

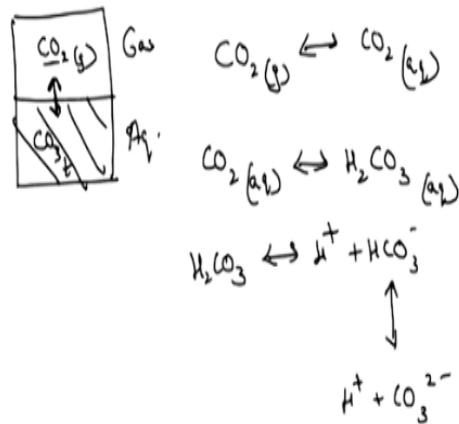
Environment Engineering: Chemical Processes
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Module No # 05
Lecture No # 24
VMINTEQ: Application Of Gases, Acid-Base Titration

Hello everyone welcome back to latest lecture session. So again we are going to briefly summarize what we have been up to in the last couple of lecture session. So I believe you are talking about the carbonate system, initially we discussed the close system as in when the relevant aqueous Phase is not open to the gaseous Phase and we are done with our analyze.

Then we moved in to the more complex system where your carbonate system in the aqueous Phase can be in equilibrium with your gaseous Phase. So you can have exchange of carbon dioxide between gaseous and aqueous Phase and tells that it increases the level of complexity in your system and we looked at the basics with respect to all copper imbalance. We looked at how to analyze the system. Let us briefly again look at that, so we have our

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System here and this is our aqueous Phase and here we have the gaseous Phase. So when you have the carbon dioxide in the gaseous Phase and you have the carbonate systems which are represent using CO₃ total here and you can have or it will have change in Phase of carbon dioxide from gaseous to aqueous. We know that carbon dioxide gaseous can dissolve to CO₂ aqueous and obviously that is CO₂ aqueous would be in the form of H₂CO₃ and aqueous.

The acid again we know that from our background H₂CO₃ can disassociate into H⁺ and HCO₃⁻ which can further disassociate and be in equilibrium with H⁺ and CO₃²⁻. So the relevant derivation might be seen relevant to complex but it is very simple, we just define everything in terms of the total component. Why is that? Because only the component is conservative.

So in the close system we only looked at H total for the liquid or CO₃ total for the liquid. But for the open system, we have another Phase which is the gaseous Phase. So we had H total or we define H total as the sum of H total in the liquid Phase and also the gaseous Phase and then we tried to correlate that with the change in CO₂ or CO₃ total or CO₂ total between the gaseous and the aqueous Phase and it is as simple as that and then we conducted the balance.

Again on H total in the aqueous Phase and we analyze for the system and went through that. So I am not going to go through the derivation again, but in last session we have looked at the application with respect to (()) (3:01) when the system is open so we will get that done now. So we will move on to V MINTEQ here.

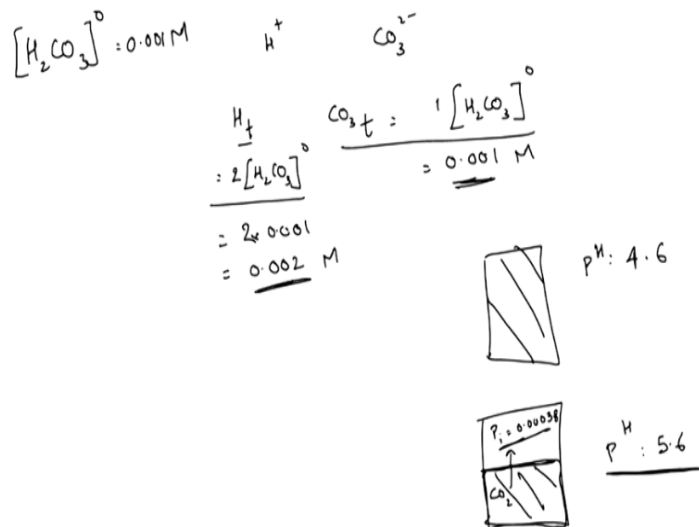
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So first we look at the simple case here. So let us say I have H two Co three in my system, I am going to take an H + and let us say the concentration that is going to be equal to 0.001 molal and add that to the list and let us say it is going to be H2 CO 3 where it is going to be two times, let me change that 0.002 add that to the list and then CO32-.

We are going to look for the component Co three two minus that is going to be at 0.001 molal and we add that to the list. Let us just check out a particular component 0.002 and CO32- is 0.001 and where did you get that?

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So we have H_2CO_3 in the system. So our components now are H^+ and CO_3^{2-} . So I am conducting the balance between H total and CO_3 total and H_2CO_3 . I am assuming that the initial concentration is equal to 0.001 molal and that is what we have, so H total will be equal to two times initial concentration of H_2CO_3 initial and CO_3 total is going to be one times the initial concentration of H_2CO_3 .

Obviously we are not going to go in detail because we have covered this in detail in previous sessions. So this is what we know putting in our system in Visual MINTEQ. So we have H total is equal to now two times 0.001 that is equal to 0.002 and CO_3 total will be equal to 0.001 molal and molal units. So now we are going to switch to Visual MINTEQ.

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Visual MINTEQ

pH: Calculated from mass balance

Ionic strength: Fixed at

Concentration unit: Molal

Temperature: 25 deg C

Add components

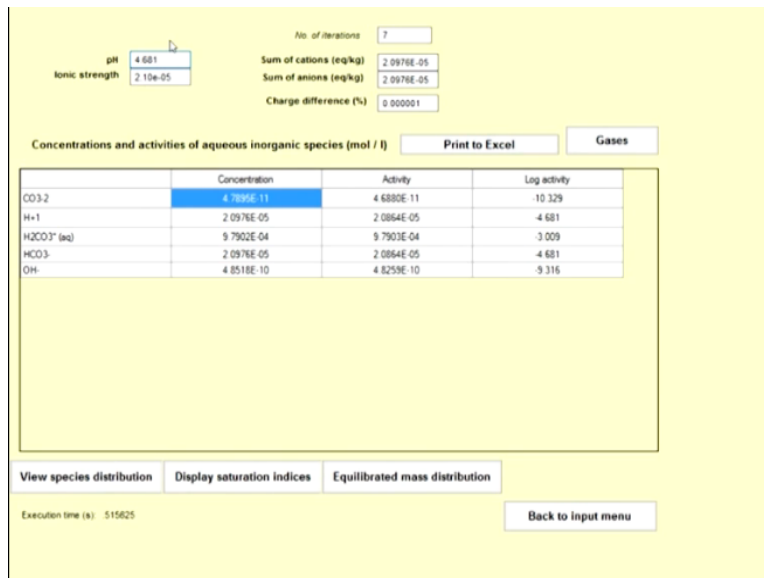
Component name	Total concentration	Fixed activity
CO3-2	0.001 Molal	<input checked="" type="radio"/>

Show organic components

Buttons: Add to list, View / edit list, Run MINTEQ, View output files, Reset, Add SOM

Let us edit our list and you all included this earlier. So going back to main menu there is obviously a close system. So for close system aqueous Phase is not open to the atmosphere. There is no gaseous Phase here, so I am going to run Visual MINTEQ add it. So I am going to run it.

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So let us see what we have, PH of 4.6 and that is expected H and we have the relevant concentration of CO₃²⁻, H₂CO₃ and HCO₃⁻. So all is expected because PKA 1 = 6.3 and PH is 4.6, you would expect the protonated form to be predominant. What is the protonated form here? It is H₂CO₃.

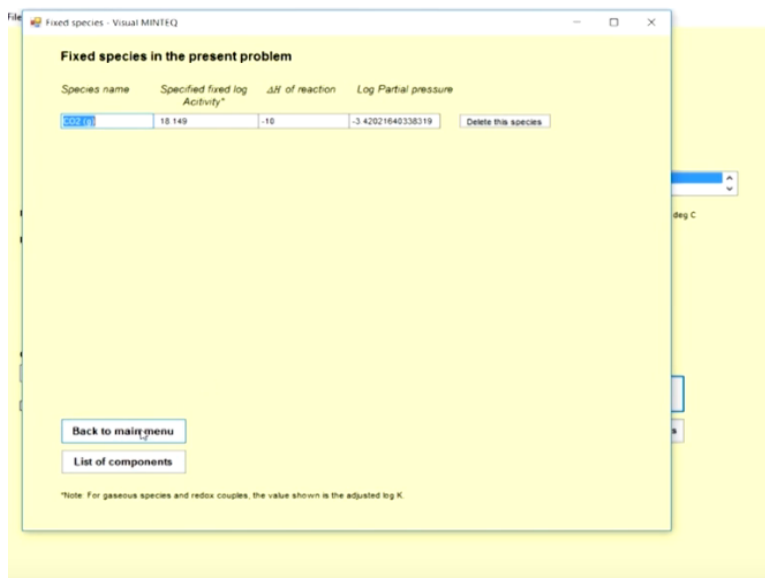
So if you look at the relevant value on V MINTEQ the result summary we will see that H₂CO₃ predominates which is what you expect. So let us look again as you see here PH 4.6 H₂CO₃ predominates 9.7 into 10. -4 and then HCO₃⁻ 10 times lesser. Obviously CO₃²⁻ the most deprotonated form is much lesser concentration.

So keep in mind the PH of this particular system is four point six eight. I am going back to the input and now I am going to change the system or I am going to change the system such that it is an open phase or you have an open system. So initially I am going to keep the carbon system concentration relatively low which would be similar to what you expect in the atmosphere.

Let us see if there is any change in PH and the second trial we are going to increase the PH of the carbon dioxide concentration that would be in equilibrium with your aqueous phase. So what would you expect from such a scenario? So if you take a few seconds you will see that carbon dioxide pressure in the axis phase increases.

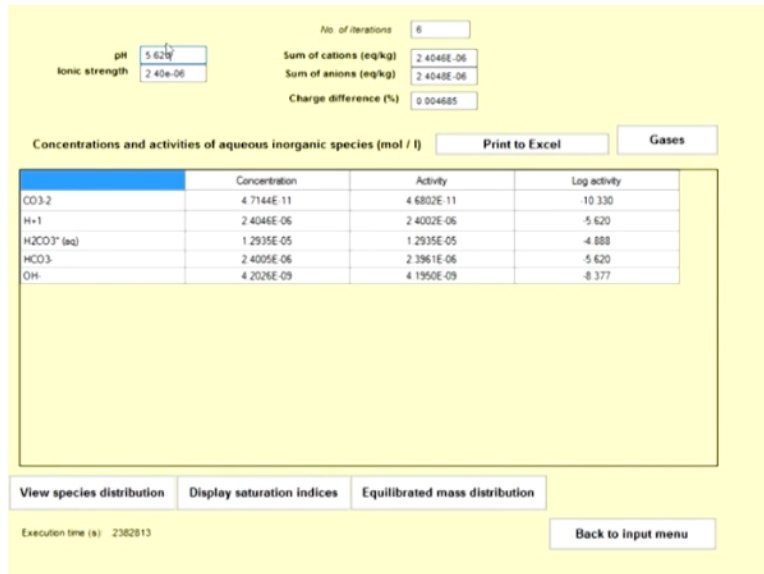
You are going to have equilibrium such that carbon dioxide is going to change its place from the gaseous to aqueous phase and then you are going to have formation of H_2CO_3 and so on. The relevant acid base dissociations and thus you are going to have or expect a decrease in pH. So let us try that now, so here when it is an open system.

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You need to go to gases and specify. So here this is the concentration in atmosphere. The partial pressure you can expect in the atmosphere. So first stick with that and try to add that and I am going to move on. Let me show you again gases specify and add. If you want to you can look at fixed species here CO_2 had is here now you have the relevant that you looked at, so back to main menu. I am going to run MINTEQ.

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We see that PH is 5.6, so what does that mean? Earlier we had Ph of four point six I believe and now we had PH of 5.6, what does that mean? So it means that the equilibrium is towards the carbon oxide or the CO3 total left the aqueous phase into and changed phase into the gaseous Phase in the form of CO2. So what does that mean? You are having a net loss of acid from your system.

So what does that translate into? It translates to an increase in the Ph. So that is what we looked at, so let us just look at that once more. So what was the case here? The earlier case when it was just the close system at these relevant concentration of 0.002 molal for H total and 0.001 molal for CO3 total, I think we calculated the PH to be 4.6.

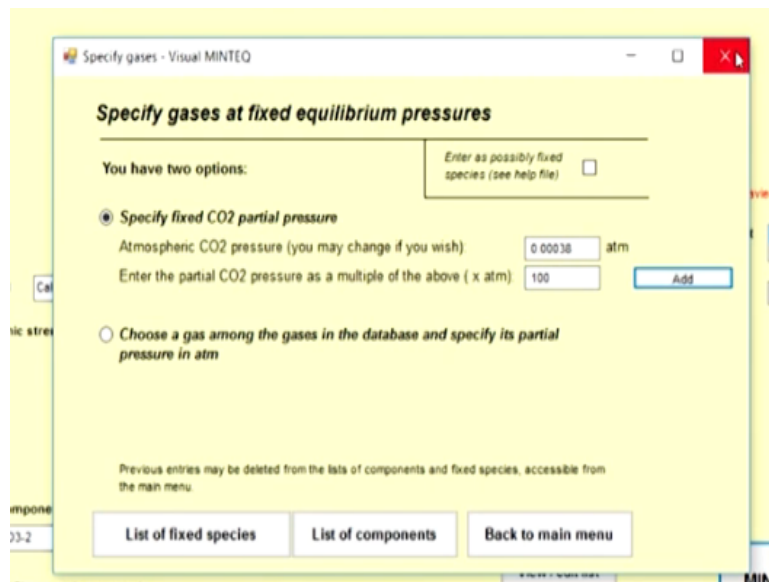
But now the same concentrations we have the gaseous phase here and we mention that the partial pressure of that particular carbon oxide was what I think 0.00038 atmosphere and so on which is similar to what you would expect in nature and when we calculate that, we saw that at equilibrium PH was around 5.6. So why that is because here the partial pressure seems to be less and you can look at the concentration so on.

We are not going to go into that so what happened was CO 3 or CO 2. Let us say you know gaseous phase. So now you have increase in your acid concentration here and that is why you see an increase in the PH. So now we will move back to open system back to input menu. So now

instead of having relatively low partial pressure of carbon dioxide, I am going to increase the pressure of carbon dioxide.

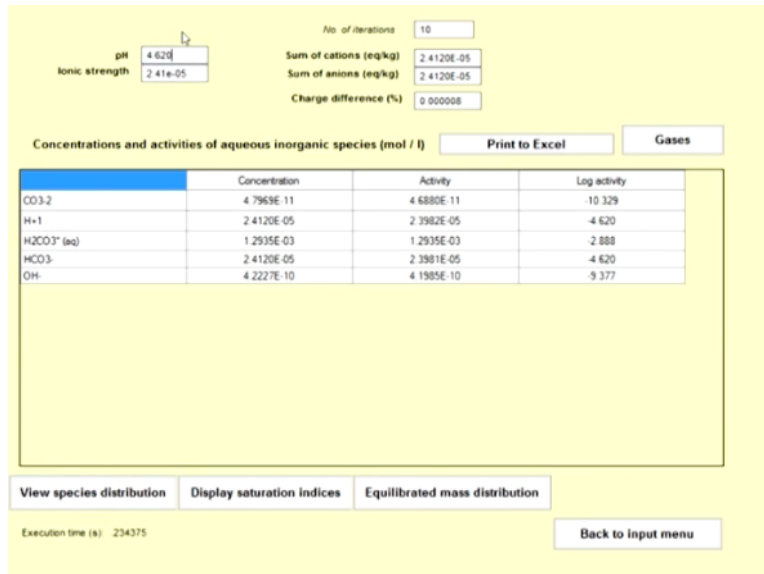
The partial pressure of carbon dioxide, so again think of this or visualize this you have lot of moles of carbon dioxide in the gaseous phase and relatively less moles of CO₃ total in your aqueous phase. So what is going to happen the equilibrium is going to shift in such a way that the moles of your particular CO₂ CO₃ total, obviously are going to change phase from the gaseous to the aqueous phase. So let us look at that we will come back to the gases here.

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I am going to specify the gases here. But this time instead of saying it one and I am going to say maybe it is hundred times. Let us see here we are just saying until the partial pressure of CO₂ as a multiple of the above. So if I want to go for zero point zero three eight atmospheres. I am going to say it is going to be hundred times here and I am going to add that and now let us us run MINTEQ.

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Now again you see that the PH has fallen down into 4.6. So what would be the carbon dioxide concentration in equilibrium with your particular system? So again we can look at that so more or less you could see that when the partial pressure was 0.038 atmosphere that is going to be in equilibrium with your particular system which is H₂CO₃ initial concentration of 0.001 molal.

You can also click on gases here and see that it is 3.8 into 10 power - 2 atmosphere. This is the partial pressure of carbon dioxide that will be in equilibrium with your system even that the relevant species concentrations are such species concentration. So again if I want to decrease the PH further what do I need to do? I obviously need to increase the carbon dioxide concentration.

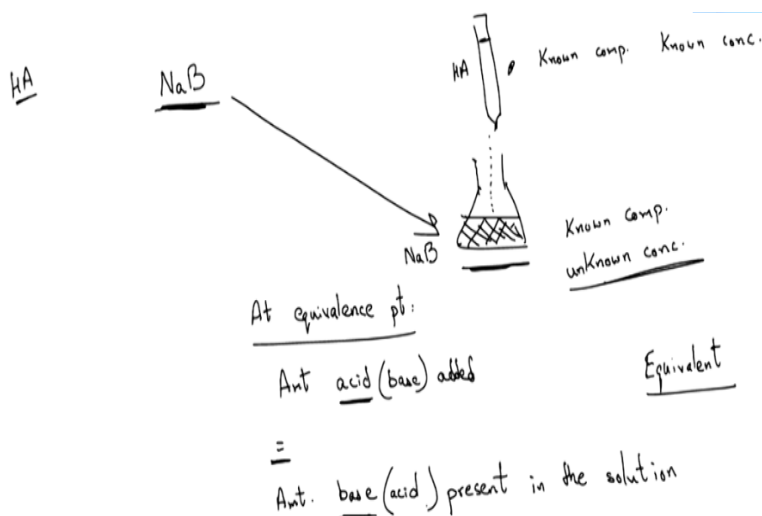
So instead of 0.038, let us look at zero point three eight. So I go back to the input menu and again back to gases and specify and instead of 100, let me try out a 1000 here add and back to main menu and going to run MINTEQ and here you see now fallen PH. Obviously why is that because now you are increasing the concentration of your carbon dioxide in the gaseous phase.

So again the equilibrium had shifted. So now to reach equilibrium again what is going to happen? The carbon dioxide from the aqueous phase is going from the gaseous phase is going to shift to the aqueous phase. So now you are going to have H₂CO₃ produced in your system and thus you are going to have a decrease in your PH.

So this is what we have observed this far and that is what we have been discussing with respect to our component balance in our earlier couple of session. So now we will move onto titrations.

So what are these titrations about? I guess if you are B tech graduate or even twelfth standard graduate, you would have some point in time connect in titration. Let us look at what we are upto here.

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So we have conical flask here and we have some solution here and then you have here burette known concentration and you know a known compound here of known concentration and here you have an known compound but unknown concentration and more or less the basic set up is you want to find out the unknown concentration of your particular compound in your conical flask.

How do you do that? You end up titrating it with relevant compound. You are going to choose the compound. But we are going to come back later. So you have an known compound in the burette, known concentration in the burette and you are going to titrate that and look at the relevant volume and then calculate the equivalent concentration. So this is the basic premise of almost all the titrations but keep in mind that there are different kinds of reactions.

We need to consider one is acid and base which were currently covered. But you can also have other reaction such as the redox reaction, the aqueous complex reaction or the precipitation reactions. But now since we are talking about the acid base we are going to look at those titrations that are relevant to the acid base reactions. In general obviously acid base reactions are the most widely used kinds of titrations and we will see why later on.

But again we are going to look at particular set of examples for acid base relevant titrations. So here, let us say I keep titrating it here with my burette and again place my band scale. We are adding, let us say I have an known base in my particular conical flask and I am titrating it with a known acid HA. Let us say I am titrating it with HA and HA is out here and NAB is out here.

So you will keep titrating, keep titrating. People in general use indicators, color change and so on so what happens at that particular point? So in general at that particular point the PKA of that particular indicator reach that particular point. So you are going to have, let us say more protonated form as you keep increasing the acid. So you can absorb a color change and so on and but what does that mean?

It means that at that particular equivalence point or that particular point where you stop the titration the amount of acid that you are adding is equal to equivalent to the amount of base in your particular conical flask. Hopefully you understand that, so let us joute them down. So at the equivalence point what is going to happen? The amount of acid added will be equal to the amount or equivalent.

I guess the key is equivalent to the amount of base that is present in the solution and because you know the concentration of acid that you are titrating it with. So then you can calculate the concentration of base present in the conical flask. So again the key is that it is equivalent concentrations and I think you are familiar with what we are talking about at this stage of the class review.

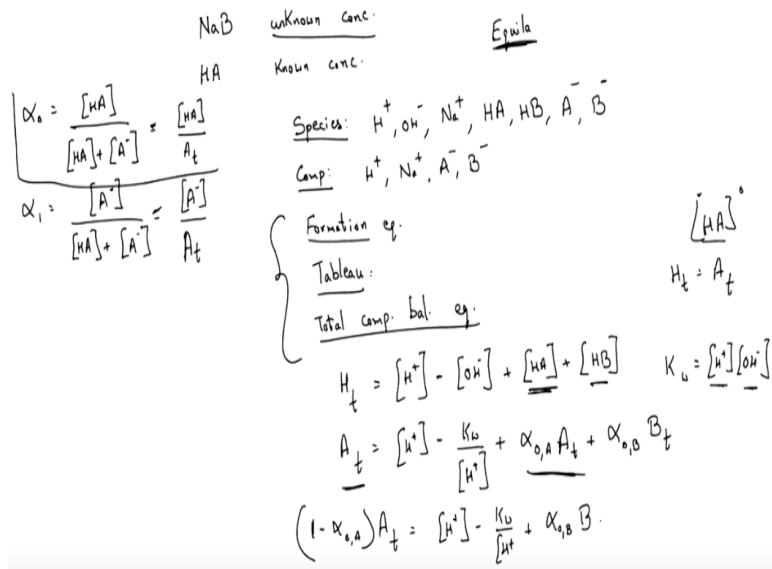
So again amount of acid added would be equal to or equivalent to the amount of base present in the solution. But vice versa, let us say if you had acid in your particular conical flask which has been titrated with the base and so then how can we transform that particular sentence here? The amount of base added would be equal to the amount of acid that is present in the solution. So that is straight forward.

So again let us look at one case and try to calculate this as equal as points. So for example people use different indicators. So why that particular indicator or search depends upon where the

equivalence points lies? So you need to know or have done prior idea about where the equivalence point is to be able to stop the titration at that particular point.

So you can both use your PH meter and stop the titration at that particular point or you can also use indicator. If this particular color change or such phenomena falls within the range of your particular equivalence points, so let us see how to go about that, we are going to look at the example where we have base

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Unknown concentration, we do not know the concentration and we want to find that unknown concentration and I am going to titrate it with an acid HA is example here of known concentration. So what am I trying to get, we are trying to get at our equivalence point. So we are trying to get at the equivalence point. So how do we do that? Again crust of the solution lies in setting up the component balance.

So let us go back to that in general. We obviously need to identify the species. Species are those compounds which we know at this stage that are at equilibrium in your particular solution and they obviously be H^+ and OH^- and I will have Na^+ the relevant salt and then you will have the protonate forms of the acid and the base protonated forms. You will also have the deprotonate forms A^- and B^- and from our previous prior knowledge.

We know we need to choose components and they always are going to be H^+ and NA^+ and A and B^- . You need to choose your component such that you will be able to arrive at your particular species and that is something we covered in great detail earlier so again skipping it. We need to come up with formation equation which we are not going to go through. Now formation equation and then we need to get down to writing our tableau and then the total component balance equations.

So at this stage we can skip this three aspect and let us write down H total would be equal to the concentration of H^+ at equilibrium that is the key here, minus the concentration of OH^- + the concentration of HA + the concentration of HB again protonate forms of A and B . So we have this particular case again. What is H total equal to? We want to transform this equation to remove those variables which are irrelevant to us and substitute them with variables that are relevant to us.

So H total is equal that would be depending upon what we are putting into the system. So what is the only source of H total if we look at HA that we are putting it in the system or HA . Let us see H total as you look at from start unit here or if you look at the component balance is going to be equal to A total. So here that would more or less mean A total is equal to concentration of H^+ - and OH^- .

The water dissociation constant is equal to H^+ times OH^- . So thus H^+ going to be KW by OH^- is going to be equal to KW / H^+ water dissociation constant by H^+ + HA the protonate form of A and HB . The protonate form of B . So in this case what aspect or what in their variables that we know that we can express in terms of ionization fraction. You get α_0 and α_1 for monoprotic acids and bases.

So is the conjugate base, so we are going to use that concept here. So let us refresh our memory briefly. So we have α_0 for particular acid is going to be equal to HA or the protonate form of the acid by the total acid as in both its protonate forms, then deprotonate forms. What is α_1 the second ionization fraction of its going to be equal to the deprotonate form by the concentration of $HA + A^-$.

So again alpha not will give an idea about the deprotonate fraction of the acid in its protonate form and alpha one will give you an idea about the fraction of the acid present in its deprotonated form. So that is what we have here alpha not and alpha one and we know that this is equal to HA by as you can see from your component balance that is going to be equal to A total and this is equal to A - / A total.

I mean this is from our previous background so I am obviously not going to go through in great detail. So HA obviously express this as I followed this particular equation is going to be equal to alpha not of A into a total + HB again alpha not of B into B total. This is one equation we have here so I am going to take this particular term out on the left hand side. So what is that going to be here?

We are now going to have 1 - alpha not of A into a total would be equal to concentration of H + - KW / H + + alpha not of B into B total and the key here is that the sum of the ionization fraction. So obviously these are fraction, so sum of the ionization fraction need to be one. So 1 - alpha not of A would be equal to alpha one of A. So we are going to substitute that here. So let us go back to that.

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$$\alpha_{1,A} A_t = [H^+] - [OH^-] + \alpha_{1,B} B_t$$

$$\alpha_{1,A} A_t = [H^+] + \alpha_{1,B} B_t \quad [OH^-] \approx 0$$

$$A_t = [H^+] + \alpha_{1,B} B_t$$

At equivalence pt.
 $A_t = B_t$

$$B_t = [H^+] + \alpha_{1,B} B_t$$

$$\alpha_{1,B} B_t = [H^+]$$

$$\alpha_{1,B} = \frac{[B^-]}{[HB] + [B^-]} = \frac{K_B}{[H^+] + K_B} \approx \frac{K_B}{[H^+]}$$

$$\alpha_{1,A} = \frac{[A^-]}{[HA] + [A^-]} \approx 1$$

$$1 - \alpha_{1,B} = \alpha_{1,A}$$

HB is a weak acid: $pK_B \gg pH \quad K_B \ll [H^+]$

Alpha 1 of A into A total would be equal to the concentration of H+ - the OH - concentration + alpha not of B into B total. So let us just check that for a second alpha 1 of A total H - 1 OH minus concentration + alpha not of B into B total that is what we have. So here we are going to

make few assumptions to arrive at alpha at answer. So here as we are adding an acid I am assuming that the equivalence point is going to be in the acidic region.

So can assume that the OH⁻ concentration is negligible. So that is something we are going to make and we are also going to assume that the acid that you are titrating solution with is a strong acid and let us see what that means. So here we are now going to assume that the OH⁻ concentration is negligible and why is that because we are adding an acid and the PH will be relatively low.

Now we are going to be left with alpha one of A into A total is equal to concentration of H⁺ + alpha naught of B into B total. So let us try to simplify this further. Now we know that we are going to use strong acid, so what does that mean? Now at almost all practical range of your PH it is going to dissociate or it is going to stay in its deprotonated form. So what does that tell you about alpha naught and alpha 1, so if it is going to stay in its deprotonate form, alpha naught more or less.

You know I guess you can guess that it is going to be equal to zero or more or less nearer to 0 and alpha 1 is going to be one why is that ? So we know that alpha 1 of A is equal to the concentration of A - by concentration of the total acid and if it is a strong acid it is going to dissociate at almost all PH range and it is only going to stay as A minus. So you see that by a minus more or less it is going to be equal to 1.

So that is what I am going to substitute here. So it is going to concentration of H⁺ + alpha naught of B into B total and now we come to the crust of the issue the equivalence point where we know the amount of acid added would be equal to the total amount of base present in the solution. So now we are going to use that to simplify our solution equation here. So now at the equivalence point and you can correct my spelling if I am wrong.

At the equivalence point A total is going to be equal to B total. So now I am going to have B total is equal to the concentration of H⁺ + alpha naught times B into B total and again taking this term out here on to the left hand side. Again it is going to be 1 - alpha naught of B and again going to be equal to alpha 1 times of B. So what are we going to have here alpha 1 of B into B total is equal to the concentration of H⁺.

So obviously we need to simplify this further and in general we are going to consider that B is a weak acid. So I am going to say that PK_B is going to be far greater than P^H , so now assuming that HB is a weak acid and from our background we know that P^H of B is going to be far greater than P^H . So the K_B is far less than the concentration of H^+ and we can we apply this. I guess so let us write this down here that α_1 of B is equal to the deprotonate form of B which is B^- minus by the concentration of H^+ naught by H^+ the protonate form of B which is HB.

B^- - and from our background we know that that is going to be K_B by concentration of H^+ + K_B . So if K_B is far less than H^+ . What does this turn out to be? I am going to say that it is going to be equal to K_B by concentration of H^+ . So if I am going to substitute this in this particular equation here let us see what I am going to end up with. So I guess I have to refer to this back and forth.

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$$\frac{K_B B_t}{[H^+]} = [H^+]$$

$$K_B B_t = [H^+]^2$$

$$\log K_B + \log B_t = 2 \log [H^+]$$

$$2 \log [H^+] = \log K_B + \log B_t$$

$$-2 P^{H_{ep}} = -P^{K_B} + \log B_t$$

$$P^H = -\log [H^+]$$

$$P^{K_B} = -\log K_B$$

$$P^{H_{ep}} = 0.5 \left(\log P^{K_B} - \log B_t \right)$$

So K_B by concentration of H^+ into B total is equal to concentration of H^+ . So let us look at that again where we have this α_1 B is now equal to K_B by H^+ into B total is equal to H^+ . So let us simplify this further K_B into B total is equal to concentration of H^+ plus square and now taking logarithm on both the sides let us say \log of K_B + \log of B total would be equal to two times \log concentration of H^+ .

So more or less transform, I am going to switch the swap the two sides. So let us write down just to simplify my particular calculation here. $\log K_B$ plus $\log B$ total and now we know that PH is equal to minus \log concentration of H plus. We also know that we are applying PK_B is equal to $-\log K_B$. So I am going to substitute those particular terms, so it is going to be -2PH at the equivalence point.

This is the equivalence point, so I will say EP is equal to $-\text{PK}_B + \log$ seems like I am in the track $\log B_T$ and so the PH at the equivalence point is going to be equal to 0.5 into \log I guess is going to be $\text{PK}_B - \log b$ total. So again this mean now if I know what the base I am looking for, you know trying to calculate the equivalence point is said to be easy because if I know the base B , I can calculate.

I know the I can get the PK_B value which is here and general as you see even though B total has an effect on equivalence point PH of the equivalence point because logarithm scale it affects relatively less. So in general if you have an idea about the base that you are titrating for let us say or against you can come up with your PH of your equivalence point and that is the crust of the issue.

Once the PH of the equivalence point is known you know when to stop the titration or you can obviously look for particular color change or an indicator. So that will have its particular color change at the this particular PH . So with that we will stop for today and I will come back to you with relevant applications of V MINTEQ in the next session thank you.