Environmental Engineering: Chemical Processes
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Lecture – 37
Aqueous Complexes: Solubility, Rate Constant & Strength of Ligands

Hello everyone, so welcome back to our latest lecture session, so in the previous session, we you know, introduce ourselves to aqueous complexes and looked at why they are relevant or we know we have been discussing that and let us take the discussion further, right.

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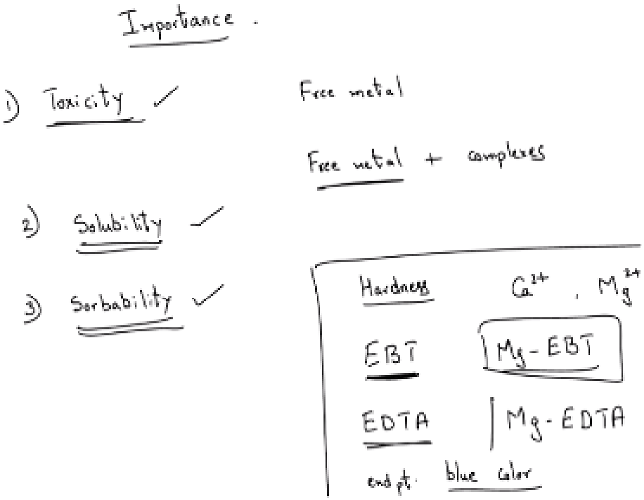

We have discussing the importance of aqueous complexes, right and in that context, we discussed that the toxicity is going to be affected right, as in now you instead of just having the free metal at relatively high concentration, if you add a ligand, you are going to have both the free metal and the complexes, right and let us say you know in general, if let us say only the free metal is what is toxic and in general, let us say if and is the decent assumption if the complexes are not toxic.

What would that mean for your particular system that the toxicity of your particular system is decreasing, right, so that is what you know, we can look at that and the second case is with respect to solubility, let us say, for example, you might have notice than neither you freshman chemistry practical class or such, you take a solution, you keep adding some salts or such, at a certain point, you are going to see residue or precipitation you know, at the bottom of your beaker or such let us say, right or the slides let us say depending on the kind of solution you are using, right.

So, let us say you know, you want to increase let us say the concentration of some protonated metal, let us say not a heavy metal that is toxic but let us say some metal that useful to you let us say, you want to increase the concentration of some metal in your particular solution but beyond the threshold sure you know that it can precipitate out right, so what can you do you; you can add a ligand, right so that the total metal concentration is going to be higher.

Without the ligand, let us say it is just going to let us say stay as the free metal or you know form precipitate and settled down or form precipitate and you know go and change into the solid phase but let us say that is not what I want, I want it to stay in solution, so what can I do now; so I can increase the concentration of the total metal; total metal, keep that in mind by adding the ligand, right, ligands as we know are more I mean the complexes as you know are more soluble, right or soluble species.

So that would in fact mean, you can increase the total concentration of the metal by adding ligands and forming your aqueous complexes, so when you want to, you know adjust the; pardon me, what is this now, the solubility of the particular metal that is something that you can take into account. The third aspect is sorbability, let us say, right, so let us say distortion or adsorption let us say, you know it depends on the relative sorbabilty of the metal let us say.

So, let us say if you want either increase or decrease the sorbabilty, you can then consider the addition of ligands to form complexes, for example, let us say if you want to increase the sorbabilty, right and let us say you know that your complex is relatively more sorbable, right, let us say the charge is such that it favours sorption, so maybe then let us say you were going to add a ligand, so that you have more complexes and that can increase your efficiency, not efficiency, I guess, the sorbabilty of your particulate system, why is that?

Because in this particular case or that particular scenario that you are considering, the sorbabilty of your particulate complex is higher but obviously keep in mind it depends on the scenario that you are looking at obviously most of them look at charge, right or charge plays an important control, so let us say if you want to decrease the sorbabilty and in different case, let us say the sorbabilty of your complex is relatively low, right.

Then, by adding the ligand and forming the complex, you can decrease the sorbabilty of your particular metal right, so again depending on relative sorbabilty, pardon me; of your complexes, you can either increase or decrease the sorbabilty of your particular metals that is one particular aspect. So, 3 major applications; one is toxicity, right, one is solubility, another is sorbabilty, right.

So, in general, now let us move on to some of the example that you might have come across at least in a lab you know, so this is something that we can look at. So, when we are trying to measure hardness, right; hardness and I think you are trying to measure Ca2+ and Mg2+, right, so how do you go about then, if people can recall that or I can have refresh their memories, you add EBT right that is again an ligand.

Eriochrome black T indicator, right, EBT, right, you add that initially, right and then you start I believe, titrating with EDTA, right until I believe a blue colour appears, right a blue colour is your endpoint, if you remember that I guess. So, what is happening here, right, so here initially, again I said EBT is an ligand and also EDTA 2 is a ligand, so Mg, EBT complexes are formed initially, okay, magnesium and EBT complexes are formed, when you initially add EBT to your solution right.

So, then you are titrating with EDTA right, so that in general, leads to formation of a more stronger or stable complex, the Mg EDTA complex right, so the ligand is replace here you know, earlier the complexes was between magnesium and EBT, now with the addition of EDTA, as you are titrating your solution with EDTA, you are now going to end up with; what is this now; Mg EDTA complex.

So, when all the Mg EBT is replaced by; the EBT is replaced by the EDTA in your Mg EBT complex that is when you end up with your blue colour, right and that is the end point that you observe, so here again, so that is one particular you know illustration of where it is, you know one of your practical applications of your particular complexes, right. So, again complexes, they are again never present in most of your titrations.

So, before move further though, one other aspect, so in your COD test, you might have seen that you add mercury, right, if you would have paid attention to your test, so why is that though; you know if you think about that; that is because you want to; what do we say take care of the interferences due to Cl- as in what is your COD test, you are adding a strong oxidising agent and you know potassium di chromate I guess, right, or di chromite.

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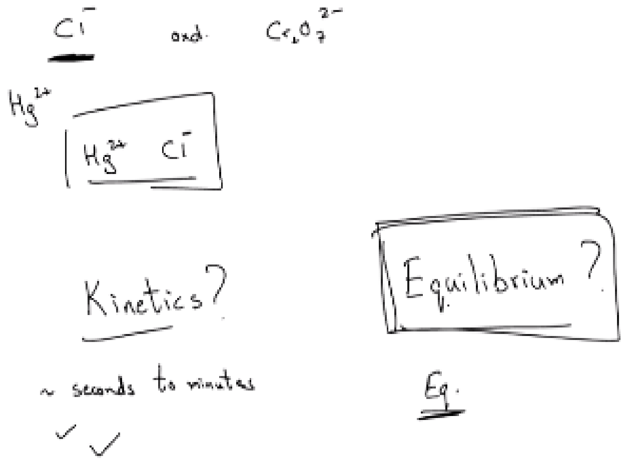

Cl^- oxd. $Cr_2O_7^{2-}$

Hg^{2+}

$\boxed{Hg^{2+} \quad Cl^-}$

Kinetics?

~ seconds to minutes

✓ ✓

$\boxed{\text{Equilibrium?}}$

Eq.

And that can oxidise Cl- right, so that can lead to over estimation of your COD, yes so you want to remove the interferences due to this Cl-, as in Cl- right, can be oxidised by; what is this now, your potassium di chromate, yes but you want to remove this particular interference, so that is why you add mercury, right, so the complexes are formed between Hg 2+ an Cl-, thus you are now removing the interference from Cl- on your COD test, otherwise, the Cl- can be oxidised to the various forms of; oxidised forms of Cl, right.

So, that is obviously another example of why you would add or you know practical example of your complexes. So, now we move on to the next aspect, we need to now decide you know am I going to look at kinetics, right or we are my going to consider equilibrium, right, or do I need to consider both the aspects, right. So, in general acids and bases we mention that the relevant half reaction lifetimes are right; half-life's are of the order of milliseconds, right.

So, in this case, they are not as fast but they are still pretty fast, they are let us say in general, order of let us say few seconds to minutes, so in general, they are still for most practical purposes, that are relatively fast, right, so seconds to minutes, unlike acids and bases, they do take more time, right the relevant reactions are relatively slower compared to acids and bases but for most practical purposes you know, the formation of your particulate complexes are relatively fast, right.

So thus you can you know consider that for most of the system that you see kinetics do not play an important role, why is that because they are so fast that you more or less mostly end up with equilibrium, right. So, again similar to acids and bases now, we are going to discuss equilibrium in much greater detail, right, again why is that; because the kinetics are in general, relatively fast enough such that you know they end up reaching or the system ends up reaching the equilibrium, right.

So, here now the major aspect is you know they are relatively fast and that is why we are going to look at equilibrium or we achieve equilibrium usually and that is why we are going to discuss equilibrium now, right.

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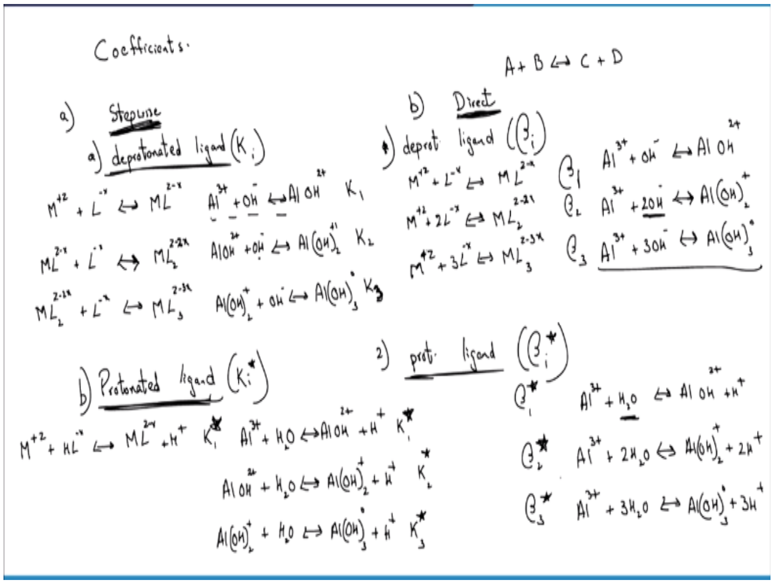

Coefficients:

$A + B \leftrightarrow C + D$

a) Stepwise

a) deprotonated ligand (K_i)

$M^{+z} + L^{-x} \leftrightarrow ML^{z-x}$ $Al^{3+} + OH^- \leftrightarrow AlOH^{2+}$ K_1

$ML^{z-x} + L^{-x} \leftrightarrow ML_2^{z-2x}$ $AlOH^{2+} + OH^- \leftrightarrow Al(OH)_2^{+1}$ K_2

$ML_2^{z-2x} + L^{-x} \leftrightarrow ML_3^{z-3x}$ $Al(OH)_2^{+} + OH^- \leftrightarrow Al(OH)_3^{0}$ K_3

b) Protonated ligand (K_i^*)

$M^{+z} + HL^{-x} \leftrightarrow ML^{z-x} + H^+$ K_1^* $Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^+$ K_1^*

$AlOH^{2+} + H_2O \leftrightarrow Al(OH)_2^{+} + H^+$ K_2^*

$Al(OH)_2^{+} + H_2O \leftrightarrow Al(OH)_3^{0} + H^+$ K_3^*

b) Direct

1) deprot. ligand (β_i)

$M^{+z} + L^{-x} \leftrightarrow ML^{z-x}$ β_1 $Al^{3+} + OH^- \leftrightarrow AlOH^{2+}$

$M^{+z} + 2L^{-x} \leftrightarrow ML_2^{z-2x}$ β_2 $Al^{3+} + \underline{2OH^-} \leftrightarrow Al(OH)_2^{+}$

$M^{+z} + 3L^{-x} \leftrightarrow ML_3^{z-3x}$ β_3 $\underline{Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3^{0}}$

2) prot. ligand (β_i^*)

β_1^* $Al^{3+} + \underline{H_2O} \leftrightarrow AlOH^{2+} + H^+$

β_2^* $Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^{+} + 2H^+$

β_3^* $Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3^{0} + 3H^+$

So, equilibrium I guess, before we go further, people looked at the relevant textbooks, I think Stumm and Morgan, right, water chemistry by Mark Benjamin and Aquatic chemistry I believe by Brezonik and Arnold, or any other book let us say. When you are discussing complexes right, you will have different kinds of coefficients here, if you remember equilibrium coefficients is one concept we looked at, right, what is an equilibrium coefficient now?

If you remember that A + B goes to let us say C + D, right and we mention that you know, equilibrium coefficient, this is going to be at equilibrium, I guess right, activity of C raise to stoichiometry of C, activity of D, raise to the stoichiometry of D, activity of A, raise to stoichiometry of A, activity of B, raise to stoichiometry of B, and which we usually approximate by concentration of C, concentration of D by concentration of A concentration of B, right, this is something we might have discussed or we did discuss in acids and bases and in an equilibrium and so on, right.

But here though, we have different ways of different types of coefficients depending on you know is a ligand and metal you know going from 1 or 2 step, right or is that let us say protonated ligand or deprotonated ligand anyway, let me write that down and hopefully, it is going to be more clear view. So, in equilibrium we are going to talk about coefficients, right, so we have different cases; one is stepwise, right and another case would be direct, okay.

And in this case of stepwise, right I am going to have a deprotonated ligand and for that the coefficient is going to be expressed as Ki, please keep that in mind, right and the other case is when I have a protonated ligand; ligand, pardon me, and that I am going to represent by K star and if I assuming it is a direct reaction again which I am going to you know explain further, keep in mind that there are different coefficients here, when we are talking about equilibrium for complexes.

One for stepwise, one set for stepwise, one for direct, one for protonated ligand, one for deprotonated ligand I guess, anyway stepwise, again here to we have; what do we have here; let us say I call this one deprotonated ligand and that is going to be beta here and here let us say, if it is protonated ligand, it is going to be with the ash, star, anyway different coefficients would be available in different books, so you just need to be aware of what it is?

Let us say, if a book says it is beta star let us say, what is it that you are referring to, which reaction are you referring to or which complex are you referring to, so the complex might be such that it depends upon the relevant products and that you can glean from the relevant coefficients. So, let us look at the examples, so stepwise; so in the first aspect, we are going to look at stepwise and deprotonated ligand.

So, you know stepwise obviously, it makes sense, it is self-estimator, let us say charge of the metal M is z and L is –x let us say, right and that confirm a complex ML z – x, right and an example will be AL 3 + is my metal let us say and it is going to react with the deprotonated ligand OH - and it can form AL OH and the charge is now going to be 2+, right, this is one complex. So, again stepwise, right so again I need to go from ML z – x + another ligand L – x, it is now going to be = ML, let us say 2 z – 2x, right.

Again, this is a generate form, you know it is obviously, flexible depending upon how you write the coefficients or such, so what is that mean? So, here it is going to be AL OH 2+ charge + OH-, again a stepwise, right, it is stepwise, AL 3+ first forms Al OH 2+ and AL OH 2+ again reacts with; not reacts with; okay, reacts with the deprotonated ligand OH -2 form AL OH twice and +1 charges, right.

And again, the next aspect will be again similarly, ML2 z – 2x + L – x can go to ML3 z – 3x and an example here, would then be now, AL OH twice + OH-, right would then go to AL OH thrice 0 charge, right, so again stepwise, so here we will have K1, coefficient for this, K2 and K3, right, K1, K2 and K3, right. So, here you have metal and you have a ligand, so here when you talk about coefficients in terms of equilibrium coefficients in terms of just K, what is that mean?

AL 3+ going to AL and reacting with OH- and going to AL OH 2+ charge and then stepwise addition one after the other, so obviously, if it is a protonated ligand, still stepwise and now we are going to talk about protonated ligand, so again that is the self-estimator, I guess, right, so it is M + z HL, I mean the charges, I guess on L going to be –x, just keep that in mind that it is an approximation here that we are writing a generic form.

It is going to be ML z – x + H+, right and the coefficient here is going to be K1 star, right and what does that mean, let us write that down, it is going to be = AL 3+ and what is the protonated ligand here; protonated means OH- has a proton, right, it is H2O and now it can go to AL OH 2+ charge + H+, right, so for this, we have K1 star, I am not going to write the generic form further but I will just write this further.

So, I can now say, stepwise next example here will be AL OH 2+, + the protonated ligand, it is protonated ligand, right +H2O can go to AL OH twice + charge + H+ and what is the coefficient here; it is going to be K 2 star, so someone talks about K2 star, right, K2 star or K1 star they are talking about the protonated form of the ligand you know forming a complex with the metal, right. So, the last set would now be AL OH twice +; + the protonated ligand, which is H2O, right, would go to AL OH thrice no charge + H+.

And that is going to be = K3 star, right, so obviously let us self estimatory, once you understand one aspect, right, now we are going to move on to the second aspect, which is the deprotonated ligand but the direct addition, I guess. Again it is self estimatory, so let us see what it is that we are up to here, so now I am moving on to the direct addition, here I looked at stepwise addition, as in one complex and then addition of only 1 ligand to that complex, again one complex, another addition of one ligand but here it is obviously going to be a direct addition, so let us look at what that is I guess, right.

So, the first example is going to be similar, right M + z + L - x is going to be = ML z –x, so the coefficient is going to be beta 1 right, again the example is let us say, similar here, and you will have write that down, you have 3+ ; + OH- goes to AL OH 2+ but let us say for the next case, let us say the formation of the next complex, it is not stepwise anymore, now it is direct addition, as in AL 3+, +2OH- goes over to form or forms, AL OH twice + charge, right a direct addition, right.

Earlier, we had only one stepwise but now, we have a direct addition and same case for the next particular complex, AL +3 + 3OH - will directly form AL OH thrice, right, so again the key is that you know, we now have a direct addition of the; or we are considering what do we say that there is the direct addition of the ligand, again beta 1, beta 2 and beta 3, right, so generate form, may be if I can write that down, M + z +2 L - x would go to ML2 z -2x, right.

Again, direct addition, right, what is the generic form M charge is +z, let us say, 3L - x would go to ML 3 and z – 3x, anyway generic forms, you can play around with it to get a form that suits you better but again, here we are talking about direct addition of the ligand, right to form the relevant complex, unlike earlier, where we just talked about a single step addition, so one complex will then lead to a formation of the other complexes and so on.

So, let us obviously again write down the protonated ligand, so that is again self estimatory, I will start with my example I guess, right, so it is Al 3+, +; what is it now; H2O, well form, what now; AL OH 2+ + H+ and what is the coefficient here, it is going to be beta 1 star, right, I am doing away with the generic form and here again it is the protonated ligand that is the key here, it is the protonated ligand and direct addition.

So, the next complex 2 can be form from the direct addition, what is that or how is that I guess that is going to be = 2H2O, right and that is again going to form AL OH twice and + charge + 2H+, right and again AL 3+, +3H2O will form AL OH thrice, no charge +3H+ and obviously, the coefficients are going to now be beta 2 star and beta 3 star, right, again you know, it might seem a bit confusing but it just combination of 2 aspects.

One is when we have stepwise and one is when we have stepwise indirect and the other is when we have protonated and deprotonated ligands, right, so you know different books have different coefficients, so you should be able to understand what is what and you know go from there but there I guess, right. So, again one other aspect that we need to consider is; when you solve for the equilibrium right, we usually choose components.

So, when you choose components, say if you choose in such a way and the relevant coefficients in such a way, you know, it can simplify your particular solution further but if you choose coefficients you know, anyway we will have an example later, I guess you know, depending on your choice of what do we say, coefficients, you can either end up with a very complex calculation or relatively simple calculation, right.

So, let us say in general I think the protonated ligand with the direct step is the easiest way to solve for what do we say; different equilibrium solutions in such, so let us look at I believe one example here, right.

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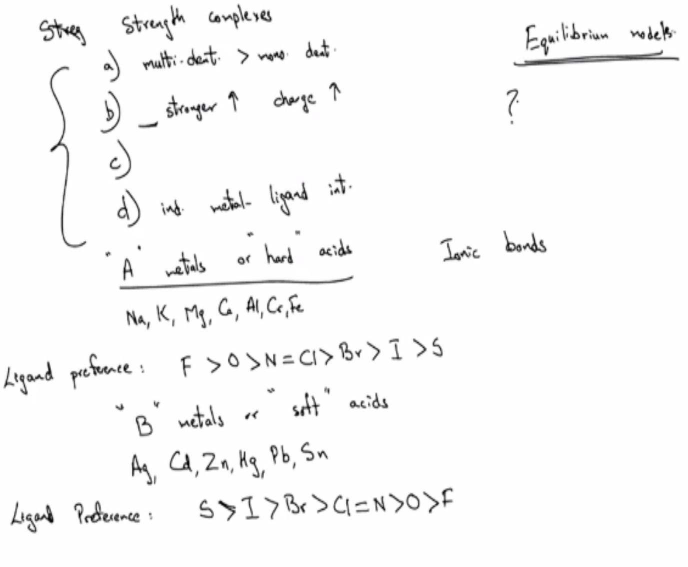

Streg Strength complexes

a) multi-dent. > mono. dent.

b) – stronger ↑ charge ↑

c)

d) ind. metal- ligand int.

"A" metals or "hard" acids

Na, K, Mg, Ca, Al, Cr, Fe

Ligand preference: F > O > N = Cl > Br > I > S

"B" metals or "soft" acids

Ag, Cd, Zn, Hg, Pb, Sn

Ligand Preference: S > I > Br > Cl = N > O > F

Equilibrium models

?

Ionic bonds

So, anyway before I go for examples I guess, I need to talk about the strength of complexes, right, so 2 generic cases, let us say a and b, so one is let us say, multi dentate, right when you have more than 1 electron or you know more than 1 binding site, right, you know those complexes multi dentate are usually stronger than mono dentate right, so that is one aspect. So, multi dentate are usually more stronger than mono dentate, right.

And b would be when let us see you have multiple charges rather than let us say charge; single charge or double charge, let us say you have charge of +3 or -3 on your metal or ligand, so the greater the charge on either your metal or ligand let us say, the strength of your complex would increase, right, so that is one particular case, I guess, so, in another case, when you are going to look at the hydrated radius, right.

So, that is the case when let us say this might; you might have come across when you looked at ion exchange process, so that is something we are going to discuss again in detail, so in this context we need to look at also individual metal ligand interactions, right as in different kinds of metals would form let us say, a stronger complex with one kind of a ligand but what do we say, not as strong with different another ligand, we are going to look at those particular cases here.

So, here I am going to come across with let us say, 2 case here, one is the A metals, or hard acids I guess, right. So, in general, what am I talking about? I am talking about Na, K, Mg, Ca, Al, Cr and Fe, right, so these in general are referred to as; what is this now? Hard acids and they usually end up forming ionic bonds, I guess due to the relevant complexation, right. So, let us look at their particular preference ideas, so the ligand preference.

So, they would prefer F > oxygen or the strength of the complex N would be greater in this order, right and usually they form; an obviously the second aspect would be, right, and here we looked at A metals are hard acids, so then we are going to look at B metals or soft acids, right and what are we referring to; we are referring to Ag, Cd, Zn, Hg, Pb, and a mercury, lead, zinc, cadmium, silver, right.

And the ligand preference in this case is usually the opposite ideas, right and here it is going to be such that they prefer to form complexes with sulphur, iodine, Br, Cl, nitrogen, oxygen and fluorine or F- I guess, right. So, here we looked at 2 cases; right, one is we defined or you know not defined I guess, this is common knowledge, we have hard acids and soft acids, or A metals and B metals, right.

So, we looked at what is it now sodium, magnesium, calcium, aluminium, and so on, so they have a particular preference for the ligands and that is something that we listed as in F > O, nitrogen, bromine, iodine and sulphur, right but if it is the B metals, usually it is the reverse order, they would form stronger complexes with sulphur than with let us say, oxygen, right, so this is something for you to keep in mind.

So, in general, what are the aspects they are; the strength of the complex are depend upon as in multi dentate is greater than mono dentate, right so that is something we just talked about. In general, if the charge on either the metal or ligand greater than or you know > 1, right, the higher the charge the better the or the greater the strength of the complex, right and then we also talked about the hydrated ionic radius, right and that is something we need to consider.

And then we talked about the ligand preference for A metals and B metals, right, so now let us go on to looking at what is this now; equilibrium models, right, again you do not need to mug this up but the key is that for you to be able to understand you know develop that intuition I guess right, for example as easily as you know which acid is let us say, stronger acid or weaker acid, you should let us say you know at the end of the course, we able to understand you know which complexes are relatively more stable.

Or you know, which are most stronger, let us say, right, now ionic radii, so it has a concentrated charge let us say, right, this small the ionic radii thus the greater are you know the stronger the complex and again that is something you would come across in ion exchange process too or obviously if the greater the charge, the greater the complex and that is something that is logical to but with respect to A metals or B metals, obviously there is a preference here.

So, now equilibrium metals; equilibrium models, pardon me and how do we go about that? Again, this is similar to what we talked about everything with respect to equilibrium models, we can solve by getting it done with respect to component balance, right again, components, you define components, right or you first identify the species, then define the components, right, get in the tableau, write the total components concentrations, right.

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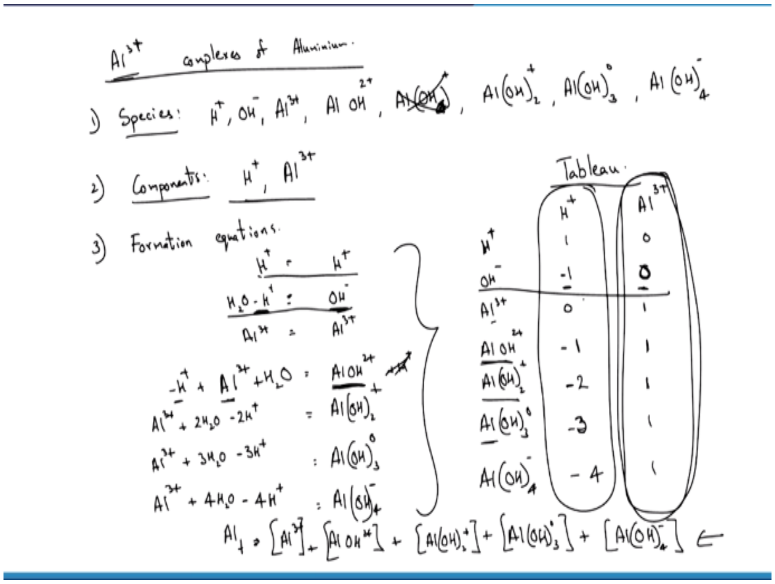

Al^{3+} complexes of Aluminium.

1) Species: H^+, OH^-, Al^{3+}, $AlOH^{2+}$, ~~Al(OH)~~, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$

2) Components: H^+, Al^{3+}

3) Formation equations.

$$H^+ = H^+$$
$$H_2O - H^+ = OH^-$$
$$Al^{3+} = Al^{3+}$$
$$-H^+ + Al^{3+} + H_2O = AlOH^{2+}$$
$$Al^{3+} + 2H_2O - 2H^+ = Al(OH)_2^+$$
$$Al^{3+} + 3H_2O - 3H^+ = Al(OH)_3^0$$
$$Al^{3+} + 4H_2O - 4H^+ = Al(OH)_4^-$$

Tableau.

	H^+	Al^{3+}
H^+	1	0
OH^-	-1	0
Al^{3+}	0	1
$AlOH^{2+}$	-1	1
$Al(OH)_2^+$	-2	1
$Al(OH)_3^0$	-3	1
$Al(OH)_4^-$	-4	1

$$Al_T = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-] \leftarrow$$

And then solve for the relevant what do we say, variables, so let us look at one example here that I have, right and I think we are going to look at Al 3+, right or complexes of aluminium I guess, right. So, how do I go about this now, so first I need to identify the species; right and what are the species here? So, first it is always going to be H+ and OH-, right and then the free metal and then you are going to list all the different complexes.

So, let us initially, you are not sure, you can look at some of the you know books that you have and list the complexes based on the number of coefficient that are listed, right, so for aluminium, you are usually going to have 4 relevant complexes, so let us list them, let say, so let us say we are just looking at it or solutions in water, right, so I am going to have H+ and OH- and then Al 3+ and you know the other after addition of one particular ligand Al OH 2+ and Al OH twice with +1 charge, this is twice, and then Al OH thrice no charge.

And Al OH4 with a negative charge, again if you look at the relevant books or look up the relevant coefficients, you would see that for aluminium, you would have 4 coefficients listed, so form that you can understand that more or less there are 4 complexes that are usually predominant for aluminium, right and depending upon the type of what do we say, coefficients listed as in beta 1 star are so on you can then try to approximate what they are also I guess, right.

So, let us we are done with that so now, I need to come up with my particular components, right and obviously again, similar to acids and bases, right what do we choose, which; these are; we are going to choose building blocks, right based upon the simplest combination, right and simplest and smallest combination of components, you should be able to build all the other species.

What are species? They are actual compounds present in equilibrium in the solution but components, they do not need to be so but they are just building blocks that you are going to use to form your species, right, so obviously you know always going to have H+ and what else is the building block here, obviously as you see it is going to be Al 3+, right, so that is what you have here. So, usually you would choose the metal and the; what do we say H+.

And in this case, the ligand is OH-, so you do not need to choose any other ligand here, you can get by with just choosing H+ because you get 2 OH- by subtracting H+ from H2O, right, so thus you do not need to choose any other ligand but let us say there were some other ligand, you need to choose that ligand as one of your components, right. So, what next now, right, you need to form your equations or the formation equations.

So, the formation equations; so what are they about obviously as we discuss earlier, so each species need to be formed from a combination of these particular components, so I am going to have my particular what do we say a species listed here, H+ OH - and Al 3+, Al OH 2+, right and Al OH twice + Al OH thrice no charge, Al OH4 negative charge, right. So, I need to form these particular species from my components.

So, 1H+ is H+ and H2O –H+; H2O is always a component, right, H2O –H+ OH-, Al 3+, well form Al 3+ and how do I end up with; here with twice Al, let us say, I can write it in different forms, so let us say I can write it as Al 3+, + H2O, well lead to Al OH twice + H+, right this something we know or I can say, here it is going to be –H+, + Al 3+, + H2O goes to Al OH 2H, right. So, next case here this particular species, how can I form them obviously, same case?

So, it is Al 3+, + 2H2O – 2H+, +2H2O – 2H+, and how I can form this, it is Al 3+, +3 H2O -3H+, right and again, Al 3+ +4 H2O - 4H +, right and now I can go ahead and get down with my tableau, right and here I am going to list all the components here and my 2 components or in this case, I only have 2 components, Al and 3+, H+ and Al 3+, pardon me and then I am going to list all the species as different rows, H+ OH- Al3+, Al OH 2+ charge, Al OH twice +1 charge, Al OH thrice and Al OH4 one negative charge, right.

So, from these formation equations, I can obviously come up with my particular tableau right, so 1 and 0 that is what I see here and here again it is -1, obviously because H+ has a -1 coefficient here and 0 and here it is going to be again, how did we come up with OH -? Look at the relevant formation equation to form 1 OH-, you need -1 of H+, right and that is why I plucked that in here and you need any Al 3+ to form OH- none, so that is why we have 0.

And this is something we covered earlier to write and for Al 3+, you need 0H+ and 1 Al 3+, how are you forming Al OH 2+, how are you forming Al OH 2+, you need 1Al 3+, that is what I am going to write here and you need -1H+, right, so similarly for all the other cases, how can I form Al OH2, I need 1 Al 3+ and 2 or -2 H+ and how do I form Al OH thrice; 1 and -3, 1 and -4, right.

So, from this let us say you know, I can now write my total component balance equation, right, so what are these total component balance equations here, we just have a 2 components here, it is going to be H total and Al total, so let me write that down here rather than next slide, so we understand that further, so I will write that Al total, right is going to present as so this is nothing but the sum of this particular set of; concentration here is going to be present as Al 3+ free metal + concentration of Al OH 2+ right, + concentration of Al OH twice +, +Al OH thrice 0 charge + Al OH4 negative charge, right.

Again, where did we get this particular equation from; from this particular tableau or the component balance right, so similarly now we are going to have H total, right, I am going to write that in the next particular slide I guess, right.

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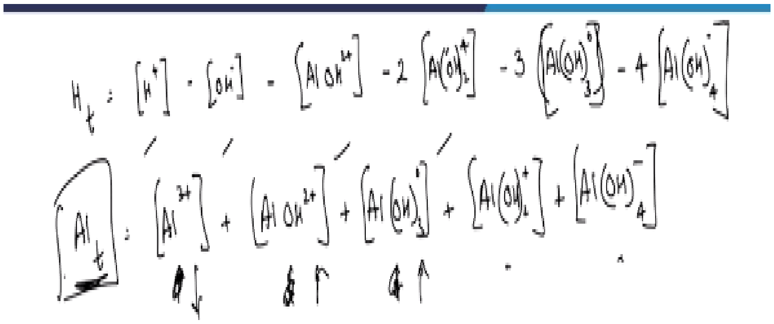

$$H_t = [H^+] - [OH^-] - [Al\,OH^{2+}] - 2[Al(OH)_2^+] - 3[Al(OH)_3^0] - 4[Al(OH)_4^-]$$

$$\boxed{Al_t} = [Al^{3+}] + [Al\,OH^{2+}] + [Al(OH)_3^0] + [Al(OH)_2^+] + [Al(OH)_4^-]$$

So, H total, was is that =? It is = H+ concentration, right, OH- concentration, right and I think nothing for Al3+ and let me just write down all the complexes, so that I do not need to go or jump back and forth, here OH, Al OH twice with a negative charge, right and Al Oh thrice with no charge and Al OH4 with a negative charge, right and obviously, the coefficients if you remove, what there were?

There were -1 here, -2 here, -3 here and -4 here, let us go back and check back, so that is what you see here, -1 for Al OH 2+, you need -2 H+ for forming Al OH2+, -3 and so on and that is what I plugged in here, H total is nothing but H total = H+ -OH- and -1 times this -2 times this and so on, right and again, where did we get that from; from our total component balance equation. Similarly, we had Al total was = Al 3+ + Al OH 2+, I am just writing in this sense, so that we can compare them here I guess, right.

Al twice 0, so I missed one here Al OH twice with the positive charge and Al OH4 with the negative charge, right. So, again how will this component balance help us, it is because let us say you know that the total aluminium is always going to be constant, I mean other the; unless you change the scenario, right, so depending on pH let us say, or such will total aluminium body or Al total change, this one change, why is that?

The individual concentrations of these variables will change, as this can increase, others can decrease and so on or this can decrease and the others can increase and so on, right but the total aluminium or the total component concentration is going to change and that is the key, I will just trying to refresh your memory, so based on this, you have different applications, so I guess we look at that particular applications in the; or those applications in our next lecture session.

And be done with our complexes and then move on to the next aspect which is precipitation and dissolution, right and thank you that is it from me for now.