Environment Engineering: Chemical Processes
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Module No # 07
Lecture No # 31
Alkalinity & Acidity: Applications

Hello everyone welcome back to our latest lecture session right so we have been discussing I believe acidity in great detail in last class and priority to that we discussed alkalinity. So obviously you know we are going to look at the applications right as in how you are going to end up using alternative mostly we will have may be a minor application with respect to acidity. So primarily today session we are going to try to understand and how to apply acidity with respect to various scenarios right.

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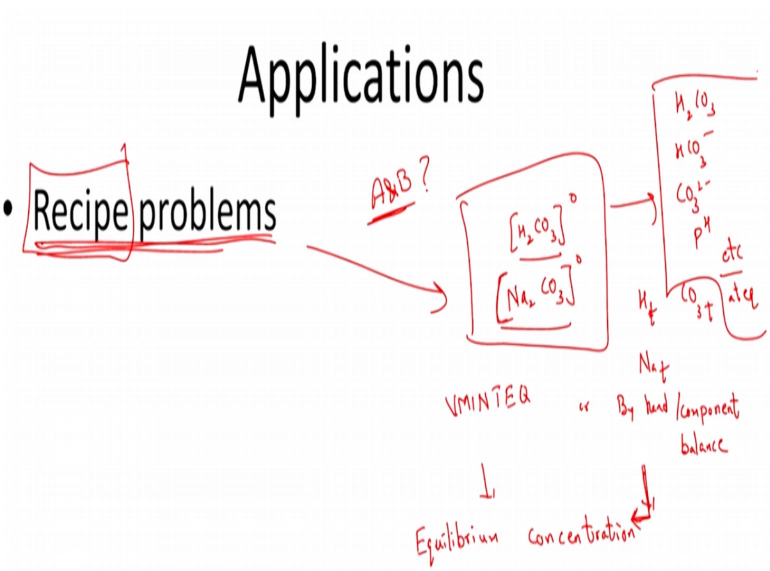

So let us get write down to it so initially what are we been until doing until now you know if our acid and base systems what kind of problems have we been looking at kind of recipe problems right recipe problems as in you know what did we look at let us say I considered different examples.

Or all the examples that we looked at so far have been you know I know what it is adding initially as in let us know the amount of acid I am adding initially or amount of base I am adding initially and I am using VMINTEQ or the component balance approach you know solving it out manually to be able to calculate the relevant species at equilibrium right so what you have been up to so let us look at minor example let us say I know H2CO3 naught present initially or NA2CO3 naught present initially right.

So from that we calculated either H total or CO3 total and NA total and either we use VMINTEQ right or by hand or component balance and then what did we solve formally we are trying to find out what would be the equilibrium concentrations right. So this is what you know we discussed in general so this will work fine whenever you looking at engineer systems right you know let us say I am conducting an experiment I know what it is putting it initially I want to know the PH that would that I would expect or the alternative that I would expect or acidity I would expect and so on right that will help with your engineering system.

But let us say if I am looking at say natural systems or real world systems or the different kinds of problem you would routine face what are they for example you know let us say I have water quality analysis right what parameter will they have? They have let us say we have PH alkalinity expressed has CACO3 or equivalence but rarely equivalence people in that in India anyway we are using units of as CACO3 and then we need to end up estimating like let us say or might need to end up estimating what are the relevant concentrations of the species.

For example let us say if you look at water quality report let us say what would you have let us say you will have certainly say PH and other than the physical parameter let us say you will also have alkalinity and let us say you will also have phosphate but it is not phosphate right total phosphate that people end up measuring.

Right so you have let us say people PH alkalinity and total phosphate but let us say I want to be able to understand what are the concentrations of the relevant species at equilibrium right what are the different species represent and what in what concentration how do I do that because here let us say we are not saying we are inputting so and so solutions.

And then I want to calculate what the or not calculate estimate more or less right what the equilibrium concentration are going to be here let us say I have a solution and the PH alkalinity and relevant total component concentration of various what do we say component are given for example in this case I mentioned total phosphate right how do I estimate the concentration of the relevant species so that is what we are going to look at in greater detail.

So this we are going to look at as water quality problems until now we looked at recipe problems I know I mean I know what it is the recipe is has in the recipe solutions you know one example is what we looked at when we added H2CO3 or NA2CO3 initially and wanted to know okay what are the concentration of H2CO3 HCO3 – CO32- PH etc at equilibrium this is what we calculate until now right yes.

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But in general what do we face we face scenario's let us say where we have let us say PH we have alternative given and then we have let us say for this example X total but let us say one example can be total phosphate present right and then let us say we are trying to estimate let us say what are the various species at equilibrium right. So obviously we are going to look at alkalinity in this case and then we are going to move to the complex system but one step at a time I guess.

So this is the case again right so again as we know I guess right what is this about what is our approach about it is about more or less able to calculate the total components right. But here if you look at this system we have PH in alkalinity but we are we do not have the relevant component their or a total components pardon me but we obviously have one other total component we have phosphate total here let us say or ex total in this particular generic example right.

So how do I go about estimating the equilibrium concentration right so what am I missing here obviously if you understand what it is we have been up to earlier trying to transform the recipe concentration express them in terms of the total component so we do not have that we have PH in alkalinity.

So what can I get from or what infirmation can I get from them right so obviously I we are looking at component balance we obviously need to try to find out H total and CO3 total why alkalinity in general we look at it in terms of the carbonate system and thus we are going to look at CO3 total right.

So first we will try the manual approach as in how to express you know or how to let us say calculate the CO3 total give an PH alkalinity relatively simple obviously and the we will also see how to use VMINTEQ which obviously you know cuts down on the time required right.

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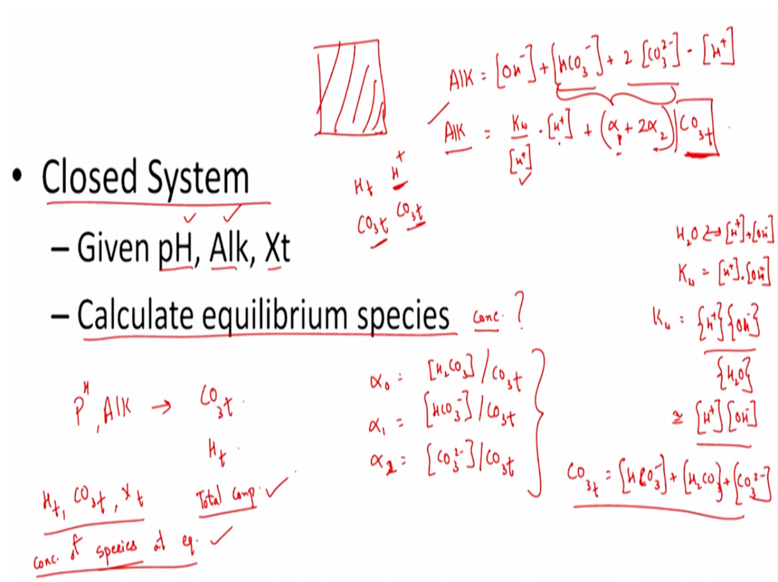

So first aspect is that you know it is a closed system right when we have no exposure of relevant solution to the atmosphere right the gaseous phase present. So here are going to consider where you have PH alkalinity H total and what I am trying to calculate the equilibrium species the concentration I guess the concentration of various equilibrium species. So how to go about this first manually I guess right so alkalinity what is our equation with respect to alkalinity now we know that it is going to be equal to what is it here please OH – right and the other basis are HCO3- + 2CO32- - H+ right.

And how can we simplify this further let us say we are trying to express everything in terms of variables such that we can end up with H total and CO3 total so obviously I need them in terms of H+ and CO3 total right so let us see how I can transform that so as it is given right so alkalinity is given case and PH is given so I want to express in terms of H+ the OH-.

We know is KW by H+ and where does this come from because you know the water can dissociate into H+ and OH- and the water dissociation constant is going to be equal to H+ into OH- right again just to you know refresh our memories fundamentally what is it KW = activity of H + right and activity of OH- by activity of water at activity of water in this dilute systems is going to be equal to 1 and we are approximate it the activities by concentration.

So right that is where we end up with or that is how we end up with this particular equation and – H+ right and how can I express HCO3- and H3CO32- in terms of CO3 total now. and obviously as we know right we took the ionization fractions so alpha naught is nothing but H2CO3 concentration by CO3 total and similarly the first second and third ionization factor in this case or what are they CO3- by CO3 total and CO32- by CO3 total.

Again just to refer your memories we talked about you know I guess quite some session ago this has in ionization fractions so what do this ionization fractions give an idea about obviously has we just try to job them down understand that each ionization fraction will give an idea about the relevant protonated and deprotonated form in terms of the total acid concentration so for example the relevant species for us are HCO3- and CO32- so how can we express them as alpha 1 = HCO3 - / CO3 total and alpha2 is CO32- by CO3 total and what is CO3 total now?

In general CO3 total if you write it down in this case should be = HCO3- + H2CO3 + CO32- right total acid concentration in this case yes. So anyway let us try to use that here so that then going to be equal to how do I transform these two variable going to be equal to alpha1 + 2 times of alpha this is alpha 2 pardon me right alpha 2 into and from this set of equations you know into CO3 total right.

So what do we see here given that you have the alkalinity and given then you have PH or H+ you can end up calculating CO3 total right you know that alpha naught pardon me alpha 1 and 2 alpha 2 or constants for given PH so you can calculate them they are more or less constants given that you know the PH and the relevant system which in this case is carbonate system so here with the PH and alkalinity we end up calculating the CO3 total and once we have that we can also calculate H total right.

So once we have H total CO3 total and X total we have the relevant total components right so once we have this obviously what can we solve for we can solve for the species or the concentration of species more or less species means what are they the compounds present at equilibrium right so we are able to solve that this is manually the right but again solving at manually obviously going to take from time right.

So let us look at one particular example or such where we going to use VMINTEQ but we should always be able to understand the basics behind is and we will see why later on when we look at a minor example I guess right.

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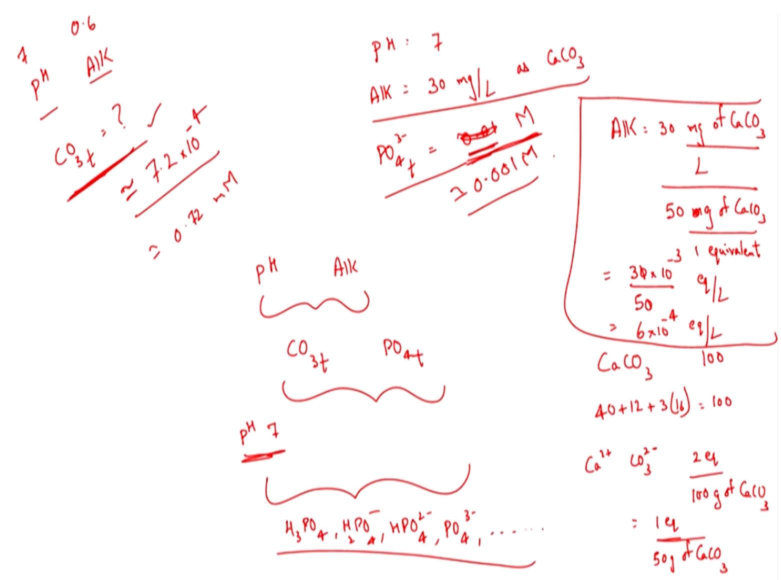

So here we are going to start looking at VMINTEQ right and let us say let us take particular case when PH let us say is 7 right alkalinity let us say is 30 milli gram per liter expressed as CACO3 right and let us say my X total in this case let us say PO43- total = let us say 0.01 molal or molar units which we are approximating = molal units in VMINTEQ if required we will change this later but for example let us take this down.

So you can either use the units of alkalinity as CACO3 we will see that right or we can transform that and how do we transform that = 30 milli gram of CACO3 at and try to express them in terms of relevant compounds so that is easy to understand per liter of water right if I want to transform that into it equivalence per liter so I am going to divide that by I know that it is going to 50 grams of CA CO3 per 1 equivalent I guess right.

So where did we get this from calcium carbonate the molecular weight is 100 I guess right 40 + 12 + 3 times 16 is I guess is 48 right 48 + 12 is 60 yes 60 + 40 that is 100 but we know that you know it is CA2 and CO32- when they can dissociate into that so more or less we end up with 2 equivalents right per100 grams of CACO3 right. So more or less 1 per 50 grams of CACO3 right anyway that is the what do we say background here so that we end up with 30 into 10 power -3 / 50 equivalence per liter so that is equal to 3/5 is 0.6 into 10 power -4 equivalence per liter so that is something that we just have as the background.

So let us now switch out to VMINTEQ right and understand the system so again what do we need to do let us switch back what do we need to do here. So we have the PH we have alkalinity right VMINEQ cannot calculate whatever it is we want run only so what we need to do initially we obvious need to calculate what is the CO3 total right so how do we do that so look at that so let us switch so here was our PH so I think we said PH was 7.

So the PH I am going to fix it is okay as 7 that is the value that we alkalinity have here and we know we have alkalinity so let us go by specifying alkalinity as you see here we have different units as milli gram per liter of HCO3- HCO32- CACO3 or milli equivalence per liter is I did not have the transform units for milligram per liter of CACO3 into milli equivalence but anyway for understand we did so that is fine.

So we transform that into equivalence per liter right so and that we end with 6 into 10 power -4 which is 0.6 mili equivalence right hopefully I am right and normal we will go through this particular case let us say again PH 4.5 because we titrated to PH4.5 and normal definition here you can understand the difference if we want to so I plug that in so and now I run VMINTEQ the number of components = number of fixed species okay.

Obviously I see that there is any issue their because as you expected right let us go back to VMINTEQ menu and we ridiculous so let us say something else need to be given here right so I need to view back to main menu let us say and also let us say I am going to have NA+ and act guess I will try to see if we can let the system guess okay again Visual MINTEQ species into input file as fixed possible finite or was not or exclude was not in the thermo dynamic database I think let me understand the system here and ok.

So CO32- NA+ back to main menu let me add H+ I think that is the reason I why we are end up with an error let us see H+ here okay add to the list we were at list let me try of this should hopefully solve this issue or I think I still need to add the CL- will back to that anyway one way would run by what do we say what we are up to anyway looks like would not H+ or deleted H+ / error we end up with issue right so where do we have this particular let us look at this species the distribution ones.

So PH you would assume that or you would expected everything would be present as HCO3- so that is what most of it as CO3 total is present as HCO3 and that is what you see here 81 or 82 % present as what do we say H2CO3- and H2CO3 is 18 % of CO3 total right that is what you expect on PH which is 7 back to main menu input menu.

And now here let us say where can I get the CO3 total here please so I can go back to species distribution not really or now I can some up the CO3 total right CO3 total will be equal to CO32- H2CO3 and HCO3- so I can sum up these three values and then I will end up calculating my CO3 total right so that is want I can see from here and new species distribution pardon me this space saturation this is when we have to look at say saturation or precipitation or dissolution which do not go into right now.

So now from this particular graph I can end up calculating you know graph pardon me from this particular set of values I can end up calculating the CO3 total right CO32- H2CO3 HC03 the sum of them will give me my HCO3 total so I input in PH at 7 alkalinity at 0.6 equivalence per liter and I can calculate my CO3 total right for sake of ease let me just take it as this is what we say 10 power okay 6. HCO3- is let us say this is 6 7.2 into 10 power -4 you know let us say 7.2 into 10 power -4.

Let me take that and then try to plug in the relevant values it is not equal we can use the excel and get the relevant values right. So again what are we up to here I am trying to calculate the component balance in terms of CO3 total and because excel and VMINTEQ can do that by itself we plugged in PH and in parameters we plugged in alkalinity in terms of equivalent per liter units and then looking at relevant species I can calculate the CO3 total right.

So let us come back to this obviously I can print it to excel and get the relevant what do we say species concentration first I go back to main menu at list so earlier am in the error of you know having inhabitant H+ that is why we lo0ked at error right and where are the output files okay here are the output files look at relevant concentration here and calculate that. So now I am going to change it such that how do I change it that I want to also put in phosphate total right.

So let us see how can we go about that specify alkalinity let us say now I can no there is no alkalinity specified in the solution we were in the hit list and now CO3 total is going to relatively what is it I think 7.4 right 7.2 into 10 power -4 right let us plug that in CO3 total back to main menu and CO3 total and key let us say I will use milli molal I just need to plug again 0.72 milli molal right.

And so here I am going to plug in 0.72 and add that to the list and what else do I have here please also have first (()) (21:09) and what is that we said was 0.01 molal that is a bit of high concentration let us look at that later so now PH is not fixed before let us say calculated from mass balance let us say let us if we are workout not read earlier PH at 7 because I know it is 37 and PO43- and I said I am going to use it at molal concentration of 0.01 right or to make it relatively similar I am going to change it 0.001 or 1 milli molal right otherwise it might be way to high.

So here I have 0.002H and so on back to main menu and PH is fixed at 7 so now I can calculate the relevant concentrations or the relevant species which are H2PO4 H3PO4 HPO42- which are unable to do earlier so I look at the relevant species distribution right so CO32- it is present obviously at 82% and HCO3- and PO43- is present as HPO24- and H2PO4- right. So let us summarize what up to right back to input menu so keep in mind that we change this particular value to make it similar.

So again manually we saw how to do that again that summarize PH and alkalinity we plugged them initially right and then we end up from this particular information calculating CO3 total and we already have PO4 total right and using this information right and also fix in the PH at the given value which is PH7 and then end up calculating all the species concentration and what would the H3PO4 H2PO4- HPO42- and PO42- and so on.

So this is what we can do obviously we need to transform and such that we get the first component that we need to look at and then go through right.

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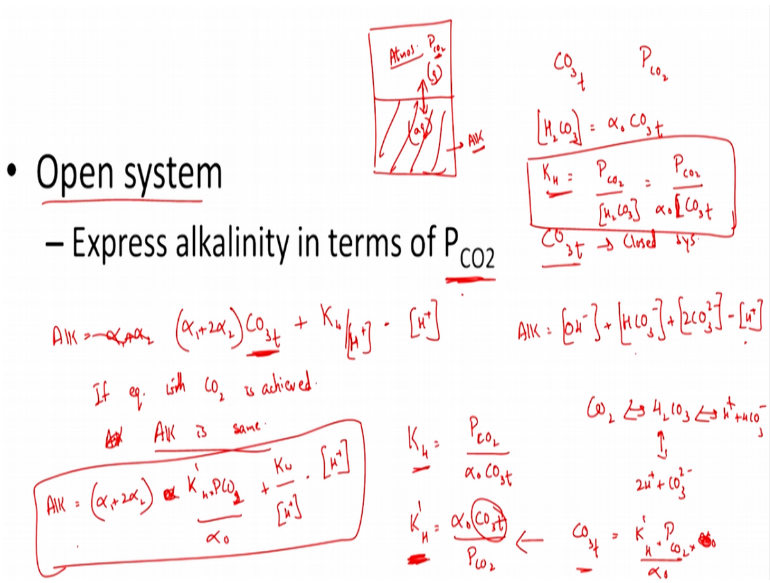

So this we have done with this now so let us move on to the open system right and where is that so open system I guess then what is about so when this case is then you have you particular system here but it is you know you know open the atmosphere gaseous phase let us say.

And here what do you have as we know the transfer of carbon dioxide HCO3 total between the gaseous and the aqueous phase. So for this we looked at the relevant what do we say transformation earlier obviously we are not going to go through that but we are going to look at applications I guess right so let us see right.

So obviously here instead of CO3 total right which we did in the closed system obviously we are going to try to express our terms of alkalinity in terms of partial pressure of carbon dioxide so let us see how it can do that I think we might looked at minor transformation earlier. So we know that alkalinity = alpha 1 + alpha 2 alpha 1 + 2 alpha2 because 2 times CO3 2- into CO3 total + KW + H+ - H+ right anyway what is this equation though?

This equation is when we have alkalinity initial I guess this is the alkalinity equation for initial cases. But let us say now we have carbon dioxide that is in equilibrium with your particular system so we will what do we need to do I guess what is the case. So here we have alkalinity here and we have let us say partial pressure of carbon dioxide so how do I go about this particular case now right.

So again the key aspect that we need to consider here is that from what we discussed the couple to sessions ago we know that alkalinity does not change when you introduce carbon dioxide into the system or remove carbon dioxide from the system right. So how was that why do we come up with that alkalinity was equal to or what now OH- and the other bases or HCO3- + 2CO2- - H+ right.

And we saw that when we bubbled carbon dioxide can go to H2CO3 or H+ HCO3- or you can directly let us say also go to 2H+ and CO32- if we plug in the relevant variables we see that you know 2CO32- and – H+ or HCO3- and – H+ so they cancel each other out right. So again if we remember what we discussed introducing or remove carbon dioxide from your particular solution will not affect alkalinity.

Obviously the PH is going to change but it is not going to change the alkalinity so this is the key here as an alkalinity before and after equilibrium with gaseous phase is going to be the same right. So let us use that so let us say if I assume that if equilibrium with CO2 is achieved right the alkalinity is still going to be the same right alkalinity is same. But obviously I want to transform CO3 total into what do we say partial pressure of CO2.

So CO3 total I want to express in terms of partial pressure of CO2 right so in this case we looked at particular case earlier so I think we talked about H2CO3 right and that it was equal to what now in terms of your total it was alpha naught into CO3 total right and then we talked about the henry constant PH right and then we try to solve for it henry constant that would give me an idea about partial pressure of CO2 / partial pressure of H2CO3 in the aqueous phase right.

So that is going to be equal to partial pressure of CO2 / alpha naught into CO3 total right this is something I believe we looked at previously. So KH is going to equal to PCO2 by alpha naught into CO3 total right but depending on the units let us say if it K dash H where in the units are moles per atmosphere this is then going to be equal to alpha naught into CO3 total by partial pressure of CO2in the case that the units are going to be or can be different right you need to look at the units whenever you are looking at henry's constant right.

Again to refresh out memory we just trying to use Henry's constant to get relationship between partial pressure CO2 and CO3 total right and what does Henry's constant give us an idea about it gives us an idea about the concentration in the gaseous phase of a compound to the concentration of the compound in the aqueous phase in this case we are talking about CO2.

So we say that Henry is constant and depending on the units is either going to be the partial pressure of CO2 in the gaseous phase to the concentration of H2CO3 in the aqueous phase or if the units of henry's constants are you know vice versa as in of the inverse let us say as in effects moles per liter at atmosphere is going to then going to be henry's constant of K dash H is going to be equal to H2CO3 concentration by partial pressure of CO2 right.

So I believe it this particular earlier so I am going to continue using this so can I express alkalinity here so alkalinity is now going to be equal to alpha1 + 2alpha2 into right where do I have that so I have CO3 total so CO3 total in this case = K dash H into partial pressure of CO2 into alpha naught so that is going to be equal to CO3 total = K dash H into partial pressure CO2 by naught into alpha naught divided by alpha naught obviously right partial pressure of CO2 by alpha naught + KW by H+ - concentration of H+ right.

So in this way was can simply the particular system further and you can solve for the relevant aspects right so again we just try to this is the manual approach so we are obviously going to look at how to get that done or it is what do we say it is the if you are trying to use VMINTEQ right.

So again what have you done here we just try to express CO3 total in terms of partial pressure of CO2 and why is that so this is a open system as in the what do we say solution is open to the gaseous phase and there can be transfer of CO2 or CO3 total obviously right from the gaseous to the liquid or liquid to the gaseous so that is the reason we looked at alkalinity and again why alkalinity because alkalinity does not change when there is any exchange of CO2 between the gaseous and aqueous phase right.

So let us try to use VMINTEQ and try to look at a particular scenario pardon me so let us go back to VMINTEQ and see how we can go through with that so now let us edit the list what we are up to earlier right. So I am going to view edit the list and I am going to delete this I am going to delete this for now and back to main menu so I am going to say this PH and alkalinity right and to PH and alkalinity specify alkalinity and there is alkalinity now let us say it is present as 3 in my case 30 milli liter as CACO3 which we looked at earlier right so okay.

And PH is going to be fixed as 7 let us say for my example right and view edit list okay it already obviously calculated the case for that back to main menu and then run MINTEQ right PH7 and so on yes and we can the CO3 total from here H2CO3 and such obviously from here what can I calculate I can calculate.

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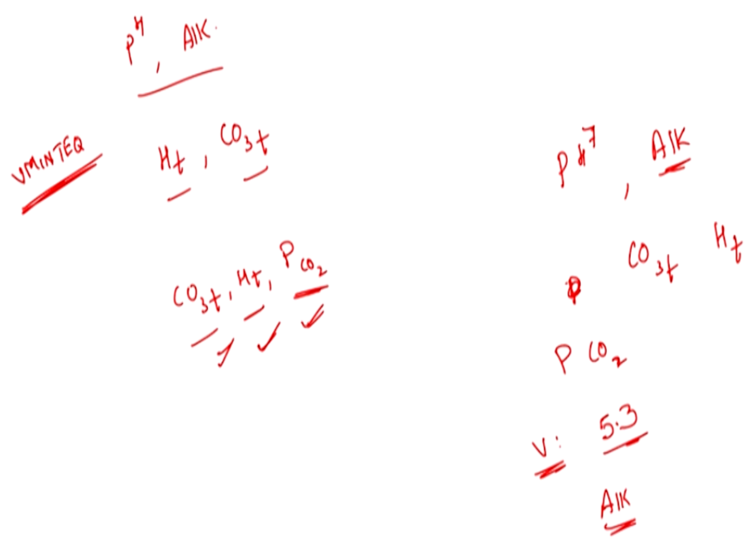

So plug in PH and what is it please alkalinity I can then end up calculating H total and CO3 total right from VMINTEQ again and now what am I going to do I am going to end the CO3 total H total and now give the partial pressure of CO2 right let us give us random value their and then we can come up with particular you know case I guess instead of calculating the aspects I am going to you know go head and get that done with some random values obviously you can calculate total and CO3 total here.

So back to input menu and view edit list so hopefully even might to be the same and what next here we are trying to input CO3 total H total and PCO2 so strictly speaking we calculate that from the previous particular VMINTEQ output but I am going to use the random value and we can see how can we go through right so HCO3 total and PCO2 let us go back to that so here now parameters i am going to say now more alkalinity now right because I am going to input CO3 total right.

But gases I know that I need specify gases how do I do that and pressure so I am going to change it let us say that we are going to be two times let us say than what I would expect in the atmosphere what is this tab here so it says specify the fixed CO2 partial pressure and atmosphere CO2 pressure is given you know which I am going to say it is constant but in my case I am going to say the partial pressure is what I would expect in the atmosphere.

So that is what we see here enter the partial pressure of CO2 as multiple of excel as going to say it is going to be equal to twice of what I would expect a let us say go with thrice or what I would expect in my atmosphere you know this is the hypothetical example I am looking it going to click at and back to main menu.

So I need to also give the CO3 total right CO3 total is that CO3 total let us say I am going with 0.001 add to list right view edit list is back to main menu and run MINTEQ okay because the charge is not balance so it is going to take CL- at particular concentration and now we can end up with relevant you know aspect after PCO2 is take into case as you say PCO2 is present as this particular partial pressure at equilibrium right.

So with that I am going to end today session again the cuts of the issue is to be transformed using PH and alkalinity we end up calculating CO3 total and then use the relevant aspect in closed system but in the open system what we are up to we are calculate OH and CO3 total pardon me H total and CO3 total from PH and alkalinity and then use that to have the pressure of CO2 why is that because an open system and the calculate the relevant species obviously in this example I did not plug in PO4 total so I could have plugged in PO4 total and so on PO4.

But here one case is that you know if I remove the PH because let us PH is not going to be constant when partial pressure is let us say changed calculate mass and charge balance run that so obviously we see that something need to be done earlier the PH is not going to stay the same which was the initial case earlier but the PH is going to fall why is that going to fall because I increase the introduce a new variable in terms of partial pressure of CO2.

As an let me just clarify that so earlier the PH was 7 right and there is a given alkalinity and then I end up calculating you know the relevant CO3 total and PH total which I assume random values I guess right which you given time may be later and then I plugged in values of partial pressure of CO2 and then ran VMINTEQ and what did I get I got a procedures around 5.2 right. But if I calculate the CO3 total or not CO3 total pardon me the alkalinity should still be the same right. So that is what we see here and with that I will end today's session and thank you.