

Environmental Engineering Chemical Processes
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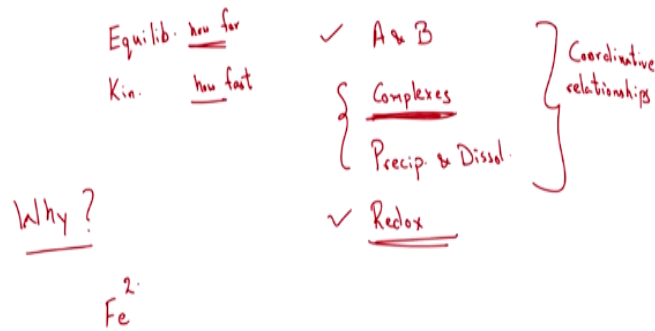
Lecture - 36
Aqueous Complexes: Application in Toxicity Reduction

Hello everyone, so welcome back to our latest lecture session. So thus far we have been discussing acids and bases and we have done with that. So now we are going to move on to the other major aspect or one of the other major aspects in our environmental chemical process and that is going to be the formation of or you know aqueous complexes I guess. So we are going to talk about aqueous complexes here.

Before that quick 2 or 3 minute what about we have been up to thus far and how you know the discussion about aqueous complexes fits into the bigger picture. So let us have a look at that.

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Aqueous Complexes



So in we talked about the basic aspects related to any chemical process so that is equilibrium. We discussed that and we also talked about kinetics. So how far can the chemical process go to let us say and how fast? How far, and how fast, and in that context we mention that we usually have you know 4 kinds of chemical process that an environmental engineer would come across. So one is obviously the acids and basis upon which we have spent considerable time.

So acids and bases are what do we say relatively fast reactions so that is why the applications of kinetics in acids and bases are negligible but equilibrium is what you would almost always observe or achieve. So thus we looked at relevant aspects with respect to acids and bases after the system reaches equilibrium. So that is what we discussed in great detail. Strong acids, weak acids, bases, acid neutralizing capacity, base neutralizing capacity, alternative which is something remarkably important because if you know it is omnipresent I guess.

And we have the applications with respect to what we have been taken and so on. So we talked about acids and bases and so now we are going to move on to complexes and then we are going to talk about precipitation and dissolution and then last major aspect is going to be Redox and we are going to spend relatively less time on complexes and precipitations and dissolution and more time acids and bases and Redox reactions I guess.

So the reason for looking at this holistic picture is you know most chemical processes can be you know very broadly classified based upon 2 aspects let us see. Again, why would what drives the chemical reaction, now let us say or chemical process now. It is because relevant molecules or atoms involved would want to have a more stable structure of form with respect to their what is now the outer shell.

Arrangement of electrons in the outer shell they wanted to be more stable. So all the chemical processes are driven towards that particular aspect. So it is more stable, yes. So in general we can broadly classify you know these what do you say chemical process into 2 aspects. One where the oxidation state or oxygenation number or oxygenation state of the relevant atom or such would change and that obviously is the Redox process when the oxidation change state would change.

And the other aspects as in acid bases complexes and precipitation dissolution these come under the process where just we coordinative I can call that coordinative relationship I guess. So you know the 3 aspects as in acids and bases complexes and precipitations dissolution you obviously would not see any change in the oxidation state, but you would see a change in the coordination number let us say.

Or in the coordination partner would change again there is no change in the oxidation state and the relevant reactions are acid basis or complex formation or precipitation and dissolution. It is more or less they are based on coordinative relationships and again that is what I am trying to point out here. So let us move on and look at it great details. So for now we are going to talk about complexes in greater detail for may be a couple of classes or probably 3 or the most.

So let us look at why they are important. First we before we are going to any other aspect so we to look at why as an environmental engineering my concern with it let us see. So in general we as environmental engineers would need to look at complex formation or consider that whenever you have any particular system that deals with metals let us see. So obviously if we have heavy metal you are concerned with its removal or remediation.

Or such and you know aqueous complexes play a remarkably important role in that particular contents or just say let us say if we are adding a coagulant let us say Fe^{2+} or Fe^{3+} , Fe^{3+} . Again aqueous complexes are formed and they play a remarkably important role in those scenarios where you come across let us see metals let us say. So again before we go further let me just demonstrate what it is.

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Visual MINTEQ - Output

File Options

No. of iterations: 3

pH: 3.000
 Ionic strength: 4.02e-03

Sum of cations (eq/kg): 2.8010E-03
 Sum of anions (eq/kg): 1.7240E-03
 Charge difference (%): 24.788858

Concentrations and activities of aqueous inorganic species (mol / l) [Print to Excel](#)

	Concentration	Activity	Log activity
Fe(OH)2 (aq)	2.1779E-18	2.1799E-18	-17.662
Fe(OH)3	7.4344E-26	6.9409E-26	-25.159
Fe+2	8.9496E-04	6.7996E-04	-3.168
FeOH+	2.9194E-10	2.7256E-10	-9.565
FeSO4 (aq)	1.0503E-04	1.0513E-04	-3.978
H+1	1.0711E-03	1.0000E-03	-3.000
H2SO4	6.9529E-05	6.1553E-05	-4.211
OH-	1.0785E-11	1.0009E-11	-10.997
SO4-2	8.2903E-04	6.2987E-04	-3.201

[View species distribution](#) [Display saturation indices](#) [Equilibrated mass distribution](#)

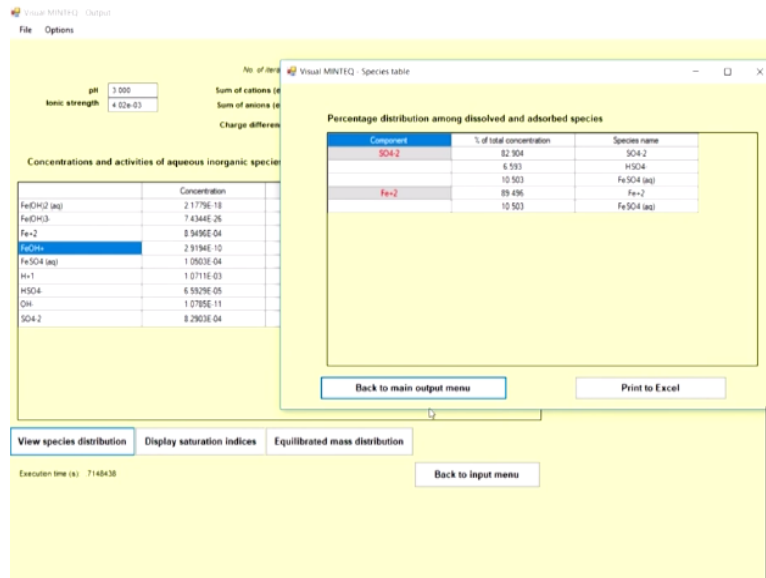
Execution time (s): 7148438 [Back to input menu](#)

I am trying to look at. So I am going to look at VMINTEQ and before we go further so I am going to put in have 2 forms of what do we say iron Fe^{2+} and Fe^{3+} that I am going to consider. So I am going to put in a random concentration of Fe^{2+} and also a random concentration of Fe^{3+} in VMINTEQ. I am going to substitute them or plug them in VMINTEQ. Ferrous and ferric I am going to plug them in at different concentrations and I am going to compare in what states are they going to exist.

So let us look at let us different pH values too. Let us have let us say the pH 3, 7, and let us say 11. So let us just look at this. I am just trying to demonstrate let us say what is that I am trying to talk about here. So let us switch to VMINTEQ here. So first I am going to go to let us fixing the pH at 3 and where is the key here 3 and I am going to put an Fe^{2+} and where is that let us see. Fe^{2+} and let us say I will say millimolar and may be 1 millimolar let us see and how come 1 millimolar add to the list and view/edit list.

So 1 millimolar I should have put in something with respect to so let us say what should be my source let us see it is going to be a FeSO_4 let us see. So to charge out to charge let us say I am plugging in I am putting in FeSO_4 . Yes, it is going to be source for Fe^{2+} and SO_4^{2-} . Let me plug that in here relevantly equivalent concentrations right so I am going to plug that in. View/edit list back to main menu and run MINTEQ. So now let us say I have the relevant concentrations at pH 3.

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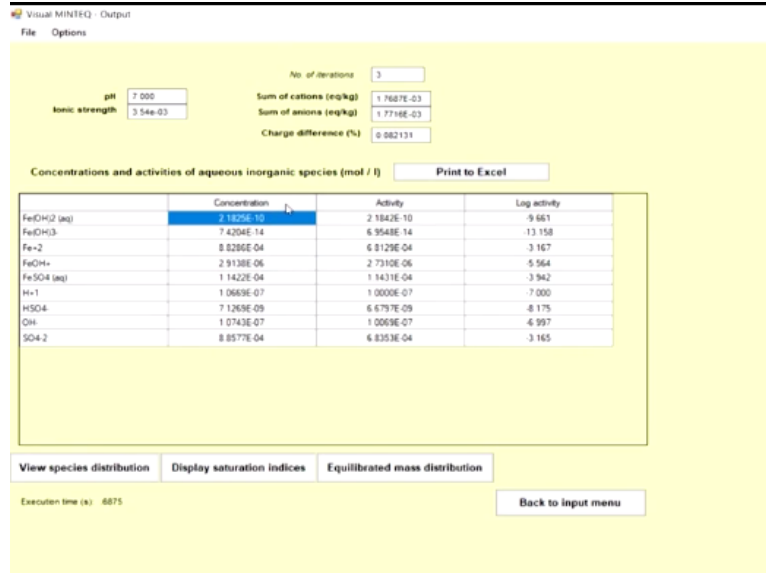
So now you see that you have Fe²⁺ and you have FeOH⁺ + FeOH²⁺ and FeOH³⁺ with negative charge. So Fe²⁺ is present in different forms here. So that is what I am trying to look at let us say and what are the complexes here that I am talking about. So here I have 3 complexes that are formed here. So the ferrous iron or ferrous is forming various complexes with OH⁻ and we see that we have I think for that particular concentration and that particular pH we have the relevant concentrations.

So what I am trying to say is we have let us see when you put in ferrous in the solution it does not stay only as ferrous it stays FeOH⁺, Fe²⁺ which is it is you know free metal and this is the free metal and these 3 are the complexes. So If I want to look at the relevant concentrations or relative concentrations part of me so I am going to look at new species distribution so looks like you know here they are not giving it to me with respect to the breakdown.

So again they are saying that Fe²⁺ will be present as you know in different forms as Fe 90% of it in different forms and this does not give me great idea here so I am going to go back to the main menu. So again if I look at the total concentration of Fe²⁺ it is present as FeOH²⁺, FeOH³⁺, negative charge, Fe²⁺, FeOH⁺ positive charge in FeSO₄, but it is present as free metal only at this particular concentration, but that is had pH 3.

Let us see what would happen if you know I increase the pH keep in mind that the free metal concentration is relatively high compared to FeOH and the other 2 complexes I guess. Different orders of magnitude so I can neglect the concentration of the complexes. So if I increase the pH what would I see here?

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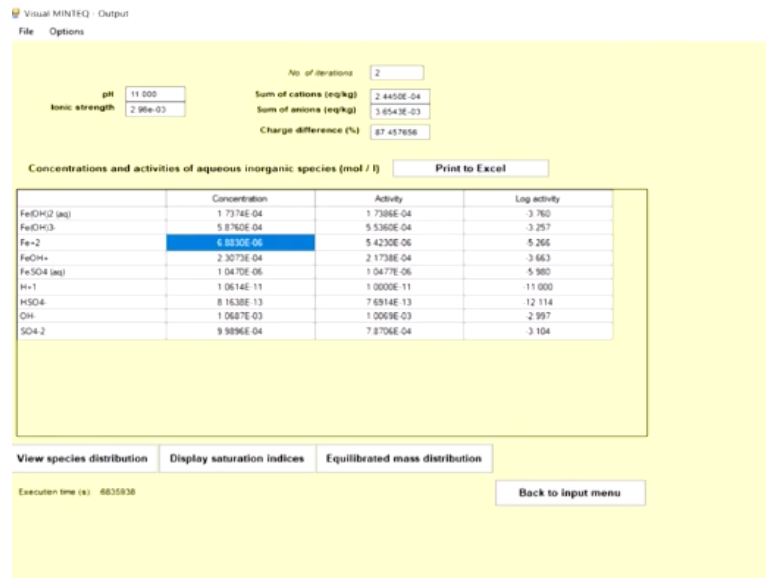
So I am going to increase the pH to let us say 7 now as we just talked about earlier and I am going to run MINTEQ and now let us say Fe²⁺ concentration is still relatively similar, but the concentration of the complexes 1, 2, and 3 complexes they have relatively increased. Why is that say we are talking about complexes here? You know metal and ligand we are going to discuss this later.

I am just trying to explain a few or help you visualize what it is that we are going to talk about. You have a metal which is electron poor compound and you have a ligand which is an electron rich compound. So a complex is nothing but let us say a soluble species formed by a combination of an electron poor compound which is a metal and an electron rich compound which is the ligand between an electrophile and a nucleophile.

Again we are going to discuss this later, but keep in mind for complex to be formed you need a metal and a ligand. A metal means it is electron poor and ligand usually is electron rich compound. So again here you see because you increase the OH⁻ concentration. When you

increase the pH from 3 to 7 what is happening. You are increasing the OH⁻ concentration. So obviously the Fe and OH what do we say complexes are going to be relatively high concentrations but you still see that compared to the free metal concentration of Fe²⁺, FeOH and FeOH₂ are still at relatively low concentrations.

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So again I am now going to change the pH to be 11 and I am going to run MINTEQ. So again I guess you still see a further increase in your particular complexes. FeOH⁺, FeOH₂ and FeOH₃ and only you see that the actual free metal concentration is much lower. So as you kept increasing the pH of your solution and you are looking at the speciation of Fe²⁺ and if you are considering the various complexes form at pH 3.

And 7 you saw that the free metal was predominant in the solution, but at pH 11 what is that you are observing. You are observing that the complexes FeOH⁺, FeOH₂ and FeOH₃ they are almost 2 orders of magnitude higher than the free metal concentration. So this is what you need to keep in mind because you know free metal concentrations are what we let us say might consider depending on the scenario.

So depending upon the pH or in this case the ligand concentration, ligand here is OH⁻. Depending on the concentration of ligand or the type of metal you know your speciation or the

relative concentrations of you complex or just the free metal they are going to change. So this is with respect to Fe^{2+} + just keep in that in mind.

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Aqueous Complexes

Why?

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

pH 3

pH 7

pH 11

Equilib. are fast
Kin. are fast

✓ A & B

{ Complexes
Precip & Dissol. }

} Coordinative relationships

✓ Redox

So now we are going to run the trial with respect to FeCl_3 . So we put in a source of FeSO_4 that is why we plugged in Fe^{2+} + and SO_4^{2-} - and if I am putting in FeCl_3 that is going to dissociate into Fe^{3+} + and Cl^- . 3 Cl^- . So that is what I am going to plug in now. I am going to check why am I trying to do so? Earlier I plugged in FeSO_4 to see what complexes can Fe^{2+} form. Now I am just trying to illustrate to you what are the complexes or what is the behaviour of Fe^{3+} .

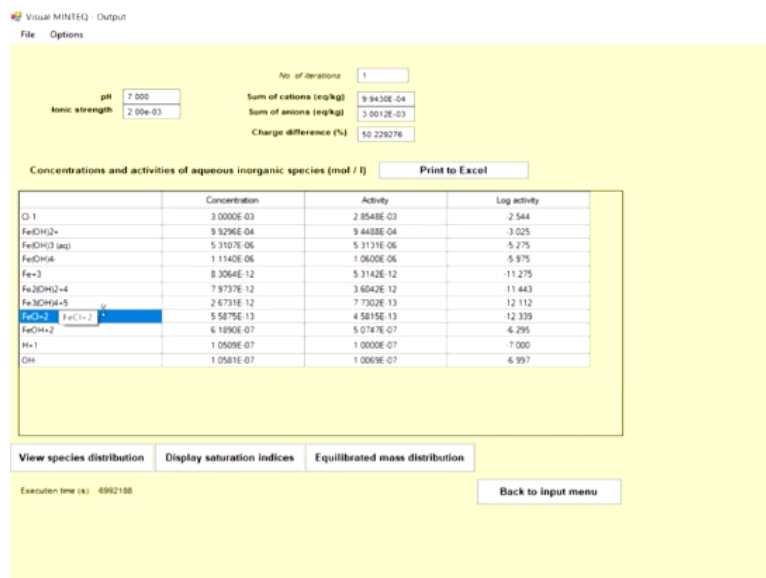
Now we are going to look at some particular relevant aspects are here. So go back to input menu. So I am going to again start with pH at 3 and now I need to edit the list. I am going to delete Fe^{2+} + and SO_4^{2-} - and back to main menu and now I am going to plug in Fe^{3+} + initially and where do we have Fe^{3+} + that is here. I will stick with 1 millimolar add to list and then Cl^- . Cl^- - and that has to be 3 though. 3 millimolar and I add that to the list. The pH e is at 3.

Let me check my components Fe^{3+} + and Cl^- . I am going to run MINTEQA2 and let us look at the output now. At pH 3 and I have free metal concentration here $\text{Fe}^{3+} + 1 \times 10^{-4}$. Earlier we had 1 millimolar and now keep in mind that is almost a 10th of it even at low pH 10^{-4} . 1 millimolar was 10^{-3} concentration total, but here you see Fe^{3+} + can form a lot many more complexes as and let us start with few OH would we have that somewhere here.

We have that here. FeOH^{2+} charge. And you have multiple complexes 1, 2, 3, 4, 5 and with Cl^{-} it can form a complex again 6. So what you see is Fe^{3+} can form a lot more complexes so even at low pH if you look at that the free metal concentration is considerably affected and some of the complexes like FeOH^{2+} with 4 charges. Fe^{2+} with 4 charge is as high concentration as Fe^{3+} and also look at FeOH^{2+} or FeOH^{2+} . FeOH^{2+} with 2+ charge.

You see that it is 10^{-4} concentration. It is greater than the free metal concentration. For Fe^{2+} you saw that at pH 3 or 7 the free metal was predominant and only at pH 11 was the free metal concentration relatively lower, but for Fe^{3+} you see that even at pH 3, the concentration of the aqueous complexes that Fe^{3+} forms are higher than or relatively comparable to the free metal concentration. So let us go back to pH 7 scenario.

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I am going to change this to pH 7 and here pH 7 and run MINTEQ. So again same case I am going to look at the relevant concentrations. So now you see that Fe^{3+} is now 10^{-12} earlier at pH 3 it was at 10^{-4} concentration. So now again you see that the complexes are at much higher concentrations and predominant complex is FeOH^{2+} with 2+ charge so again what is this tell you. So if you put in a source of Fe^{3+} let us say pH 7 it is not going to stay as Fe^{3+} .

It is going to form multiple complexes and one of those complexes is going to be predominant in concentration. So let us say if you have some other reaction that depends on the free metal concentration is that going to be relevant not really why is that because the free metal concentration Fe^{3+} staying as Fe^{3+} so is remarkably less which is 10^{-12} in this case and one of the complexes is at concentration of 10^{-4} , 8 orders of magnitude higher.

So that makes it a critical difference in your particular system or the interactions there in. So again obviously if I keep increasing the pH 2 to pH 11 obviously again that trend is going to worsen further as in free metal concentration is still going to be pretty low and the aqueous complexes. Here because I am only changing the pH or the ligand concentration which is OH^- - Cl^- that is why we are looking at only a few OH obviously you can have a metal and different ligands to as in here I guess we even had Cl^- - I can call that I guess as complex 2.

So let us go back, change the pH to 11 and run MINTEQA2 and what do I see here and I see that Fe^{3+} concentration is now almost 10^{-13} times lower than what it is was at pH 7. So what is this telling you now that may be Fe^{3+} would stay as Fe^{3+} at lower or acidic pH but in neutral or basic pH or basic solutions the free metal concentration is going to be negligible, but only the concentration of the complexes is going to be relevant.

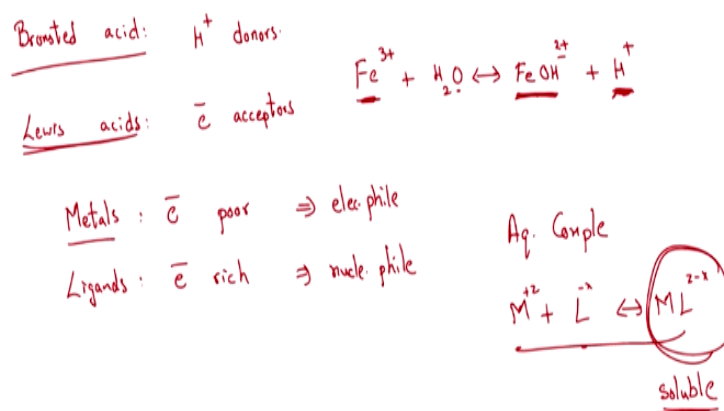
So which complex is predominating you $\text{Fe}(\text{OH})_4^-$ with a negative charge is what seems to be predominating and it is more or less $= 10^{-3}$. 1 millimolar was what we put in initially of Fe^{3+} so here it shows as that you know $\text{Fe}(\text{OH})_4^-$ with a negative charge is almost = the total iron that you put in initially make sense hopefully. All the free metal that you initially plugged in is now present as this kind of a complex.

So any interactions or any reactions that you think might occur with that particular Fe^{3+} . They are now going to be negligible. So again this is what we are going to talk about I just took example of ferrous and ferric iron to illustrate the example here. So let us go back to our particular case. So Fe^{2+} we saw that it is considerable quantities at pH 3 and pH 7 and so, so at pH 11, but Fe^{3+} is at considerable quantities only at pH 3 and at pH 7 and 11 it is at remarkably low concentrations and that is what we observed here.

So again Fe^{2+} is in general you know does not form a lot of complexes as you just observe, but Fe^{3+} really stays as free metal it forms complexes. So that is one peculiar aspect. So again let us again look at the bigger picture. So forming an aqueous complex you need a metal and a ligand and a metal is an electron poor compound let us say and the ligand is an electron rich compound. So thus you need a combination of these 2 a metal and ligand to be able to form your relatively more soluble species which is your aqueous complex.

So let us go further and discuss some of the basic aspects.

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So if you remember particular definition of bronsted acid. How do you define acids in our acids and basis? We mention that there would be H^+ donors, but in same case we also looked at Lewis acids and we define them as electron acceptors. So here we can understand the aqueous complex formation in terms of Lewis acids or basis or electron acceptors or donors. So let us look at 1 example here let us see.

So 1 of the example I guess I have here which is $\text{Fe}^{3+} + \text{H}_2\text{O}$ so if I put in Fe^{3+} into the solution and H_2O and let us say at a particular concentration or such it can or it will be in equilibrium with FeOH^{2+} and thus the charge is going to be $2+$ and now it is going to obviously release the

H⁺. So going by the definition of bronsted acid you know Fe³⁺ can act as an acid because it is leading to or it is donating a proton here.

It is ending up increasing the concentration of H⁺ that is why you can call that as a bronsted acid or obviously as a Lewis acid because Fe³⁺ which is electron poor where pull the electrons from the oxygen atom yes and form a complex. Again it is accepting the electron here let us say in a way and that is why you can call that as a Lewis acid 2 makes sense hopefully. So here you have electron acceptors we remember or you know refresh your memory.

We looked at acids and 2 definitions 1 is bronsted acids where we say if a particular component is donating H⁺ we classify that as an acid or if it is accepting an electron we can call that as a Lewis acid or an acid let us say. In general, bronsted acids are subset of Lewis acids. So obviously here the example we have here is Fe³⁺ in addition to water. So Fe³⁺ is electron poor and oxygen is electron rich.

So it accepts the electron let us say kind of accepts you have done that is for your particular understanding let us see and it forms the complex FeOH²⁺ with a 2⁺ charge and in the process releasing H⁺. So this is 1 particular example that we look at. So obviously what do metals look for let us see because they are electron poor they are electron poor that means they are electrophiles and ligands are electron rich or nucleophiles, phile means you have tendency to I think attract or such.

You can look at the definition for the root word phile means so a metal when we saw it is an electrophile or an electronphile. So it wants to attract electrons so now it is an electron acceptor. So that is what we look at. So your aqueous complex you need a metal and a ligand, electron poor and electron rich and you will end up forming a complex let us see + Z and - x charge you know I am just going to say generic term is the charge is at - x and in general your aqueous complexes are relatively more soluble.

The aqueous complexes are relatively more soluble. Keep that in mind because we are going to look at that later on I guess. So let us move on.

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Terminology

- Complex = soluble specie formed by combination of electron rich compound (ligand) and electron-poor compound (metal)
- Central atom = electron-poor compound in complex
- Ligand = electron-rich compound in complex
- Co-ordination number = number of ligands per central atom

So we are going to look at few terms I guess and with respect to terminology what is a complex obviously. It is a soluble species and it is formed by combination of electron rich compound which is a ligand and a electron poor compound which is the metal so 3 aspects here first you see more soluble species and you need an electron rich compound which is your ligand, electron poor compound which is your metal and ligand has a generic example.

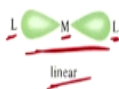
You know water you have OH⁻, but you have various other ligands you know Cl⁻, CO₃²⁻ and so on. And any what let us look at what else we have here. You need an electron. We have a something called central atom so that is the electron poor compound in your complex which usually means it is the metal. So central atom is the metal here in general electron poor compound next aspect is ligand it is the electron rich compound in the complex this is something we discussed earlier.

Electron rich compound in the complex and here now we come to a particular aspect a co-ordination number. So co-ordination number gives us says an idea about number of ligands per the central atom and that helps us in understanding the structure of your compound again if you remember we classify acids and basis, aqueous complexes and what else now precipitation and dissolution as being based on coordinative relationship.

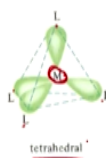
And in that case we also talked about coordination number and such. So coordination is nothing but number is nothing but in the context of aqueous complexes, number of ligands per central atom. So it can have different numbers so based on the different coordination numbers you will have different structures so let us look at some of the usual coordination numbers and structures.

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Co-ordination number



Two:
linear complex (L-M-L)



Four:
tetrahedral (L at edges of pyramid, M at middle, equal distance between each L and M)

So if you have 2 ligands the 1 central atom usually we have a linear complex and this is the structure that you would observe yes 2 and in general most of the complexes you have would be would have even coordination numbers. Some might have 5, but that is relatively rare or very rare though. Usually you will have 2, 4, or 6.

So 2 it is going to be linear and that is what we see here and if it is 4 there are 2 kinds of shapes or 2 structures I guess, 1 is tetrahedral with LLL edges of pyramid and central atom, the metal is here and the other ligand here more or else a pyramid and equal distance I guess are equidistance between the metal and the ligand or the central atom and the ligand. So tetrahedral shapes usually more stable

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Four:

square planar (L at edges of square, M in middle)



Six

Octahedral (L at corners of square and above and below, M in middle)

And second aspect or second kind of shape with 4 central atoms is the square planar again self explanatory in the same plane, 4 ligands per central atom so the coordination number is 4 and square planar I guess and 6 obviously so we have an octahedral shape usually you know 4 in 1 plane and L and L above and below.

4 ligands in 1 plane and the other 2 ligands 1 above and 1 below. So again what is the coordination number, number of ligands per central atom and central atom is the electron poor compound in your particular complex and that is what we looked at here. We usually come across what are the complexes with coordination numbers of 2, 4, or 6. So let us move on look at what else we have here.

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- Monodentate = one electron-rich structure per ligand, i.e. one binding site
- Multidentate = more than one electron rich structure; tend to be stronger
- Chelate = multidentate complex

Few terms nothing to mug up but let us say if somebody is speaking about it you need to be able to understand what is that they are referring to so we have a few what do we say terms here monodentate, multidentate and so on let us see what it is that we are about. So monodentate is when we have 1 electron rich structure per ligand. More or less it means 1 binding site. So if it has your particular structure has you know electron rich structure has 1 binding site you will call that a monodentate obviously if it is more than 1.

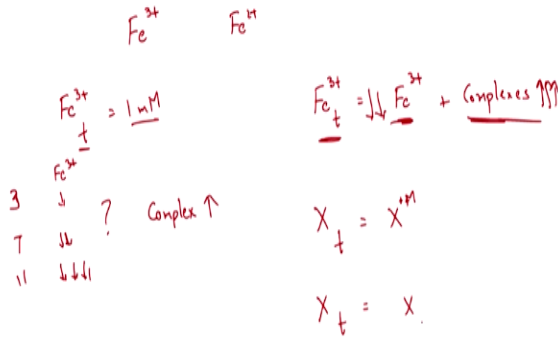
If you have more than 1 electron rich structure you would obviously call that to be a multidentate and obviously they will tend to be stronger. So monodentate, bidentate, tridentate and so on more or less means either 1 binding site, 2 binding sites or 3 binding sites and respectively. So the next aspect would be looking at Chelate. Chelate is a complex first keep you understand that it is a complex which is formed with a metal or a couple of metals let us say or more than a few metals and is multidentate I guess.

So it is a complex that has more than or that involves more than 1 binding site and these are called the Chelates and they are relatively more what is now stable. So let us move on. So again what is the importance of these particular aqueous complexes now? So we will briefly touch up on that for today's session. So again we are talking about metals. So let us consider 2 aspects let us see 1 one would be let us say we are talking about heavy metals.

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Importance

(total concentration of metal not equal to concentration of free metal)



And in this case let us say we are talking about total concentration of metal is not equal to concentration of free metal that is what we discussed earlier when we talked about Fe^{3+} and Fe^{2+} . For example, I put in Fe^{3+} total was 1 millimolar, but I saw that at different pH either 3, 7, or 11 my actual Fe^{3+} concentration Fe^{3+} total is still constant there is still 1 millimolar, but Fe^{3+} concentration was decreasing and further decreasing with increasing pH and why is that because the concentration of the complexes was increasing.

For example, let us say to simplify that Fe^{3+} total or Fe^{3+} total let us say is = the free metal Fe^{3+} + all the complexes let us see. So obviously here for Fe^{3+} though we saw that in general the concentration of the complexes is much higher and the concentration of the actual free metal is relatively lower, but obviously the total free metal concentration is going to constant let say. So let us see you know with this in mind let us say when is this an issue let say.

Let us say you have a heavy metal and let us say that the free metal is toxic. If your free metal is toxic so then let us see how would your particular system be affected by formation of complexes now. So keep in mind there let us say if in that particular system or that particular heavy metal if the free metal is what is toxic and if you add ligands what is going to happen you are going to have complexes being formed and what will that lead to it can lead to the decrease in the free metal concentration.

So let us see initially we had only let us say it consists some metal x , X total was = the x free metal let us say $+ Z + m$ charge, but after adding a ligand what can have what can happen x total will be now = x_1 m of free metal concentration which is going to be lower because now I am going to have formation of complexes. So thereby you are reducing the free metal concentration thus the toxicity of the particular solution decreases.

So with that I guess I will end today's session and we will continue this forward we will talk about or have a brief discussion about the importance how solvability is affected and so on and also look at some of the practical applications with when you would come across in titration and then move on to the equilibrium aspects and so on and with that I end today's session and thank you.