficients, so the way we wrote down the formation equations, you might need to change them slightly if required.

Because I guess we had the protonated form addition here, right in this case of what is it now, a deprotonated form addition but beta 1 star would require the addition of the protonated form of the ligand, which is HF, so then you would have –H+ here, so that is something you need to take into account, right, again with that we will end today's session and we will; and in the next session, we will look at a few examples where we will look at VMINTEQ and also supplication of this particular aqueous complexes, I guess right. So, with that I will be done for today and thank you.