Environment Engineering: Chemical Processes
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Module No # 04
Lecture No # 17
Introduction to VMINTEQ

Hello everyone welcome back right so we are talking about I believe acids and basis and this in this context we are discussed kinetics and we have talked little no aspects covered little to know aspects in respect to kinetics why is that because the acids and basis are in those systems I guess the kinetics is so fast but in general you will almost always end up HAV equilibrium to analyze the system now right.

So we did away with kinetics and we started analyzing equilibrium always looking at various aspects with respect to equilibrium. So equilibrium again what does that give you an idea about the state at which or the state achieve as the system as gone to the maximum extent of for those extent possible under the given condition of temperature and pressure right. So in that context we have moved forward I believe we looked at various examples or importance of acid base system and PH specially and why it is master variable.

So think or air and oxygen right and it is the source of life now so similarly PH as it hand in each and every system with environmental engineering systems. As we go further down and look at most of the application we will see that I guess and in that case we want to be able to be relate let us say which acid is going to be present as the protonated form or deprotonated form and in what fraction right.

Because you want to know can it be removed by ionization fractions or such and thus you want to look at is charged or uncharged and release the proton or can I actually as an acid at that particular PH yes or no so to be able to cover these aspects or understand these aspects we looked at Henderson Haselbach equation and what is that give an idea about. It give us an idea about PH (()) (02:13) to PKA and the concentration of the deprotonated form A - / the protonated form HA so that is the aspect their right.

And then I believe we moved on to discuss the ionization fraction in the last lecture class so we are done with more or less being able understand the background with respect to the acid and basis and one particular aspect that we come across is the acid dissociation constant KA right and in this context KA or PKA value which is the negative logarithm of KA gives you an idea about the strength of the acid so what do I mean by that let us say PK of HCL I think 0 or less than 0.

So what is that mean so it has almost all the PH values because PH 12 HCL is going to dissociate into H+ and CL – or it can actually donate the proton or it will act and acid but for an example if I acetic acid PKA is 4.76 I guess so PKA or PH3 the acetic acid cannot donate its proton or only some of it are small fraction of it because we call that or else truly I guess weaker acid right all these terms are relative.

So how do you quantify that we can look at that with respect to PKA right so now what we are going to discuss now I guess he is you know you have multiple systems out there in nature either in water air and so on let us say. So for example a particular concentration of a particular acid is introduced in the system what is my equilibrium is going to be with respect to change in PH or the change in species concentration species as in concentration on compounds presented in equilibrium.

So this is where the cracks of the what do we say class wise we want to be able to quantify the changes and what you would expect at the equilibrium.

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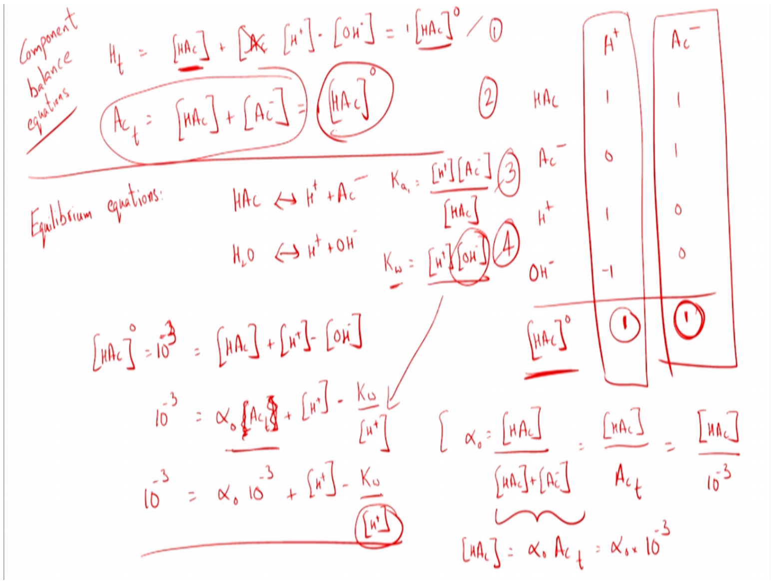

So in that case let us go on I guess so now we are going to start looking at developing models especially when you have multiple reactions right and in that context we already discussed the models and I believe we talked about this model physically the component balance component balance we introduce the concept of this building block called the component in terms of equilibrium.

So we are not going to that in detail again but we are going to have a problem solving session throughout the class we are having some problem solving session but this time we are going to have it in tandem with the lecture session I guess right. The component balance I guess let us look at an example that I have here so looks like an example that I am going to we are going to look at is the first one is going to be a single acid.

So if you have or if you know that the concentration of your particular solution is such that after adding acetic acid it is going to be at 10 power -3 molar right acetic let us say right I want to know what are the equilibrium concentrations of the various species right. So again this is a simple example we are going to start with right now assume a case or look at a case where you have added acid or acetic acid in this particular case 3COOH which we are for which we are using nomenclature HAC right.

So you added HAC such that concentration of the acid in that particular system is 10 power -3 molar so I let us see we are going to start with baby steps so first I want to be able to calculate the PH for this single acid base system and then I will also want to calculate the relative concentration not relative pardon me the relevant concentrations from the various species has not this compound that would be in equilibrium in that particular solution.

So let us go ahead and identify the species so what are the species I have let us say right and in this case we are only assuming that it is HAC and then let us have a two water right so has we know from our background right any acid you have an acid let us put into solution it can be it stay has protonated form all the deprotonated form. So in this case what do we have we have acetic acid CH3COOH or HAC and it can deprotonated and then form a state ion AC – so that is what we have here.

So we have H+ and AC – so obviously the species what can they can be the protonated form of the acid the deprotonated form of the acid and you will always have H+ and obviously if you have H+ we will have OH- right. So these are the species of the compound that you would expect you have at your equilibrium and so what next now we need to identify the components.

And so again a deep refresh here what are these components they are the building blocks right so think of your the game that you played in your child would if any I guess right. So you have this blocks let us say blue colored blocks red colored blocks yellow colored and you can choose from individual blocks or colored individual differently colored blocks and form different shapes right.

But if I look at the total number of the blocks of blue, red and yellow we still going to stay the same right. So these blocks are components conservative right so that is the concept we are going to use to the able to solve any and all equilibrium based portions. So again components we choose components I guess you are going to choose the H+ in general always if you want to you can choose other components too but choosing other components might require additional calculations.

So a good thumb rule is always to use the proton or H+ and then to choose he most deprotonated form of the acid and in that case is going to be AC- right so also I guess a care needs to be taken with respect to choosing components is that you need to choose minimum possible member right and also keep I mind that cannot choose component which you can use to form the third component itself.

For example component 1 and 2 cannot be used to form 3 they need to independent of each other right. So that is obviously the case here so once I have done with that components I guess we need to write the formation equations the formation the formation equations as in I want to find the species which I am going to list here from my components. In general always components means it is always H_2O goes without add or without saying that water is always a component right.

And again we do not list it as species because water concentration in dilute systems we assume that it does not change right so that is the reason why we do not list water as the species and water is always considered a component though so here we are trying to form the species here from the various component so let us see how we can form that and here we have H^+ 1 component and AC^- required to form a HAC keep in mind that these are not chemical reactions these are literally H^+ AC – going to HAC or = HAC.

And you only need 1 AC – to form 1 AC – 1 H^+ to form 1 H^+ and H_2O – H^+ to be able to form here OH^-. So once you are expert let us say not even expert once you are comfortable with your component balance equation so in such you can I guess if you want to skip the formation reaction or equations pardon me not the reactions formation equations and directly move on to the Tableau.

So what is the tableau about this is where the crux of the matter lies tableau we have the component listed here H^+ and AC – and this here is the tableau and here we are going to have our species and what are they are HAC AC – H^+ and OH^- right and now from your formation equations you are going to populate the relevant functions here. S how many H^+ required to form HAC as you see it is 1 so that is 1 and how many AC required to form AC that is 1 again or let us be done with H^+ first how many H^+ do need to form AC^- none.

How many H^+ to form 1H^+ 1 and in this case -1 and so again same case with a state AC^- 1 0 and 0 and obviously the last equation or the aspect that we need to look at is what is the source of all these components right what is that now keep in mind that the initial question was from we added acetic acid we know that source the only source of these components is from the initial acetic acid you add in.

So that is recipe species so that I going to be we added HAC so AHC naught again same case we need 1H to form HAC and again AC – to form HAC. So now we have done with the tableau and now we are going to move on to the balance equations right. So first obviously looking at component balance equations so it makes sense to be able to write these component balances now.

So how many component balances equations do we have so they will be equal to number of components that you define so in this case we define two component they are H+ and AC- and so you are going to have two components balance equations right so let us look at what they are? So I believe H total right = something else and AC total these are the total balance equations so if I am not wrong they are going to be equal to the concentrations of to be able to assist us further I am going to again re write or re write the tableau here and this is the recipe species the source of everything.

So this is my component balance now for H total that is equal to 1 times HAC concentration and what is this HAC? This is the equilibrium concentration right so H and AC- there is nothing in AC - + H+ - OH – and state or AC total and that is here and what is that equal to? Equal to HAC and AC – and what do we understand from these particular component balance right if you look at the first equation or H total we see that H is only present or can you know transform between HAC H+ and OH – right.

It can you know transform between these three species and the estate can transform between HAC and AC – but the total is always going to be the constant or be a constant and again as we discussed earlier what is the source of these components now keep in mind that we added estate initially right acetic acid and that is what we have here HAC naught and that is the source here we have 1 so it is one times HAC naught and this your known value obviously and here to it is going to be equal to 1 times HAC naught.

So here now how many equations do we have two equations but how many unknown we have four unknowns HAC, AC-, H+ and OH- and what are these? These are the concentration at equilibrium so we are still missing to further equations anyway let us label these please this is the component balance equations right this is what we have so we have done with that and the next aspect is going to be the equilibrium equations.

Again we are trying to solve for a system that is at equilibrium so obviously you are going to have equilibrium equation to assist you in your solution right. So let us look at what they are and we know that we have two particular dissociation here with respect to acid and base they are HAC going to H+ and AC- and H2O dissociating into what is it H+ and OH –.

And we have the relevant dissociating constant KA1 that is equal to concentration of H+ into concentration of AC- / concentration of what now HAC and here we have acid dissociation constant for water and that is going to concentration of H + into concentration of OH- and obviously concentration of water is going to be equal to 1 that is we do not list it here. So here now we have two other independent equation and so in total we have 1, 2, 3 and 4 equations right.

So we have four equation that are independent equations and four variables and thus we can solve for your solution now but before we go further I guess the point of this class not for you to only be able to concept the number and you know blow some of the mind right so you also want to develop the intuition with respect to what it is you would expect in nature or what would expect to see as in you know that what are we plugging here yet.

You are adding 10 power -3 or you want to estimate the concentration of 10 power -3 molar acetic acid and you always –plug this in or now we are also start looking at in the visual software that I requested the people install the visual WINTEQ software we are going to look at that too but you should also be able to guess your particular value the PH at least right. So we are going to do that let see how we can solve this particular aspect I guess right.

So what is that here and here we are going to solve for H+ that makes everything easier so we have HAC naught right and that we know 10 power – 3 molar we are going to use that is going to be = HAC + H+ - OH – right. And so obviously now what else can I list this as though so here we have four independent equation but if you remember we already solve for ionization fractions right.

Ionization fraction what do they give an idea about they give you an idea about well let us say the fraction of particular protonated or deprotonated form in relation to or with respect to the total acid. So here let us try to use that so we do we have here we have 0 power -3 = alpha naught into total what is that I guess that will be a total in this case you will see Y + H+ estate total not the concentration obviously – KW by H+.

So let us see where we go this particular term from so these is from here so OH – concentration = KW / H+ and let us see how we end up with it here we know that alpha naught = concentration of HAC / concentration of HAC + concentration of AC – and what is that equal to concentration of HAC / and look at these term sounds or seems familiar and that is nothing but equation number 2 equation number 2 here and so that is hesitate total right.

And again you know that hesitate total into HAC naught so that is going to be equal to HAC / 10 power -3 again HAC = alpha naught into estate total or that is equal to alpha naught here into estate total into 10 power – 3 so we have plug that in here 10 power – 3 = alpha naught into 10 power -3 into estate total + H+ - KW + H+ and I guess now you are going to have a quadrature equations and you can end up solving for this particular equations right.

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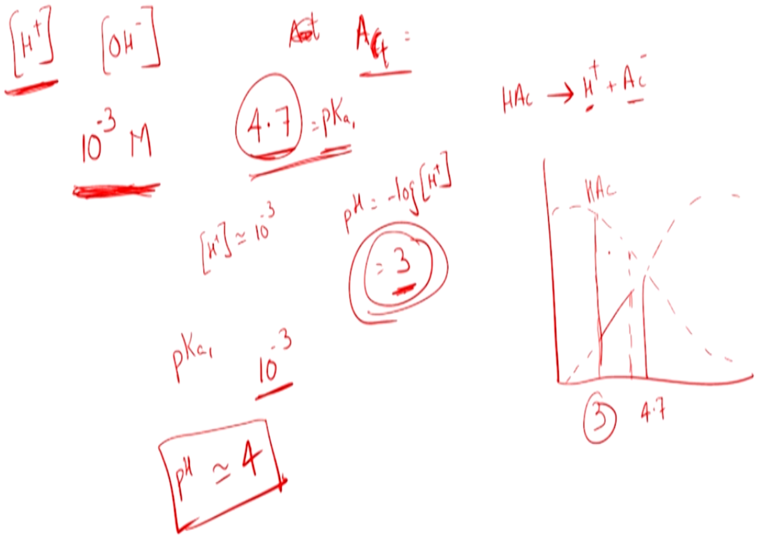

So once you have H+ let us move on once you have or you solve that H+ form that particular equation you can immediately solve for OH- right and once you have we know that estate total or you can solve for the relevant two equation from KA- let us say and equation 2 and equation 3. So before we go further we also going to look at visual mintech briefly today right let see what it is about?

But before we go further let us see if we can estimate let us say the PH I guess let us dig up the solution but in the meantime let us say if we can also estimate the PH of the solution or concentration of H+ so this is to develop intuition let us see how good or bad we are. So we know that we are concentration of the acid it is 10 power -3 molar the total anyway the total is 10 power -3 molar and the other crucial piece of information is 4.7 is the PKA or the relevant PKA or the acid dissociation concentration right so we have these two aspects yes let us see what we can estimate here.

So one case is that estimate is that all the acid that I put in is going to dissociate or assume HAC is going to completely dissociate into H+ and AC- right but that is not going to the case so let us see what the PH will be a that particular case PH will be so if you completely dissociation H+ is let us say 10 power -3 approximately = 10 power -3 and then the PH will be equal to – log activity or concentration of H+ in this case = the PH will end up being 3 right so think of this though.

Do you think by adding acetic acid which as a PKA around 4.7 do you think the PH can be brought down to 3 not really and why is that as you know we looked the species diagram and what do you see 4.7 and you need enormous amount of acid to be able to bring that to 3 why is that PH3 why is that and most of it stays as HAC and it does not dissociate into H+ and AC – but out assumption when getting up PH3 value what is that I guess?

I assuming that all the acid or all the acetic acid dissociated into H+ and HAC – and then we can calculate the PH accordingly right but that is not the case here though why is that because PK is 4.7 so certainly the PKA would not be or PH would not be as low so a best it is going to be near or PKA but because we added considerable quant is which is 10 power -3 or considerable concentration PKA.

So let us go ahead and assume that the PH is going to be relatively near PH4 right is going to be below 4.7 right somewhere over here but it is not going to be as far as PH3 so this is particular you know one solution I guess right. So let us see how we can which is a tool or software that will help you predict the concentration of most scenarios especially with respect to acid and base complexes precipitation and design the solution at equilibrium.

So I believe we requested to source the software again I repeat it is visual MINTEQ of VMINTEQ that is available for free to download 10 or 20 MB.

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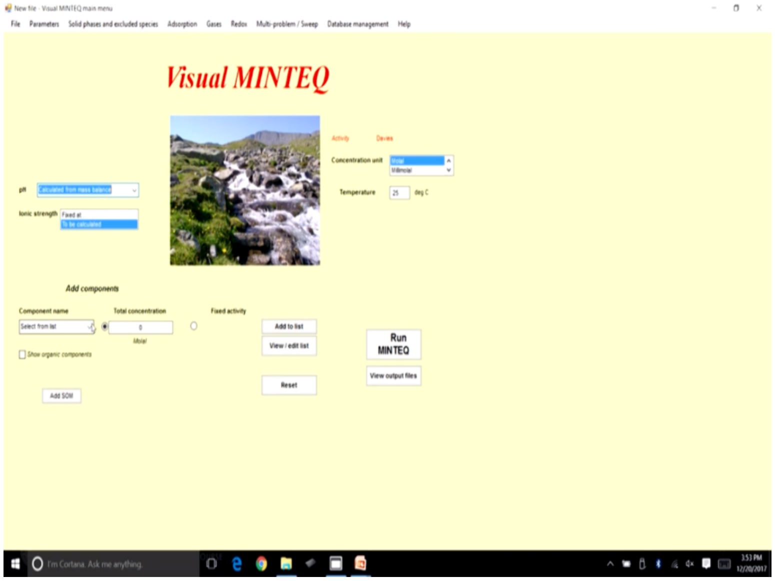

And I guess let us look at that particular interface now okay so here I guess so I am now if you download different versions but this is the version if I have here. So I believe what do we have here let us look at the software here for now so I have file you can open input file and such if you want to and parameters if I specify some of parameter such as alkalinity which will discuss later.

PE and EH their relevant to your reduction which we are not go into go into detail now but at the fag end of the class and If you are talking about precipitation and dissolution for example you know as solid precipitating you know dissolved compound one to threshold is increase let us say right you are going to have precipitating and inverse let us say dilute let us say you are going to have the solid dissolving into the aqueous form right.

So that is what we are going to have here and so this particular phase relevant to that so you can always have surface complication or absorption cam model SCM are going to discuss that later on at the end of the class so that is surface completion reaction I believe and gases your particular system with in equilibrium with gases right phase equilibrium.

So that is what we discussed earlier so this particular aspect is with respect to phase equilibrium again redox as in you are going to specify redox couple so you will have the oxidized form and the reduce form and you can specify your what your couples are going to be similar to your conjugate acid and base you are going to call the relevant what do we say oxidized and reduce form in couple so that is what we have here.

So again we will discuss those at the fag end of the class so multiuse problem let us say and what is happening please cancel back right maltase problem so here if you want to look at sweep or titration let us say you know let us say you want to see how the system changes with PH let us say or some such variables now.

So let us select that let us say is so you can see right are you can define the system in such a way that you have a particular solutions and add the titan it or you know change the PH how is my PH is going to change so that is what you can see here with respect to your titration and sweep 2 I guess with greater functionality you can vary either PH PE or so or any other concentration. So with the change in so think of this now.

So let us say you have waste water and let us say as you change the particular concentration of your compound any compound let us say ligand you want to know how the system changes so you can use the sweep here. So anyway we will discuss this in great detail later on for now I can move back and we are going to approximate the value of your particular solution or simple what do we say solution or simple what do we say solution that we looked up.

So right I am going to look at various aspect so here in one aspect and here it PH it is fixed or calculate from mass balance so right now we do not know the PH do we so I am obviously go into fix it so I am going to say the calculate from mass balance right and ionic strength it can be fixed at a particular value or you can it is going to be calculated I am going to leave it as calculate but at our system at ionic strength is not going to play huge role because it a dilute system anyway right.

So let us look at what else so here we have look at the variable + units their molal, milli molal, micro molal, milli gram per liter micro gram per liter log molal and so on. Again as we discussed earlier with respect to activities so right the concentration units or molal units and that is what you see here their molal units but obviously you can use molal units but the error is going to be around 3% because the density of the water is not exactly 1KG per liter I guess right.

So the temperature is standard temperature which is 25 degree centigrade so let us move on I guess PH calculate for mass balance ionic strength is calculated and now I need to choose my component add components so for this I need to able to look at the tableau. So let me look at my tableau where is my tableau here and here is my tableau and it is shabby manner let me have that.

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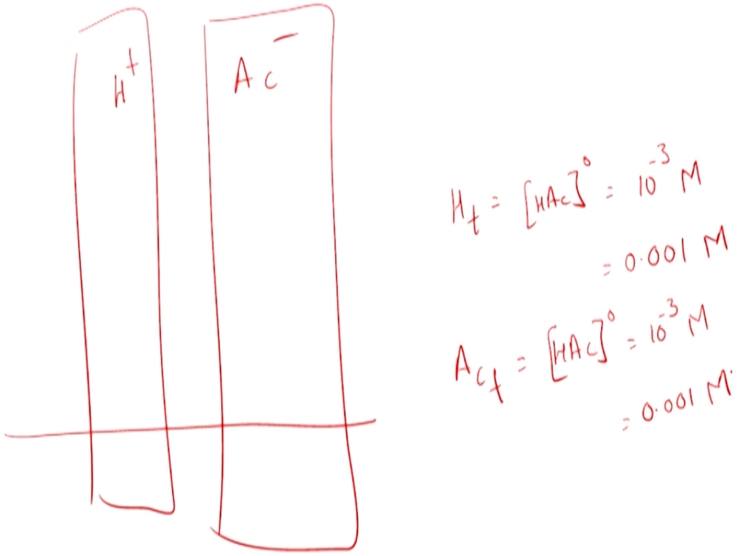

$$H_t = [HAc]^0 = 10^{-3}\,M$$
$$= 0.001\,M$$
$$Ac_t = [HAc]^0 = 10^{-3}\,M$$
$$= 0.001\,M$$

And the slide I guess i have my tableau H+ AC- right and I have relevant tableau here so my two components is going to be H+ let me choose H+ I drag down and I go to H+ and the concentration of H+ of the total concentration what is that = I guess so we know the H total as we looked H total is equal to HAC naught and that was equal to 10 power -3 molar.

So 0.001 molar right same case with estate total or AC total = HAC naught that is again equal to 10 power -3 molar and that is equal to 0.001 molar I guess right and let see plug this obviously to be able to use VMINTEQ you should at least be able to calculate your total component concentration as it at least be able to identify the components and then be able to give the tableau or form the tableau yourself and then come up with the relevant component balance right so let us look at what we have here.

So we are trying to help that list we will add the so this is going to be key 0.001 and I am going to add this to the list and we are going to check that later and so because acetic acid estate organic compound I need to choose that sure organic compounds and then AC- is the short cut or estate issue organic compounds and AC- is the short cut or estate okay here estate here and again same concentration right estate total is also again 0.001 molar.

And I am going to add that to the list and as it check and I am going to go move edit less and here i see H total is 0.001 molal and estate total is again 0.0001 molal and I am done with that now I will go back to main menu right let us see where we have now and now I will run VWINTEQ right and let us look at what we have let us look at this now the PH is 3.9. The first aspect to look is that we approximated the PH earlier right and that we said was going to be around 4 right.

So let us check out value what we have here and you see that PH they calculated they pardon the moral calculation is 3.9 so we were relatively no remarkably close or you know you are able to put remarkably or we did a good job in the PH value right so you should try to develop the particular intuition as you go along and ionic strength as you see here you know it is relatively low yours that something you would expect and here now in this particular section you see the concentration of various species what were the four species that are particular solutions they were estate are and acetic acid H+ and OH – and that is what you see here.

And obviously the system also gives you the activity and because the ionic strength is low you more or less see the concentration and activity of the relevant compound or more or less the same but if the ionic strength is high the activity is going to then the low right so this is something that you need to understand. So let me also look at few species distribution so this is the tab here few species distribution what is that give me an idea about.

So I want to look at in which form the estate is going to be in so it lets us only 12% of the total estate is going to be at AC- and 87% of estate is going to be in the form of HAC right so this is what we understand to right and let us look at what we have here I guess that to main output menu and if I switch what do we see here this is our system HAC and this is AC- PKA is 4.7 right and what was out current PH value I think is somewhere around 5.9 so 3.9 so what do you see here.

You see that most of it is present as HAC and little or only some of it present as AC – so let us check out values here and display and this is where it shows only 12% is present as deprotonated form or estate and 87% is present as the acid right so that is what we would expect and that is what we would observed to right come back to here and you can look at equilibrium mass distribution but not of great use in acid base system it is because everything is going to be in the dissolved form right.

So take our message here is that take the concentration you can get the PH right and you can also get the species distribution not species I guess speciation and also the relevant concentration of all your species. So today we were able to install a simple example with respect to adding an acid at known quantity of acid to water and then calculate what is the PH and the equilibrium concentration of all the various species there.

And then we also looked at how to use VMINTEQ and we are going to use visual MINTEQ throughout the class right that going to help you right you want to connect and experiment yes sure we have lot of time the sources and you have I am sure you do not have lot of time to spare so obviously visual MINTEQ is going to help you cut down on the calculation and your elaborated time right.

So at the next class again we are going to go through next lecture session again we are going to go through with our or more complex or slightly more complex examples and for this session I am done thank you