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Lecture - 32 Mixing of Two Solutions and Conservative Quantities – I

Hello everyone, so welcome back to our latest lecture session. As is our customary let us have a quick recap of what we discussed in the previous session. I believe we are trying to look at applications of VMINTEQ with respect to closed systems initially and then also open systems and we looked at how the relevant values for pH would change let us say when you have system in equilibrium with partial pressure of carbon dioxide or in equilibrium with carbon dioxide in the gaseous phase.

And more or less in the last session, we spent time about how to you know look at using VMINTEQ to cut down on your time for analysis yes. So in today's session, we are going to move forward and look at some more practical applications and I guess one common aspect that people come across is you know you have solution A and solution B, you mix them up and what are the properties of the solution C let us say or the mixture now right.

So obviously you can again conduct the relevant titrations or analysis and get it done or if let us say the quantities are conservative, this is something we are going to come back to, keep in mind that if the quantities are conservative you can look at the relevant balance on the conservative quantiles right. So let us just look at what we are trying to you know analyze here. So here we have let us say an example right.

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And here we are talking about mixing problems now yes here let us say we have an example and let us say we have solution at volume V right and pH is 6 and again let us say pH is 8 of a second solution again with let say for ease of understanding again the volume is the same V right. So now we have two solutions each of the same volume, one at pH 6 and one at pH 8 and obviously let us consider or resume that you have the different other what do we say compounds present in these two solutions now right.

So let us say if I am concerned with okay what is the pH of this solution going to be now right you know that is something that would be required let say for further analysis. So what are the different ways people look at let us just have a look at what people are up to in general right. So one case is right taking the average of the 2 pH values, pH 1 and pH 2 right or 6 and 8 and people say we end up with 7.

That is one thing that people do often okay. Let us go step by step (()) (02:53) so why is this not true though, now this is not the true value and why is this? So in the first case you know this is pH logarithm of H+ so it is not something that you can just you know sum up right or add or take the average of right. So that is something that fails right there, so then what do people try to do?

People try to calculate the concentration of H+ for solution 1 right and also concentration of H+ for solution 2 and then take the average of these values right and then get the pH of the mixture now, this is one way. Again this would work if H+ concentration was a conservative

quantity but as you now know with some or considerable background in the acid-base reactions in such you know that H+ is not conservative that is it.

There are other compounds let say any other bases present let say that can take up your H+ or such so you cannot just take the average of the 2H+ concentrations and you know try to get at or try to use that particular methodology to calculate your pH though right. So obviously the key here is you are going to look at balances on conservative quantities and pH and H+ concentrations are not conservative quantities.

So looking at what we have been through recently let say what have we discussed now, you know what are some of these conservative quantities? So again the whole key is that we look at components as you know the total component concentrations are going to be constant. So for example CO3 total is something that is going to be constant and similarly you can also consider let say something relatively new that we discuss in last couple of sessions alkalinity ideas right.

So let say depending on your particular scenario alkalinity let say is going to be constant and you can consider the use of alkalinity to be able to be arrive at your particular variable. So let us just have a quick look of about what we are discussing I guess right.



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So how can you go about that let us see. So as we just discussed what are the conservative quantities that you can use or conservative quantities what are they right? So obviously from our component balance obviously we know that the total components are going to be a

conservative quantity and what else have we discussed recently, we looked at alkalinity and obviously we also talked about or discussed about acidity right.

So these are variables that you can you know conduct the balance on because they are conservative quantities right. So let us just look at one particular scenario right we are going to look at how to solve a particular system by hand right and another case how to solve it by VMINTEQ let us see right and we are going to look at how to solve it by hand even though we can solve it easily by VMINTEQ because we need to understand the fundamentals of the basics here right.

So by hand so what are we trying to look at here, let say we have pH of solution given right and also alkalinity of a solution given pH 1 and pH 2 right and also let say also have pardon me alkalinity 1, pH 2 and alkalinity 2 let say you know let say have 2 solutions and I want to know let say the pH of the mixture now right. So how do I go about it by hand that is what we are going to discuss that right?

So again by hand now let us look at some of the equations that we are aware of and what we do we know? We know that alkalinity is equal to what now all the bases let say HCO3- +2 times CO3 2- and why do we go with 2 because CO3 2- can neutralize 2H+ or 2 protons and OH- and then -H+ and this obviously the theoretical definition of alkalinity which consider that only the carbonate species or the predominant acid-base species right.

So this is the particular equation that we have let say so for solution 1 right and that is going to be equal to what now alpha 1+2 times+alpha 2*CO3 total+Kw water dissociation constant/concentration of H+ -concentration of H+ and how do we end up with this, just a quick recap again. Ionization fraction alpha 1 what would that be equal to? HCO3-/H2CO3+HCO3-+CO3 2- right.

That is nothing but=HCO3-/what is this denominator, it is nothing but CO3 total right and similarly what is alpha 2 pardon me, it is going to be=CO3 2-/CO3 total and while we are not using this particular alpha 0 let us see what that is equal to, that is obviously equal to H2CO3/CO3 total right to refresh our memories. So again plug in these values of alpha 1 and alpha 2 in this particular equation here we end up with simplified form alpha 1+2 alpha 2*CO3 total and so on and so forth.

So again let us look at what we have here, what are the knowns and unknowns? So here alkalinity is the known value because it is given here right. Alkalinity is a known value and CO3 total is an unknown right, it is a variable but you know the pH right so H+ is a known value here, here and for a given pH you can calculate obviously alpha 1 and alpha 2 right and that is something we are aware of I am not going to again plug that in here.

So from here what can I calculate, I can calculate the CO3 total 1 right, I can calculate that. Similarly, for solution 2, I am going to go ahead and calculate CO3 total 2 in the same manner right and now what can I do now let us see right. Now I am able to calculate CO3 total of 1 and CO3 total of the second solution. So how do I go ahead further by trying to solve the solution for pH by hand?

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The keys we are still looking at by hand, so again what is this particular case that we know we know that again alkalinity is equal to alpha 1+2 alpha 2 times CO3 total+Kw/H+ right -H+. So let say now this is for the mixture now right, the mixture where we mix up one and two let say right and how do I go about calculating it now right. For this case, you know I can calculate alkalinity.

How do I calculate alkalinity now? I can say V1*alkalinity 1+V2*alkalinity 2 is going to be equal to V3 or the volume of the mixture right*alkalinity of the mixture right and we know volume 1, alkalinity 1, we know volume 2 and alkalinity 2 Vm is nothing but V1+V2

obviously right. So here what is this equation expressing? It is that we are balancing the total alkalinity right.

So the alkalinity of the mixture is now going to be calculated from this equation. All the others are known variables right and similarly I can also calculate the CO3 total of the mixture and how do I do that again? Just plug the relevant values in CO3 total 1+V2*CO3 total 2=volume of the mixture*CO3 total of the mixture right. Again V1, V2, Vm we know those values.

CO3 total 1 and CO3 total 2 we calculated them earlier right from this particular case here right we calculated them and now by the balance on CO3 total I can come up with calculating the CO3 total of the mixture right, that is something that now I am able to calculate. So now what do I have please? I have the alkalinity of the mixture and I also have CO3 total of the mixture. Again the key is trying to understand why am I only balancing the relevant conservative quantity.

So again the key is that the conservative as the name indicates right. So if you are looking at H+ though and if you are trying to do the balance on H+ let us say as in V1 H1+V2H2=V3H3 what is going to be the issue now right. You do not know or you know because here we do know that we have CO3 2- or HCO3-, the H+ can either be taken up by them or release from H2CO3 and so on, there are other interactions here.

So you obviously only can conduct the balance on the conservative quantity and as we know from our background CO3 total that is not going to change right, whatever happens the total CO3 is going to be the same and same case with alkalinity. So that is why we need to consider only the conservative quantities when we are looking at the balance and thus in this case where we had the alkalinity we first calculated the CO3 total of both the solutions.

And then looking at the balance on both the solutions with respect to alkalinity and CO3 total, we end up with calculating the alkalinity and CO3 total of the mixture right that is what we have here and once we have this what can I do? I can again go back to this equation right and what do you have?

I have the alkalinity of the mixture here, I have the CO3 total of the mixture here right, Kw is the known value so what is the only unknown here it is H+ right. So from this I can end up calculating what is the H+ right and once I have the H+ obviously I can calculate the pH right and again alpha 1 and alpha 2 are as you either of functions of H+ so that is something you can plug in.

So what can you use? I think one way obviously by hand might be a bit difficult so in excel you can go to solver, there is function called solver right. It should be in add-ins I guess and with that you can be able to easily solve for what do we say H+ here in this particular equation yes. So we just looked at how to solve this by hand, again what was the (()) (13:30) what do we say methodology I guess that we are going to conduct a balance on conservative quantities.

So now let us try to see or try to understand how we can use VMINTEQ to cut down on our time and get at the same solution right. So again let me just go back here.



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So what do we have? We have pH and we have alkalinity right, pH 1 and 1 and again pH of a second solution and alkalinity of a second solution right. So again what can I do here? So I can this is by VMINTEQ, they approached by VMINTEQ right. How do I do that? So for the first solution I am going to plug in pH and alkalinity right as known values and from the relevant concentrations what can I calculate now?

I can calculate CO3 total and H total right and same case here I will plug in pH 2 and alkalinity 2 for the second solution and what can I calculate? I can calculate CO3 total and H total right. So then again what can I do now H total again is a conservative quantity, so V1*H total 1+V2*H total 2=volume of the mixture*H total of the mixture right. So from this particular balance equation, we can now calculate H total of the mixture right.

So unlike H+ concentration, H total is a conservative quantity. H+ is not a conservative quantity but the total H is a conservative quantity and that is why we applied relevant mass balance here not mass balance pardon me the component balance and we now can calculate H total of the mixture right and similarly I can conduct the balance on what now CO3 total which we looked at earlier and I can then calculate CO3 total of the mixture right.

I can have that too and again what do I have H total and CO3 total. So I can just plug in these two values in VMINTEQ and what will I end up with I will end up with the pH of the mixture. So again I will just see you know unless you have the understanding of the fundamentals here with respect to the conservative quantities or such you cannot or it would be relatively difficult for you to look at or using VMINTEQ.

But obviously something that takes you around half an hour or 40 to 50 minutes to work out by hand you know by VMINTEQ you can cut down the time to 5 to 10 minutes right. Again so let us now look at an example problem right and let us see how we can analyze that particular problem I guess right.

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So let us first understand the question that we have. So obviously it is similar to what we just discussed. So it says we have 2 liters of solution A and 3 liters of solution B right and we have the pH or this is the analysis for the individual compounds or the solutions pardon me and for the first one is pH 7.2 and alkalinity is 200 milligram per liter as CaCO3 and again water 2 or water B I guess it is 8.4 pH and 400 milligram per liter.

Again I guess the first question should be something that we should be able to solve easily and then I guess there are a few more questions here which might require a bit more understanding I guess. So let us go through and try to solve this particular question. So we have pH 7.2 and 200, this is for water or solution 1 and 8.4 and 400. So by hand we are going to try to solve this by hand right.

So how do I solve this by hand now right and we just looked at that earlier so I have the pH and I have the alkalinity right so how did we try to solve this now? I believe we try to solve this by calculating the CO3 total right and how do I solve that. I said alkalinity was equal to right alpha 1+2 times alpha 2 yes*CO3 total+Kw/H+ and what is this nothing but OH- right-concentration of H+ right.

So from here what can I calculate here, I know alkalinity I know alpha 1, alpha 2, H+ and Kw so I can calculate CO3 total of solution A right but thus it is going to take some time right and what can you use to solve for this let us say you can use excel and in that particular case you can look up solver, a function called solver yes and use that to solve this but obviously it is going to be a big tedious now and I am not going to go through that right.

Again same case, how do I do the same case I am going to repeat that for CO3 total B and I am going to calculate CO3 total A and similarly I am going to calculate CO3 total B yes. (Refer Slide Time: 18:31)

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And then obviously what next let us just try to write this down right. So I have V1*alkalinity 1+V2 alkalinity 2=V3*alkalinity 3 right. So here V1 should be 2 I think and this was 200 milligram per liter and this particular V2 was I believe 3 liters and alkalinity 3 was 400 milligram per liter as CaCO3 if I am not wrong.

And V3 is nothing but V1+V2 because we are mixing the two solutions so it is 2+3=5* alkalinity 3 and alkalinity of this particular solution or the mixture what is that now 400+3*4 is 1200/5 and anyway that is going to be=1600/5 and you can end up calculating that particular value I guess yes and similarly applying the same particular balance on CO3 total right.

I will end up calculating CO3 total of the mixture, let me write it down as mixture right okay CO3 total of the mixture in the same particular equation applying the similar equation I guess and I have alkalinity of the mixture and CO3 total of the mixture now right and how do I proceed further as we looked that earlier again alkalinity of the mixture is going to be=alpha 1+2 times alpha 2*CO3 total of the mixture+Kw/H+-concentration of H+.

And what is the only unknown here, it is only H+ right because you have alkalinity of the mixture which you calculated here right, CO3 total of the mixture which you calculate here and as we know alpha 1 and alpha 2 are nothing but functions of H+ but again solving this by hand is going to be tedious and you can use excel solver or you know if you have any other mathematical tools or such at your disposal you can use them to solve for this particular function.

So anyway that is by hand but obviously it is going to take quite some time so at least we are going to work through it in detail with respect to how to solve it by VMINTEQ right. So let us look at the solution again not solution pardon me the question again and let us just see what we are up to.

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So we have pH and we have alkalinity and what is that of the mixture and what was the approach earlier right. We need to calculate the CO3 total and H total of both the solutions right, CO3 total and H total of this particular solution and same case CO3 total and H total of this particular solution and how are we going to do that? We are going to use VMINTEQ I guess 7.2 and 8.4 and 200 and 400.

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So let me see how to use VMINTEQ right. So first we need to set up the relevant aspect, so the first one is pH is fixed at I believe it was 7.2 right, 7.2 yes and what else do we have? We have alkalinity and I think we can specify that in parameters and alkalinity was as CaCO3. I do not need to change the units because I have them, I have the relevant units mentioned here and I believe it was 200 milligram per liter right.

So I am going to say okay so alkalinity is specified in this problem yes and so on normal and okay and I am going to say run VMINTEQ.

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And I have the relevant species concentration of the different species here. Again what is this mean? These are the different compounds that are going to be present at equilibrium right and these are the relevant concentrations that VMINTEQ calculates and again the binding one of the boundaries that we specified was pH is 7.2 and alkalinity obviously. So first now we need to calculate CO3 total and H total right obviously there is no shortcut we need to go to print to excel.

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And that is how here and how do I calculate this particular CO3 total right. That is going to be equal to this particular CO3 2-+ H2CO3+HCO3- right and enter so what is this equal to again. If you look at this, we know that CO3 total is nothing but H2CO3+HCO3+CO3 total. So to calculate CO3 total what did I just do? We just summed up the concentrations of the 3 what do we say species relevant of the carbonate systems H2CO3, HCO3- and CO3 total right.

And so the CO3 total that we end up with these after summing up CO3 2- H2CO3 and HCO3- that is equal to enter please, 4.5*10 power -3.



So let us write that down somewhere, so we end up with 4.5*10 power -3 right and let us look at H total, same way CO3 total let us just try to refresh our memory I guess. So we have

H+ components and CO3 2- right and what are the species they are H+, OH-, H2CO3, HCO3- and CO3 2- and how many H+ here, 1, -1, H2CO3 is 2, 1 and here it is 0 and CO3 2- here it is 0 0 1 1 1.

So what did we just do or how did we calculate that? We just did the total balance on the component CO3 total and that was equal to 1 times H2CO3, 1 times HCO3- and 1 times CO3 2- right and with that we end up with the value of 4.5*10 power -3. So similarly we need to calculate what it is now H total and what is that equal to H+ +2 times H2CO3 1 times HCO3- and –OH- so let us see if we can calculate that right.

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So that is equal to please okay and we had it=H+ + what else please HCO3-+2 okay 2 times*H2CO3-OH-. So what do we have here? We have H+, we have H++ HCO3- +2 times H2CO3-OH- right, enter please and so now we end up with the H total of let us say 5.1*10 power -3 let me plug that in here. So now I end up with the value of 5.1*10 power -3 right now approximately.

Let us check that again, so 5.1*10 power -3 and earlier we ended up with 4.5*10 power -3. So with that we have done with the analysis for part A or solution A. Now we need to repeat the exercise for solution B and what do we have, 8.4 and 400. So let us just close this excel and anyway that is fine will close this excel and will move on to VMINTEQ here back to input menu.

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And now I need to change it such that this particular pH is now 8.4 I believe 8.4 right and then parameters we are going to specify the alkalinity and the alkalinity now was or is pardon me going to be equal to I believe 400 right and 400 and okay.

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And sometimes we need to be careful about this so let us go back here and then run VMINTEQ and now again we see that a pH is fixed that is why the pH does not change and we have again the relevant species. So again need to repeat the same exercise as earlier. We need to go to print to excel.

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And I am doing that here right so first you are going to calculate the CO3 total, so that is going to be equal to CO3 2-+HCO3-+H2CO3 and enter and we are now having something like 7.9*10 power -3 so let us just write that down first.

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A volume of 2 liter of a	water A is mi 45.10 ^{3-51.10⁵} (0st, ¹⁴) 4 Water A	xed with ⁽⁰ sit, ^h t Water B	3 liter of water B. μ^* (\tilde{c}_3) \tilde{c}_4 (\tilde{c}_3) \tilde{c}_5 (\tilde{c}_5) (\tilde{c}_5) \tilde{c}_5 (\tilde{c}_5) (
pH	7.2	8.4	10 10	<u>`</u>
alkalinity (mg/L as CaCO ₃)	200	400		\bigcirc
a) what is the pH of thb) what would be thedioxide in the atmosplc) what would be theequilibrated with the a	the mixture? pH of the mix- here ($P_{co2} = 3$ pH of the solu- through the solu- the solu- through the solu- through the solu- the solu-	sture if it .8 E-4 atr ation if 1	were to equilibrate with carbon n)? E-3 M HCl were added after it	

So it is 7.9*10 power -3 that is the CO3 total of the second solution which is B and let us again go back.

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003-2	0.00011262	0.000085318	-4,069																			
H+1	4.26721-09	3.9811E-09	-8.4			0.00794	1															
H2CD3* (aq)	0.000064818	0.00006487	-4.188			0.00785	1															
HCO3-	0.0077658	0.0072451	-2.16																			
OH-	2.71098-06	2.52910-06	-5.597																			

And what else were we considering I believe we need to go back to excel and same case as earlier we need to calculate the H total and that is equal to H++ 2 times*H2CO3+HCO3- and what we are missing -OH- right so enter please and again it is relatively similar value 7.9*10 power -3. So let us just check if we have the right calculation here so we said H+ and -4H- that we are done with 2 times H2CO3 and B5 is HCO3- yes so we are on the right track enter please.



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And we are going to approximate by 7.9*10 power -3 right. I am going to have this same H total is again 7.9*10 power -3 right. So now what next, we need to calculate the CO3 total of the mixture right and also H total of the mixture and how do we do that based on the balance that we talked about earlier which is nothing but V1*CO3 total 1+V2*CO3 total 2/V1+V2 which is I believe 2+3=5 right, 2 liters and 3 liters.

So let us just plug this in for both the cases and see what it turns out to be right. So let us go back to excel hopefully we can remember the values or we can come back to this particular slide. So first we are going to try to calculate CO3 total of the mixture right.

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So we are now going to calculate CO3 total that is=V1 which is 2*and let us check the value of our CO3 total and that was 4.5*10 power -3 right and + and volume towards 3 so 3*and let us check CO3 total once and what was that, that was 7.9*10 power -3 right. So enter so I am going to say this, I need to divide this by the total volume which is 5 that is equal to this cell by 5 divided by 5 and enter.

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So now I end up with the value of 6.5*10 power -4, so let me write that down so the CO3 total of the mixture that I now have as 6.5*what was the values 10 power -3 pardon me 10 power -3. So I am done with this. Similarly, I need to repeat the exercise for H total right. So let us have that particular case here.

So H total that is equal to 2 times and let me switch and see what the H total value is when we have that here, it is 5.1*10 power-3*10 power -3+3*3 is again the volume right let us check the value of H total here that is equal to 7.9*10 power -3 and enter please and now we are going to have to divided by V1+V2 that is equal to this cell divided by 5 that is equal to 6.8*10 power -3 approximately.

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So let us plug that down somewhere, 6.8*10 power -3 so now we have 2 values. What are they here, H total and CO3 total of the mixture right. Now I can easily calculate the pH of the solutions.

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So we are going to plug in the two components, they are CO3 2- and I am going to use the accurate values not the approximate values that I used earlier. So from my calculations we will end up with 6.61*10 power -3 so I am going to add that to the list and then again H total and where is that here, that is somewhere out here and H total the accurate value should be 6.76*10 power -3 and where is this, we have to change it to 76 that 6.76*10 power -3 yes that is right.

So I am going to add that to list, so one key aspect is you need to remove the alkalinity from this particular iteration because we add alkalinity earlier and you cannot have that given that here which already dead.

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So I am going to run it now right and now we end up with pH of 7.8 right. So again 7.2 pH was our initial case right. Let us just look at our question here, so 7.2 and 8.4 but alkalinities were 200 and 400 milligram per liter, 2 liters and 3 liters right. So with this particular VMINTEQ we can cut down on the analysis time yes and now we know that the final pH of our particular solution is going to be 7.8 right and obviously if you want to look at the species concentration we again have that here.

So at 7.8 you would expect most of it to be present as HCO3- just for quick understanding let us look the distribution.



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So as you see HCO3- predominates that is 96 or 97% right, so that is what you see. Again the pH is 7.8 and this is what we want to calculate. So we are done with part A of this particular example problem and we are going to continue working on part B and C in the next lecture session.

And once we are done with that we will then further look at how to calculate or how to analyze the system let say when your theoretical alkalinity does not suit your present scenario as in theoretical alkalinity and your titrated or measured alkalinity are relatively different. So we are going to look at those examples and with that I am done for this session and thank you.