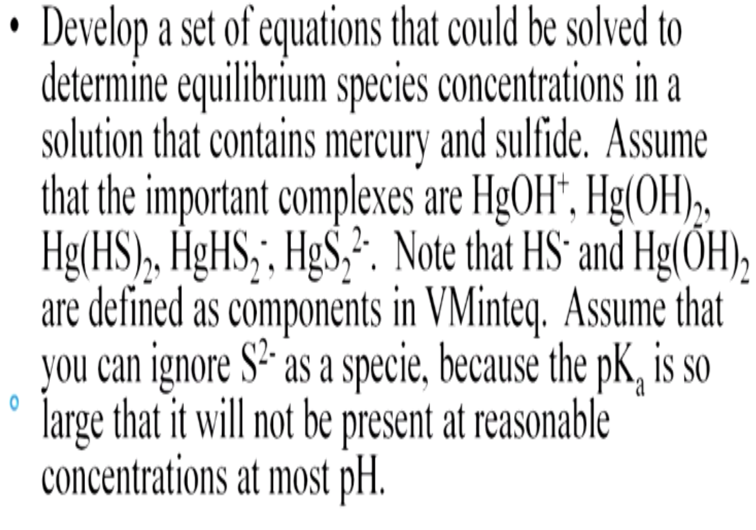
Environmental Engineering: Chemical Processes
Prof. Bhanu Prakash Vellanki
Department of Civil Engineering
Indian Institute of Technology – Roorkee

Lecture 39
Aqueous Complexes of Mercury (Hg)

Hello everyone, welcome back to the latest lecture session. We have been discussing aqueous complexes and I believe we are going to look at a couple of examples today. One we are going to set up the equations manually and based on that we are going to look at the applications in VMINTEQ I guess. We are going to wrap up the aqueous complex based relevant sessions, but hopefully this particular session should help you understand or get a holistic view of what it is.

We are trying to talk about or discuss in relation to the aqueous complexes. Here I have an example. Here we are going to first set something up manually.

(Refer Slide Time: 01:02)



- Develop a set of equations that could be solved to determine equilibrium species concentrations in a solution that contains mercury and sulfide. Assume that the important complexes are $HgOH^+$, $Hg(OH)_2$, $Hg(HS)_2$, $HgHS_2^-$, HgS_2^{2-}. Note that HS^- and $Hg(OH)_2$ are defined as components in VMinteq. Assume that you can ignore S^{2-} as a specie, because the pK_a is so large that it will not be present at reasonable concentrations at most pH.

Because you need to understand how it is going to be relevant to the second question, which we are going to look at in a minute time. Here we are going to develop a set of equations, so that you can determine the equilibrium species concentration and what does the solution contain. It contains mercury and sulfide, toxic heavy metal and sulfide, again a ligan. This is the electron pore compound and the electron rich compound here.

But here one aspect would be that there are multiple or remarkable number of feasible complexes with respect to HgOH, Hg and OH or Hg and S, but here I guess you known we cut down on all the relevant complexes, but we are only going to look at those complexes, which are going to be at relatively higher concentrations. Those higher concentrations I guess are those complexes, which are going to be at higher concentration or going to be HgOH+.

So two forms of HgOH complexes and three forms of Hg and S complexes. Again we need to develop equations such that we need to solve for these particular species as in their equilibrium concentrations. So here obviously I guess we have some other relevant right appear, but the P is that in general, say, from our background what you would usually choose as your components now. What is the approach here. You list the species.

The species are already given based on the relevant prior experience, I guess and then we are going to list the components, but in general based on our particular background thus far, what would we usually choose. We would choose the metal, which would be Hg2+ and then the ligan as 2- and H+, but that can lead to what do we say complexities in solving this particular solution and here let us say we can look at the usual components that we may take into uses.

So once we look at that, let us say it can aide us in choosing the components for solving by hand too. So you can choose those components Hg2+, S2- or S with a negative charge of -2 and also the H+, but it can take longer to arrive at your particular solution. So obviously we can look at what are the component VMinteq chooses and looks like VMinteq chooses HS – or has HS- and HgOH twice as its components. So let us just check that.

(Refer Slide Time: 03:40)

Visual MINTEQ

Activity Davies

Concentration unit: Molal

pH: Calculated from mass balance

Ionic strength: To be calculated

Temperature: 25 deg C

Add components

Component name: Select from list

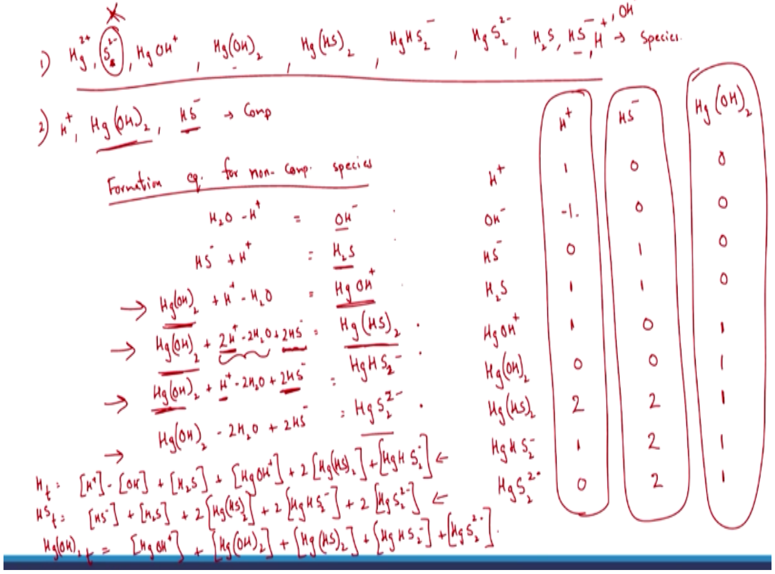
Total concentration: 0 Molal

So we are going to look at, do we have HS- here, there we have that. Let us check if we also have S-2, we do have S-2, but for this particular case, it makes more sense to choose HS- and where do we have the HgOH twice here. So we have HS- and HgOH twice here. So we are going to choose these as components, because in general that will lead to let us say easier solution or faster calculation, let us see.

We are going to move, so again here we are going to choose HS- and HgOH twice as the components. Another aspect is the question says S2- can be ignored because PK is so high, that it will not be presented most pH. S2- as we know that S2 has the acid base, HS- and S2-, lets us. So this will obviously from your acid base background too, you know that this will be present only at what do we say pH greater than the pKa.

But we are saying that, the questions says that the pKa is so high that in general you can neglect S2- as species. With this set of information, let us go through. First let us write down these particular species and their HgOH+ and HgOH twice and what else, HgHS twice.

(Refer Slide Time: 05:29)



1) Hg^{2+}, S^{2-}, $HgOH^+$, $Hg(OH)_2$, $Hg(HS)_2$, $HgHS_2^-$, HgS_2^{2-}, H_2S, HS^-, H^+, OH^- → Species

2) H^+, $Hg(OH)_2$, HS^- → Comp

Formation eq. for non-comp. species

$H_2O - H^+ = OH^-$

$HS^- + H^+ = H_2S$

→ $Hg(OH)_2 + H^+ - H_2O = HgOH^+$

→ $Hg(OH)_2 + 2H^+ - 2H_2O + 2HS^- = Hg(HS)_2$

→ $Hg(OH)_2 + H^+ - 2H_2O + 2HS^- = HgHS_2^-$

→ $Hg(OH)_2 - 2H_2O + 2HS^- = HgS_2^{2-}$

$H_t = [H^+] - [OH^-] + [H_2S] + [HgOH^+] + 2[Hg(HS)_2] + [HgHS_2^-]$ ←

$HS_t = [HS^-] + [H_2S] + 2[Hg(HS)_2] + 2[HgHS_2^-] + 2[HgS_2^{2-}]$ ←

$Hg(OH)_{2,t} = [HgOH^+] + [Hg(OH)_2] + [Hg(HS)_2] + [HgHS_2^-] + [HgS_2^{2-}]$

	H^+	HS^-	$Hg(OH)_2$
H^+	1	0	0
OH^-	-1.	0	0
HS^-	0	1	0
H_2S	1	1	0
$HgOH^+$	1	0	1
$Hg(OH)_2$	0	0	1
$Hg(HS)_2$	2	2	1
$HgHS_2^-$	1	2	1
HgS_2^{2-}	0	2	1

HgHS2-, HgS2-, is that what we have. That is what we have. Then what are the other species obvious to that you need to choose. Again the key is that this mentions that assume that the important complexes, these are only the important complexes. Obviously you need to choose the relevant conjugate acid base species and the other metal too. So you are going to have Hg2+ you are also going to have S2-, but the question says you can neglect S2-.

So this is something I am going to neglect and the other five species are mentioned because these are the only predominant species. There are many other species feasible that will occur or you would come across in the solution, but these are the species that we are considering because they would be presented relatively higher concentrations and then obviously the conjugate acid-base H2S and HS-. So these are the relevant species and what are the components here.

Again, the question mention that using VMintiq, we can choose the relevant components and I believe that asked us to choose H2S, is it, HS-, I guess. Choose HS-and HgOH twice as our components HgOH twice and HS- as our components and why is that. Again because VMintiq chooses these as components. HS-and HgOH twice. So because let us say we are going to look at the second question using VMintiq to be able to solve for this particular solution.

So it obviously again makes more sense to set up the total component concentrations. In those components, which you can obviously translate to in VMintiq. So HS- and HgOH twice are the components here. So these are the components and these are the species. So let us go with the formation equations for the non-component species formation equations for non-component, species. So first let me list those species, which are non-component.

They are going to be OH-, let us say H2S, HgOH+, HgHS twice. HgHS2- and HgS2-. So these are the non-component species, so how can I form them. Here obviously it is H2O-H+ will lead to formation of the OH-, so here now I am trying to form H2S, but my component here is HS- so how do I manipulate HS- to arrive at H2S, so I can then add obviously I need to have H+ as my component. It is always a component. H+ is always a component.

HS-+H+will lead to my H2S. So I am done with that and here I am now with HgOH, but the relevant component that I have is HgOH twice. So how do I manipulate HgOH twice to be able to arrive at HgOH, so if you look at, it is more or less equivalent to addition of one particular proton or removing OH-. If you think of it, how do I go from HgOH twice to HgOH+ now. I know either addition of H+ or which more or less transforms to removing OH-.

So that is nothing but addition of H+ and to balance it out I obviously need to write in the water. So that is what we have here. The next equation is now going to be equal to what is it here please, HgHS2. Again how do I end up with HgHS2. So again the relevant component I am going to start with is HgOH twice, so now look at what it is that I need to transform it into. I have HgOH twice as my building block, but I need to end up with HgHS2.

More or less here we have HgOH twice and we want to go to HgHS2, so in effect means I want to replace the 2OH- with 2HS-. So that is what we have here. So obviously I need to remove the 2OH- and that is in effect going to be equivalent to adding 2H+-2H2O, so this is in effect removing the OH- and obviously to be able to arrive HS, I need to add HS is again my component here, so I need to add 2HS-.

So that is what I have here and with that again, if you look at it HgOH twice, I need to remove the 2OH-, so that is what I am doing here by addition of 2H+ here and I need the HS, so that is why I am adding 2HS-. So again what are we trying to develop. We are just trying to develop what is our intuition about how different complexes can be formed from the components here. So again here same case, I am going to try to repeat that here.

Here again, I am going to start with HgOH twice, but here compared to the earlier species, we have 1 less H, so I am going to add only 1 less H here, so that is going to be H+-2H2O+2HS-. What is the only difference between here and here. As you see there is 1 less H, so that is obviously here I am going to decrease the number of protons that I need to add compared to the previous scenario.

Again same case here compared to the previous preceding species, I need to have 1 less H+. So again I am going to decrease this 1 H+ here, so it is going to be equal to HgOH twice -2H2O+2HS-. So with that done, I am able to form all my non-component species. So again what did we just try to illustrate now. So usually we choose Hg2+ or H2- and H+ or we would have chosen them, but because we are going to look at VMintiq later and VMintiq choose these components, we are trying to choose those components, which we usually do not.

Because VMintiq chooses them, we are looking at them and we are trying to come up with relevant species from these unique components that we have not come across. So let us write the total component equations here. H+, HS- and HgOH twice. So now let me list all the species. They are going to be H+, OH-, obviously I should have listed H+ here and OH- as my species. You will always have H+ and OH- as your species.

Here is something that we missed earlier, so H+ and OH-and then the relevant what do we acid bases HS- and H2S. We would have had S2-, but as the question indicates S2- is at very negligible concentrations, that is why we are not having S2- here and these are the 2 acid-base species that we are going to consider instead of the 3. Then, I am going to list all the 4 complexes here, so they are going to be HgOH+, HgOH twice, HgHS twice and HgHS2- and HgS2-.

So from the formation equations, let us write them down. It is going to be equal to H+ here and 0, how do I form OH-, I need -1 here, 0 and 0 here, how many HS- do I need usually I guess, yes, but here HS- itself is a component, so it is going to be HS- is 1 and 0 and 0 and how do I form H2S, so I need 1H+ and 1HS- and this is going to be 0 and how do I form my HgOH+, looks like I need 1H+. I am looking at this equation and I need 1HgOH twice.

I do not need any HS- and then HgOH twice and that itself is a component. So that is going to be 0, 0 and 1 and we need to look at HgHS2 and that is this equation. So what do I need here. I need 2H+ as we see here and how many HS-, again I need 2HS- and what else here, I also need 1HgOH twice. The next aspect would be HgHS2- and from this equation, I need 1H+ as I see here and 2HS- as I see here and 1HgOH twice as is obvious here.

Same case as here, so I do not need any H+ for forming HgHS2-, but I need 2HS- and 1HgOH twice. So now I am done with writing the tablo. So if you remember what are we trying to solve for, we are trying to solve for at least the minimum set of equations that can help us get at the equilibrium species concentrations. So obviously what is the key here. The key is always to write down the total component balance equations.

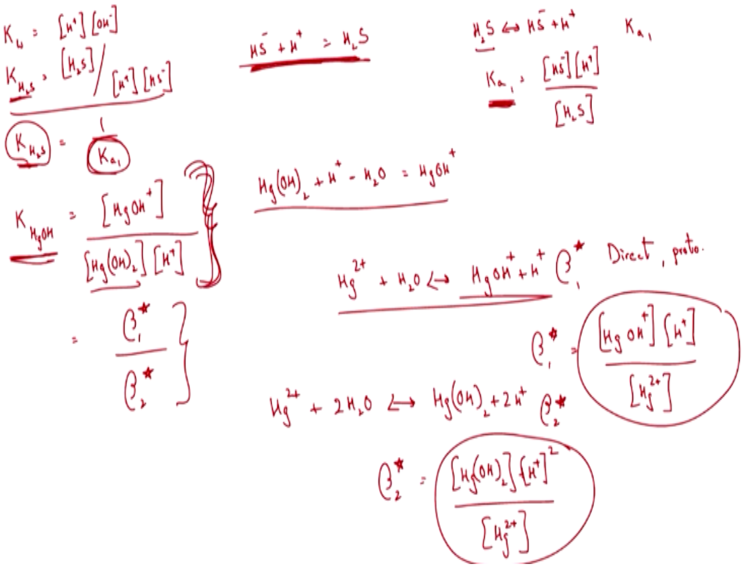
So I just need to plug in or write down the total component balance equation. So what would H total be equal to here, let us see. Let me see if I can sneak that up in here because I am limited in space. What would H total be equal to, H total will be equal to H+-OH- and 1*H2S+1*HgOH+ +2*HgHS twice and 1*HgHS2-. How did we get this equation obviously only from this particular total component balance here. Similarly we are going to write down for HS-, I guess. HS total that is going to be equal to HS-+H2S+2*HgHS twice+2*HgHS2-+2*HgS2-.

Just the coefficients and the relevant species here. Lastly we have HgOH twice total, that is going to be equal to 0, 0, 0 here, so it starts from here, it is going to be equal to HgOH++HgOH twice, +HgHS twice +HgHS2-+HgS2 2-. Thus we have the 3 total component equations. Now if we can express the different variables in terms of let us say just H+, HS- and HgOH twice, we will have 3 unknowns and 3 equations.

So right now, we have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 unknowns, but right now we have only 3 equations. So obviously we need to come up with 7 more equations, and where do we get these equations from, 2 from acid base, for H2S and HS- from acid base and for all these other 5 complexes, we can get them from our complex based equilibrium coefficients for the complexes and in general obviously we would like to express them as beta 1 star or beta star, beta 2 star and so on, but here as you see, they are bit garbled.

They are not as straight forward as with the aluminium and hydroxide relevant complexes that we looked at earlier. So let us just look at 1 particular aspect, so what are the relevant equilibrium coefficients.

(Refer Slide Time: 19:49)



Let us say they can be Kw=H+*OH- that is for one equation, let us say. I need 7 more equations. So another would be KH2S that is = H2S by H+*HS-. Where is this equation from. This is similar to the transformation equation, the formation equation that I have here. So K of H2S is going to be = K activity of concentration of H2S. Let me write down the equation here. This is relevant to this particular equation, HS-+H+=H2S.

So the KH2S for this particular case would be H2S/H+ and HS-, but you would not find such a coefficient in your particular relevant standard tables. So you need to transform these coefficients for these equations into those coefficients, which you can find from the standard table. So obviously as you know for acids what would be the standard value that we can look for. We can look for the acid dissociation constant.

So that is going to be equal to, for H2S it is going to be = HS-+H+. We know that this Ka1= the concentration of HS-*H+/H2S. As you see, we can just express KH2S = 1/KA1, so we would not find this particular value. Again where is this particular equation from, from your formation equation here. That is the relevant equilibrium quotient for this equation, though, but I want to express this particular constant in terms of constants, which would be available in my standard tables.

As we can see here with minor manipulation, we see that we can express it in terms of KA1, which is the acid dissociation constant for H2S and so on and so forth. So I can do that and transform that, so I have a relevant equation here. So let us move, let us see I can also have KHgOH and that is for which equation now, HgOH would be this equation here and how did you form that equation here. We had to come up with HgOH twice+H+-H2O=HgOH+.

So here I guess how do I go about writing this, so this would now be equal to concentration of HgOH+/HgOH twice*H+. This is for this particular equation. Again this is not in the standard form, so you would not find it in the standard tables. Now we need to be able to transform this into some products of, let us say, the standard forms, which we usually come across are beta1, beta2, beta3* and so on. So let us see how I can express this as that particular form.

If you look at in relevant detail, it is nothing but equal to beta1*/beta2*. Let us just see how that comes about. How do we know a complex can be formed by direct addition, let us see HgOH+, so direct addition again and if it is beta* what is it going to be now. It is going to be direct. I want to express it in terms of beta1*. It is going to be direct, but the protonated form of the ligan. So that is going to be = what now and what do we have here.

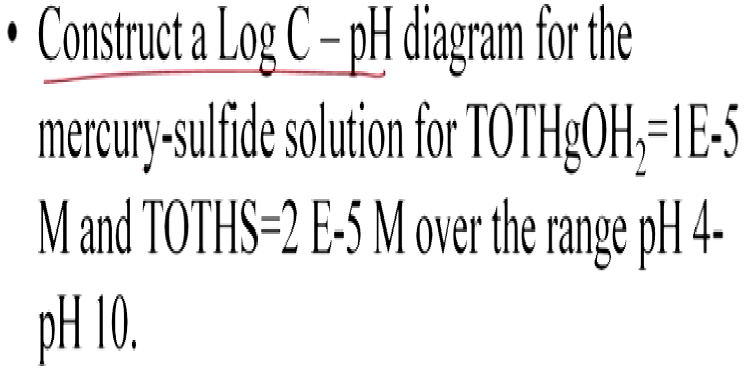
The protonated form will be equal to +H2O, then be equal to and I need to reason H+ and hopefully it is balanced now. So now we see that this is beta1* and what is beta1* obviously. It is equal to HgOH+*H+/Hg2+ and what would it be for HgOH twice. I am now trying to form HgOH twice, similarly I guess Hg2++2H2O, would be in equilibrium with +2H+ and this would be beta2*. Beta2* is obviously = HgOH twice*H+ square/Hg2+.

Obviously the division of beta1*/beta2* what do see that, that is nothing but equal to this particular set of terms. So now again I can express KHgOH in terms of beta1*/beta2*. Look at this dividing beta1*/beta2* what would that lead to, this particular set of variables. I now have KHgOH. Similarly I can calculate the relevant coefficients in terms of standard coefficients and so I can come up with 7 more equations.

If you remember earlier, we had 10 unknowns and now we had 3 component balance equation and with the relevant coefficients and equilibrium coefficients, or acid dissociation constants, I can come up with 7 more equations. So now I can express all the equations in terms of just what is it now, H+, HS- and the other component, which is I believe HgOH twice. So once I do that, I can solve for the relevant system and with that we are done here.

Now we will move on to the last example and that is going to be the case where we are going to look at application in VMintiq. Let us see where I have the example here.

(Refer Slide Time: 26:16)



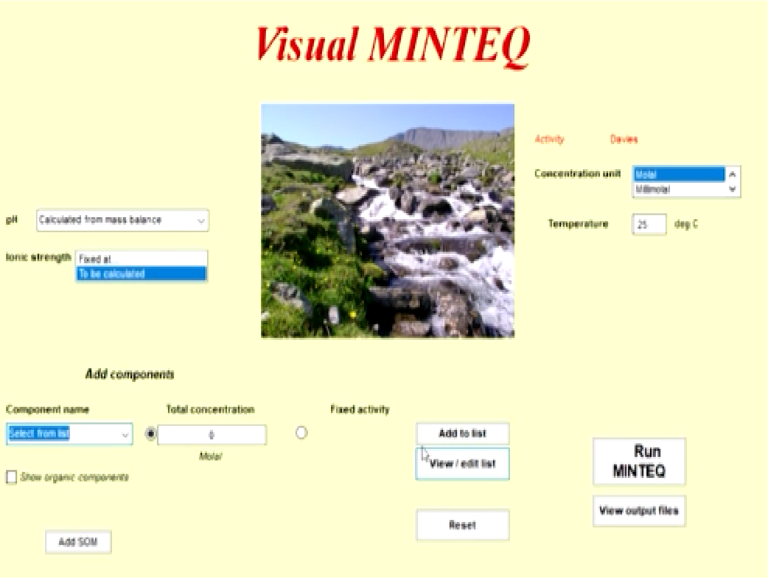
- Construct a Log C – pH diagram for the mercury-sulfide solution for TOTHgOH$_2$=1E-5 M and TOTHS=2 E-5 M over the range pH 4-pH 10.

Here we are going to look at constructing a log C pH graph. So if you remember in acid base reactions, we came across this that people look at log CpH graph to understand or have a snapshot or take a holistic view of your particular system. There are different ways obviously you can solve that by hand as we try to set up earlier. So let us say for example construct a log C pH diagram for mercury-sulfide solution when total HgOH twice is so and total HS is this value.

Let us say over range of pH4 to pH10, so you can solve this by hand based on what we just did earlier, but obviously for multiple range of H+, pH4 to pH10, it is going to be remarkably time consuming. You have better ways, what is obviously the better way, you can just plug in the relevant components in to VMintiq and how do you get the pH graph though. You know that multi sweep allows you to change 1 parameter and in this case we are going to change pH.

Rather than doing it by hand, we need to do what it is that we did earlier at each H+ concentration or at each pH, we need to solve for it and then develop the graph with log C here and pH here, so as we just looked at it that takes remarkable time, so what are we going to do. We are going to look at using VMintiq and use the multisweep problem. Let us see where we are up to, here already the question says, we have total HgOH twice as 10 power -5 molar and HS as 2*10 power -5 molar.

(Refer Slide Time: 28:01)



Visual MINTEQ

Activity Davies

Concentration unit: Molal

pH: Calculated from mass balance

Temperature: 25 deg C

Ionic strength: To be calculated

Add components

Component name: Select from list

Total concentration: 0 Molal

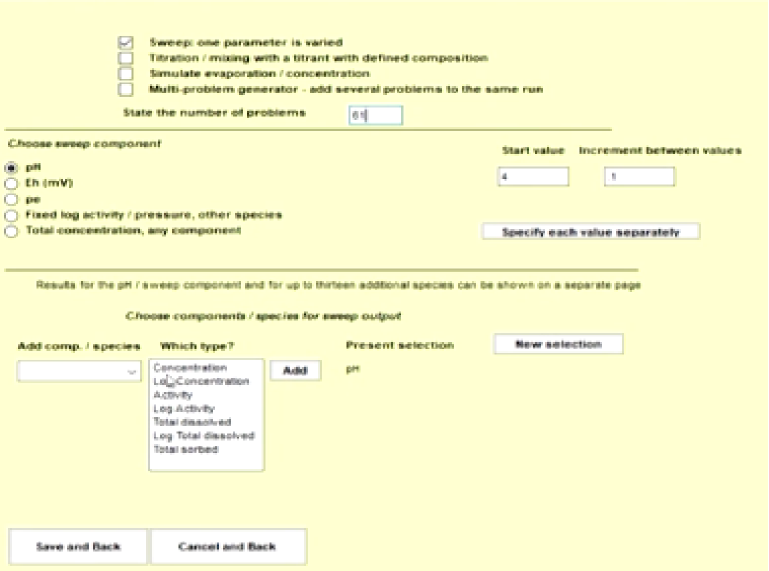
Let us switch to VMintiq here. The components are HS-, where is HS- here and what is the concentration of that HS- is 2*10 power -5, so we need to write that here, so molar and here it is going to be 2E-5, so VMintiq will take that as 2*10 power -5 add that to the list and then I believe it is HgOH twice and what is the concentration here. Total component for HgOH twice is 1*10 power -5, so 1*10 power -5.

So I am going to delete this here. This VMintiq takes E-5 as 10 to the power of -5 as excel 2, I guess. So add to list, let me just look at that, so I have HS-total component as 2*10 power -5 and HgOH twice as 10 power -5, so back to main menu. Now obviously multisweep problem and here I am going to sweep with sweep where 1 parameter is varied. Because the question, what is the question asked for, if you remember that?

It wants us to get the relevant information for pH4 to pH10. So I am going to vary the pH and ask VMintiq to do the job for me. Number of problems, obviously we are going to look at that. So increment value would be let us say, start value would be 4, increment value would be let us say 0.1, so 4.1, 4.2, 4.3 so on until pH10. So 4-10 would 6, 6*10 would be 60 and 1 addition, because we need to start with 4, it is going to be a total set of 61 problems.

So the number of increments between 4 and 10 includes of both the two values, so that is with that we can end up with 61. Because we are going from 4, 4.1, 4.2, so on until 9.9 and 10. So let us go with that.

(Refer Slide Time: 30:22)



☑ Sweep: one parameter is varied
☐ Titration / mixing with a titrant with defined composition
☐ Simulate evaporation / concentration
☐ Multi-problem generator - add several problems to the same run

State the number of problems: 61

Choose sweep component

● pH
○ Eh (mV)
○ pe
○ Fixed log activity / pressure, other species
○ Total concentration, any component

Start value: 4
Increment between values: 1

Results for the pH / sweep component and for up to thirteen additional species can be shown on a separate page

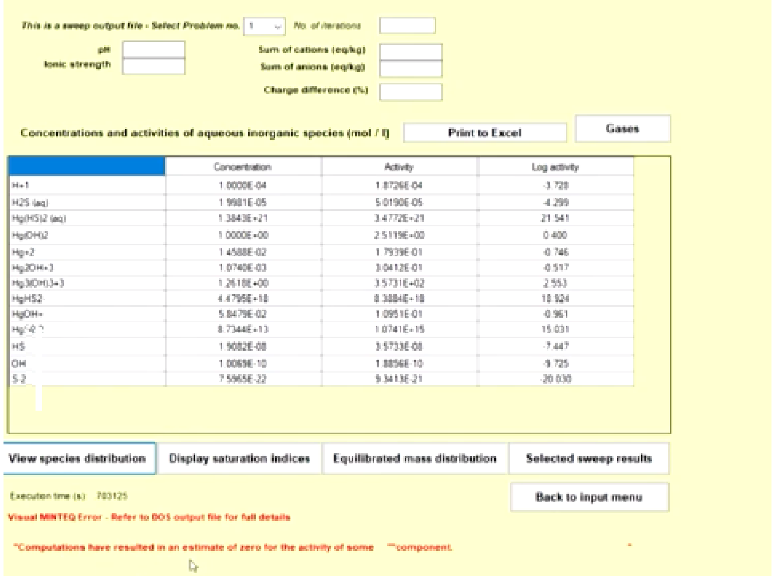
Choose components / species for sweep output

Present selection: pH

Obviously what am I looking for log C and pH. So let me add the relevant species here. We already have pH, so I am going to look at HS-, let us say log concentration because it is log C pH and what else, HgOH twice add and HgOH+. I am not going to add all the species, I am going to add those species which we know from our previous question that are going to be predominant, so they are going to be let us say HgHS2 and what else please.

These are not going to be predominant, so only the HS, HS2, we have this and S2-, so 1, 2, 3, 4, 5, and what else are we missing H2S and anything else that we are missing out here. That seems fine, so I am going to save and back and I am going to ask, so view at least we looked at that, run Minteq, that is it.

(Refer Slide Time: 31:25)



Concentrations and activities of aqueous inorganic species (mol / l)

	Concentration	Activity	Log activity
H+1	1.0000E-04	1.8726E-04	-3.728
H2S (aq)	1.9981E-05	5.0190E-05	-4.299
Hg(HS)2 (aq)	1.3843E+21	3.4772E+21	21.541
Hg(OH)2	1.0000E+00	2.5119E+00	0.400
Hg+2	1.4588E-02	1.7939E-01	-0.746
Hg2OH+3	1.0740E-03	3.0412E-01	-0.517
Hg3(OH)3+3	1.2618E+00	3.5731E+02	2.553
HgHS2-	4.4795E+18	8.3884E+18	18.924
HgOH+	5.8479E-02	1.0951E-01	-0.961
Hg[illegible]	8.7344E+13	1.0741E+15	15.031
HS	1.9082E-08	3.5733E-08	-7.447
OH	1.0069E-10	1.8856E-10	-9.725
S-2	7.5965E-22	9.3413E-21	-20.030

Execution time (s) 703125

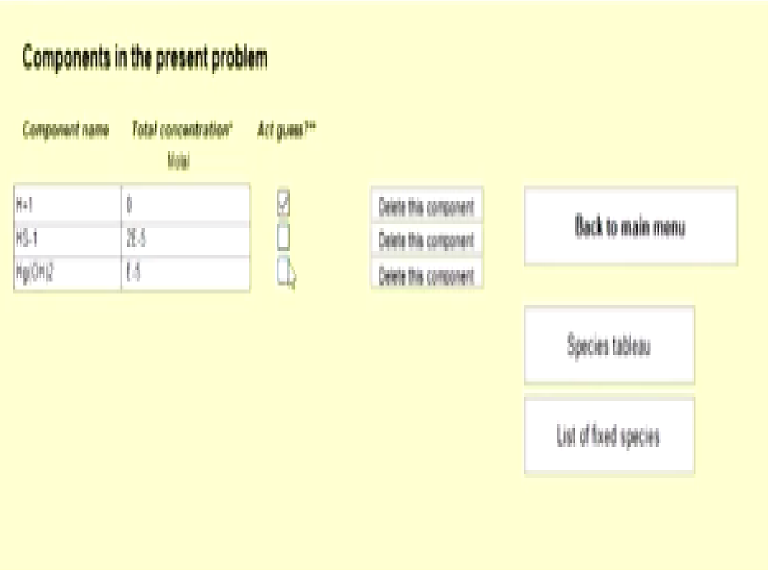
Visual MINTEQ Error - Refer to DOS output file for full details

"Computations have resulted in an estimate of zero for the activity of some ""component.

Here there is some issue here, what is the issue there, so computations have resulted in an estimate of 0 for activity of some components. Anyway the system that is used spacewide is remarkably complex, so that is why you know VMinteq itself had trouble arriving at the solution. For that, you need to provide some assistance to VMinteq as you need to have initial guess of some of the species. So let us look at how we can help with VMinteq with that.

So I am going to go here and when I do view list, can the activity be guessed for these 2 species.

(Refer Slide Time: 32:02)



Components in the present problem

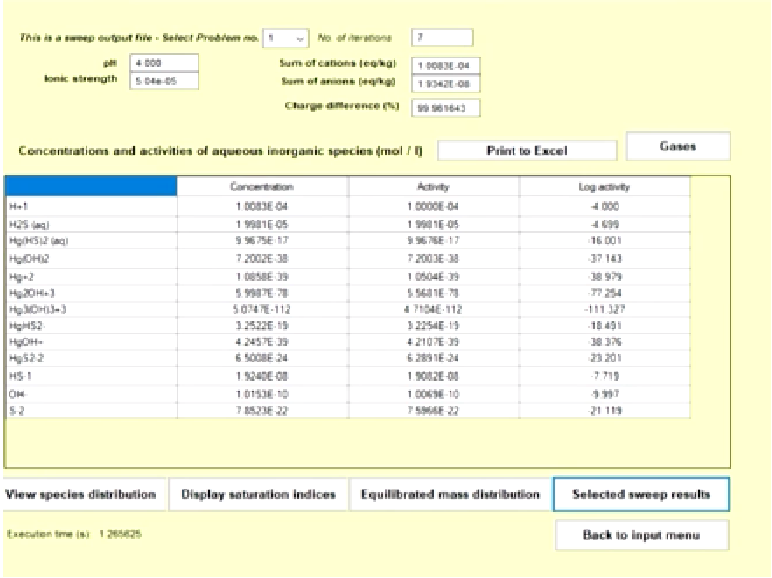
Component name	Total concentration* Molal	Act guess?**
H+1	0	☑
HS-1	2E-5	☐
Hg(OH)2	1E-5	☐

These are components, but as you see these are also species. If I uncheck this mark, what does this mean. No tick in this box means an activity guess of 10 power -16 molar. So what this means is if I uncheck this box, these components, which are also present as species, the VMinteq will start with an initial guess of 10 power -16 molar concentration, so that will be the basis for it to be able to solve for the solution.

It will arrive at the solution, but you are providing some assistance to it. Let us say obviously that is going to be the case for pH4, for obviously pH4.5 what is VMinteq going to do. it is going to use the results from pH4 to be able to solve for 4.5 and again 4.2 results will be based on 4.1 and so on, but if you give a huge gap between incremental pH values as you initially calculated pH4 and want the system to calculate pH5, then the calculations will be off.

So that is one of the reasons why we chose an increment 0.1, as in 4.1, 4.2 and so on rather than 4, 5, 6, and soon. So again, we are asking VMinteq to go up with a guess initially, so it is going to be that case, so run Minteq.

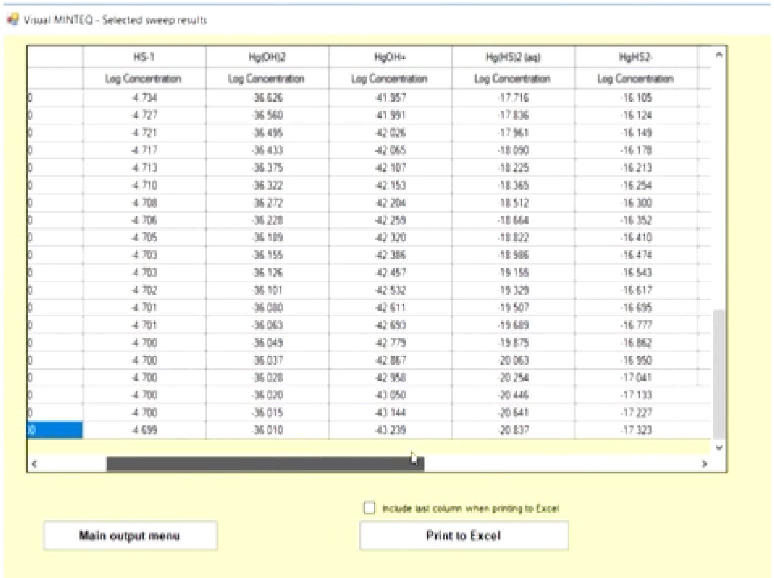
(Refer Slide Time: 33:16)



	Concentration	Activity	Log activity
H+1	1.0083E-04	1.0000E-04	-4.000
H2S (aq)	1.9981E-05	1.9981E-05	-4.699
Hg(HS)2 (aq)	9.9675E-17	9.9676E-17	-16.001
Hg(OH)2	7.2002E-38	7.2003E-38	-37.143
Hg+2	1.0858E-39	1.0504E-39	-38.979
Hg2OH+3	5.9987E-78	5.5681E-78	-77.254
Hg3(OH)3+3	5.0747E-112	4.7104E-112	-111.327
HgHS2-	3.2522E-19	3.2254E-19	-18.491
HgOH+	4.2457E-39	4.2107E-39	-38.376
HgS2-2	6.5008E-24	6.2891E-24	-23.201
HS-1	1.9240E-08	1.9082E-08	-7.719
OH-	1.0153E-10	1.0069E-10	-9.997
S-2	7.8523E-22	7.5966E-22	-21.119

So we just have the results here for different iterations, so 1, 2, 61. So I land in virtue of 50, so that is for 8.9 pH again there are the results. So obviously I want to look at the holistic picture, so I am going to look at selected sweep results. The selected sweep results are out here.

(Refer Slide Time: 33:38)



HS-1	Hg(OH)2	HgOH+	Hg(HS)2 (aq)	HgHS2-
Log Concentration	Log Concentration	Log Concentration	Log Concentration	Log Concentration
-4.734	-36.626	-41.957	-17.716	-16.105
-4.727	-36.560	-41.991	-17.836	-16.124
-4.721	-36.495	-42.026	-17.961	-16.149
-4.717	-36.433	-42.065	-18.090	-16.178
-4.713	-36.375	-42.107	-18.225	-16.213
-4.710	-36.322	-42.153	-18.365	-16.254
-4.708	-36.272	-42.204	-18.512	-16.300
-4.706	-36.228	-42.259	-18.664	-16.352
-4.705	-36.189	-42.320	-18.822	-16.410
-4.703	-36.155	-42.386	-18.986	-16.474
-4.703	-36.126	-42.457	-19.155	-16.543
-4.702	-36.101	-42.532	-19.329	-16.617
-4.701	-36.080	-42.611	-19.507	-16.695
-4.701	-36.063	-42.693	-19.689	-16.777
-4.700	-36.049	-42.779	-19.875	-16.862
-4.700	-36.037	-42.867	-20.063	-16.950
-4.700	-36.028	-42.958	-20.254	-17.041
-4.700	-36.020	-43.050	-20.446	-17.133
-4.700	-36.015	-43.144	-20.641	-17.227
-4.699	-36.010	-43.239	-20.837	-17.323

From pH4 at 4.1, 4.2, so on up to 10 and the relevant concentrations of the species that we requested. We only ask for a few species, because we know that the others are not going to be at comparable concentrations. So they were HS-, HgOH and blah, blah, so this is from the question 1, if people can remember that. So now I am going to look at the graph. I am going to print that to excel and then plot, which I have just done.

So here we are now going to look at log C pH graph and here again pH and HS-, HgOH twice and blah, blah. They are all the other species and here we now have the log C pH graph. Logarithm of the concentration on the y axis and pH on the x axis from 4-10.

(Refer Slide Time: 34:40)

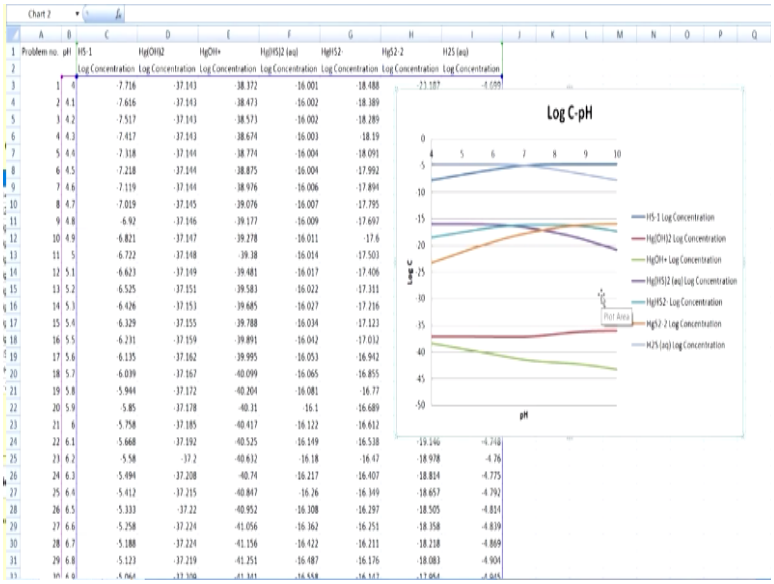


Chart 2

	A	B	C	D	E	F	G	H	I
1	Problem no.	pH	HS-1	Hg(OH)2	HgOH+	Hg(HS)2 (aq)	HgHS2-	HgS2-2	H2S (aq)
2			Log Concentration	Log Concentration	Log Concentration	Log Concentration	Log Concentration	Log Concentration	Log Concentration
3	1	4	-7.716	-37.143	-38.372	-16.001	-18.488	-23.187	-4.699
4	2	4.1	-7.616	-37.143	-38.473	-16.002	-18.389		
5	3	4.2	-7.517	-37.143	-38.573	-16.002	-18.289		
6	4	4.3	-7.417	-37.143	-38.674	-16.003	-18.19		
7	5	4.4	-7.318	-37.144	-38.774	-16.004	-18.091		
8	6	4.5	-7.218	-37.144	-38.875	-16.004	-17.992		
9	7	4.6	-7.119	-37.144	-38.976	-16.006	-17.894		
10	8	4.7	-7.019	-37.145	-39.076	-16.007	-17.795		
11	9	4.8	-6.92	-37.146	-39.177	-16.009	-17.697		
12	10	4.9	-6.821	-37.147	-39.278	-16.011	-17.6		
13	11	5	-6.722	-37.148	-39.38	-16.014	-17.503		
14	12	5.1	-6.623	-37.149	-39.481	-16.017	-17.406		
15	13	5.2	-6.525	-37.151	-39.583	-16.022	-17.311		
16	14	5.3	-6.426	-37.153	-39.685	-16.027	-17.216		
17	15	5.4	-6.329	-37.155	-39.788	-16.034	-17.123		
18	16	5.5	-6.231	-37.159	-39.891	-16.042	-17.032		
19	17	5.6	-6.135	-37.162	-39.995	-16.053	-16.942		
20	18	5.7	-6.039	-37.167	-40.099	-16.065	-16.855		
21	19	5.8	-5.944	-37.172	-40.204	-16.081	-16.77		
22	20	5.9	-5.85	-37.178	-40.31	-16.1	-16.689		
23	21	6	-5.758	-37.185	-40.417	-16.122	-16.612		
24	22	6.1	-5.668	-37.192	-40.525	-16.149	-16.538	-19.146	-4.748
25	23	6.2	-5.58	-37.2	-40.632	-16.18	-16.47	-18.978	-4.76
26	24	6.3	-5.494	-37.208	-40.74	-16.217	-16.407	-18.814	-4.775
27	25	6.4	-5.412	-37.215	-40.847	-16.26	-16.349	-18.657	-4.792
28	26	6.5	-5.333	-37.22	-40.952	-16.308	-16.297	-18.505	-4.814
29	27	6.6	-5.258	-37.224	-41.056	-16.362	-16.251	-18.358	-4.839
30	28	6.7	-5.188	-37.224	-41.156	-16.422	-16.211	-18.218	-4.869
31	29	6.8	-5.123	-37.219	-41.251	-16.487	-16.176	-18.083	-4.904

So let us just try to understand what it is that the system is trying to tell us. Obviously log C pH graph will allow us to take a holistic view of the system here. Let us just try to identify which species in general are at high concentrations and which species are at remarkably low concentrations or at negligible concentrations. Here as you see, we have 2 species that are predominant. What are they?

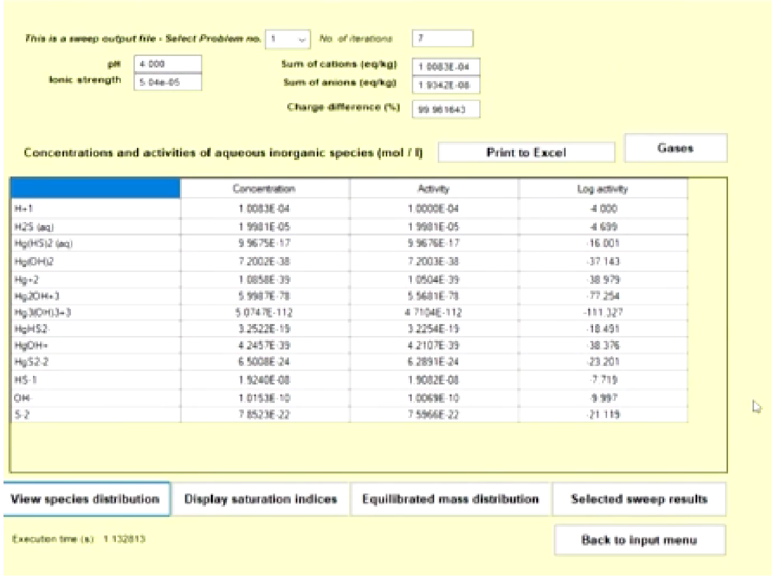
They are HS- and H2S, they correspond to these 2 particular graphs here over the range of 4 to 10. Obviously, as we keep increasing the pH, we know that the protonated form of the acid is going to decrease in concentration, that is why you see H2S decreasing and obviously HS- concentration will increase, maybe the pKa is around 7.1 or something like that and then the next major aspect that we need to look at is there are different complexes.

I think we considered 5, 2 complexes are between mercury and OH- and the other 3 complexes are between mercury and sulfide. So as you can look at this particular, a bund of 3 are here and a bunch of 3 are somewhere out now. Keep in mind that this is a logarithmic scale. So the order of magnitude difference is almost 15 and 40, so that is 25 difference, if I am not wrong. So 25 order of magnitude are 10 power 25 times smaller here.

So these 2 complexes, which are relevant to HgOH twice and HgOH+ are 10 to the power of 25*lesser than these 3 complexes, which are between mercury and sulfide. So the take home message here is that in which forms will mercury be predominantly presented. It will be present in what is it now, complexes as Hg and sulfide and though they will be present, mercury will also form complexes with OH-. The mercury-hydroxide complexes are at very low concentrations.

So that is what we are trying to look at here and so this obviously gives you an idea about what is happening in the system. So I believe I should also have asked the system to calculate Hg2+ concentration are plotted here, so let us go back and ask VMinteq to do that, so that we can know back to input menu and multisweep problem, I am also going to ask for the free metal concentration to be plotted, which is something I should have done earlier, so add that, save and back and I am going run Minteq.

(Refer Slide Time: 37:20)



This is a sweep output file - Select Problem no. 1
No. of iterations 7
pH 4.000
Ionic strength 5.04e-05
Sum of cations (eq/kg) 1.0083E-04
Sum of anions (eq/kg) 1.9342E-08
Charge difference (%) 99.961643

Concentrations and activities of aqueous inorganic species (mol / l)

	Concentration	Activity	Log activity
H+1	1.0083E-04	1.0000E-04	-4.000
H2S (aq)	1.9981E-05	1.9981E-05	-4.699
Hg(HS)2 (aq)	9.9675E-17	9.9676E-17	-16.001
Hg(OH)2	7.2002E-38	7.2003E-38	-37.143
Hg+2	1.0858E-39	1.0504E-39	-38.979
Hg2OH+3	5.9987E-78	5.5681E-78	-77.254
Hg3(OH)3+3	5.0747E-112	4.7104E-112	-111.327
HgHS2-	3.2522E-19	3.2254E-19	-18.491
HgOH+	4.2457E-39	4.2107E-39	-38.376
HgS2-2	6.5008E-24	6.2891E-24	-23.201
HS-1	1.9240E-08	1.9082E-08	-7.719
OH-	1.0153E-10	1.0069E-10	-9.997
S-2	7.8523E-22	7.5966E-22	-21.119

Execution time (s) 1.132813

Now I am going to go to selected sweep results and print to excel. I just want to look at what is the case when I consider the mercury concentration 2, to know what is the free metal concentration. Anyway the graph is not going to be as clear as earlier, but let us see if it can be done with that. So again it is from 4 to 10 and where is the mercury concentration out here, though. Anyway the mercury concentration is so low as compared to the other complexes that the graph is not capturing it, makes sense hopefully.

Let us just look at the numbers now. Here let us say at pH4 Hg2+ is already at -38 and while the others are at -7, -37, and so on and may be that is the reason why the graph is not plotting that. I do have Hg2+ and as you see it is remarkably low concentration. So if I look at the x-axis from pH4 to pH10 you see that the free metal concentration is remarkably low. What do we understand here.

First the free metal concentration of mercury is negligible and that HgOH complexes are formed, but not at very high or significant concentrations, but mercury would in general be present as in forms now, the mercury and sulfide complexes. That is what you understand from this particular graph here. The mercury and the mercury hydroxide complexes are at very low concentration, but the only relevant forms of mercury that are at relatively high concentrations are the mercury-sulfide concentrations.

This is one way I guess where you can look at the toxicity or affect the toxicity of mercury, the free metal mercury toxicity, I guess. For example, if we know that mercury is toxic, Hg2+, but by adding HS- let us say the sulfide as a ligan, you can reduce the toxicity, why? As you see here the free metal concentration is remarkably low. Again we are assuming that the Hg and sulfide complexes are not toxic, which I guess is a decent assumption to make.

With that, we will be done with the aqueous complex based aspects. From next session, we are going to move on to the next major aspect, it is going to precipitation and dissolution. With that, I am done for today and thank you.