Environment Engineering: Chemical Processes

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Module No # 04
Lecture No # 19
Mixing Problems

Hello everyone welcome back to our latest lecture session I believe we have been discussing acids and basis in great detail and looking at started looking at applications right. I believe we started looking at you know estimating the PH and the aqueous phase concentration of a particular what do we say acetic acid base example I guess right.

And then the second example we looked at was when we had the relevant base right just the estate of sodium estate their and then we are going to move on I guess to bit more complex systems as in how do we go about evaluating the system when you have let us say volume particular volume of one particular solutions ad another volume of another solution. So I want to know what is going to be the case or what the relevant aqueous equilibrium concentrations of the relevant species right of these mixtures.

So again I have beaker 1 and beaker 2 various consequence and both the beakers and I want to know what is the relevant aqueous concentrations at equilibrium for this mixtures right so again before we go further let us quickly have a look at what we discussed earlier. So I believe we looked at ionization fractions and what are these ionization fractions they will give an idea about fraction of that particular protonated for deprotonated form over the fraction of it over the total acid right.

So in that case I believe we are going to now look at example or refresh or memory with respect to an example we looked at previously.

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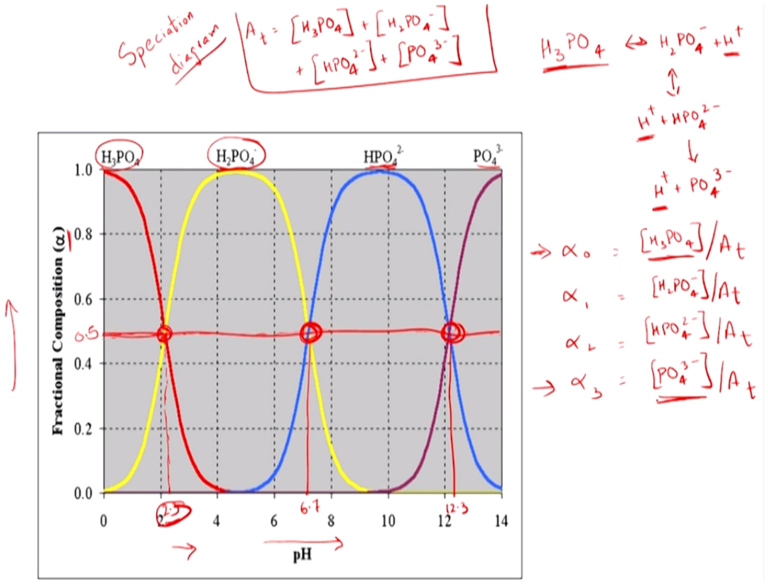

So we are going to look at tiprotic acid right here we have an example of tripotic acid and that is H3 PO4 so 3 proton so tripotic so again it is more or less end up or dissociate into H2 PO4 - + H+ and this H2PO4 can again dissociate into H+ and HPO4 now 2 – or negative charge 2 negative charge obviously and HPO4 2 – for the dissociate into H+ and PO4 3 – right so it can give a total of 1, 2, 3 it has H3 PO4 can donate 3 protons depending upon the PH obviously.

So you cannot just say H3PO4 is tripotic acid so let us say I can use that to adjust my PH based on the assumption that the phosphoric acid is going to dissociate itself in such a way that you are going to have release of 3 moles of H+ for 1 mole of phosphoric acid right and that is not the case because now with your background you know that H+ is released depending on the PH and also the PKA of that particular compound right.

So it depends upon PH and PKA only then you know how many moles of H+ will dissociate its parent aspect. So let us look at our example here again so I believe here we have phosphoric acid right and here we have the ionization fraction on the Y axis and we have YH on the X axis phosphoric acid can dissociate or you know donate 3 protons in total depending on the PH so here we end up having 3 PKA values right. and I think they are 2.3 I think they are 6.7 or 7 I am not sure I need to check that I guess 12.2 or 12.3 anyway approximate values here.

So what do we have here we have 3PKA values you know that when PK is less than PKA the system is going to the system as acid is going to stay you needs protonated form so the H+ is not going to dissociate right. As it approaches the PKA value it as the system approaches the PKA the value or PH approaches the PKA value you are going have dissociation right and at the PKA value what would you observe you observe that the deprotonated form is going to be equal in concentration or it is relevant personated form right.

So that is what we are going to see here so at this particular PKA value or the PKA 1 or I look at the ionization fraction that is equal to 0.5 here and what is that mean the concentration of H3PO4 and H2PO4 – are going to be equal when the PH of the solution is equal to the PKA 1 which is 2.3 right and then more or less as you move to your right or keep increasing the PH or it keep moving away or further away from PKA value what did you observe.

You observe that most of the particular acid would stay in it in deprotonated form what is that mean when the PH is greater than PKA the acid will be dissociate and donate the proton right. So that is the key here more or less PKA and again in this context we now know that PKS will give an idea about the relative strength or weakness of the acid again strength and weakness are relative terms subject to terms right.

So you want to be able to terms right so you want to be able to quantify that or be objective so you are always going to look at PKA right. So someone ask you what is the how can you let us say particular acid is strong or weak you would say going to look at the PKA value right so in this case we have its tripotic so we have 3 PKA values that is what we have highlighted here so at each PKA value the relevant protonated and deprotonated form are going to be equivalent concentration form and that is what you seen here in this graph right.

So this is the speciation diagram let us say this is the speciation diagram I called as speciation diagram right and again same case here with respect to PKA3 it is going to be at HPO2- and PO4 3- right. So again let us move on so now we are now talking about ionization value right and for tripotic acid you are going to have 4 each one of the each species.

So that is going to be H3PO4 by the total acid what is the total acid obviously some of the concentration of all the three species all the four species pardon me at equilibrium and we know that the relevant four species are going to be H3PO4 H2PO4 – PO43 – HPO4 2 – this is the total acid here right this is the denominator here and same case going to have H2PO4 - / total acid HPO4 2 – by the total acid and PO4 3 – by the total acid again.

So we discussed this right so what does alpha naught give an idea about it gives an idea about what fraction of your total acid is present as H3PO4 and if you look at alpha what will that give us an idea about it will let you know what fraction of your total acid is present as most deprotonated or as PO3- right.

So once you have your compound right as in what does it mean once you know you compound it mean you know your relevant PKA value and let us know you know the PH of solution that you are looking at right. You can automatically calculate alpha naught 1, 2 and 3 or you know depending upon if it is diprotic if it is going to be just alpha naught alpha 1 and alpha 2 right mono protic just alpha naught alpha naught and hence so forth.

And I believe we looked at the relevant derivation we are not going to go through that in detail but obviously the relevant ionization fractions are going to depend upon H+ or PH and KA or PKA right so we are done with that and so let us move on to a next example right.

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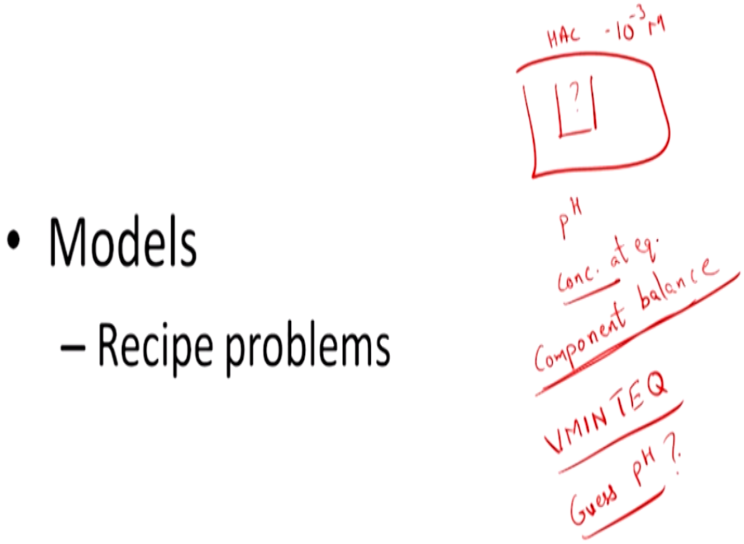

- Models
  - Recipe problems

We are looking at different recipe problems as in you add something and in general we looked at first example was HAC such that the concentration was 10 power -3 molar and how do we go about this system how do we calculate the PH how do we calculate the concentration of the compounds at equilibrium. So there are two ways 1 by hand and in general we use components balance and this almost always with which is not almost pardon me this always works right.

So even if you come across let us say even you know different methods out their this is the fundaments what do we say method or the basic method which would work always now there might be short cuts but in general there are short cuts which is applicable to particular scenario or such that but in component balance in general when you are trying to look at let us say or trying to estimate what is concentration of particular compound at equilibrium let us say in general component balance will always work.

And then the other way was obviously t use the software VMINTEQ and we are comparing our vessels and we are also trying to gas at our particular PH in general so that we develop out intuition right we also want to be able to what do we say develop the intuition with respect to be able to estimate the parameters right at least at these stage you should be able to estimate the PH I mean depending upon the complexity of the system.

Obviously and also at least if you have the PH you should now be able to what do you say estimate once you given the PKA value the relevant fraction or percentage of the personated and deprotonated forms right of the acid and base anyway.

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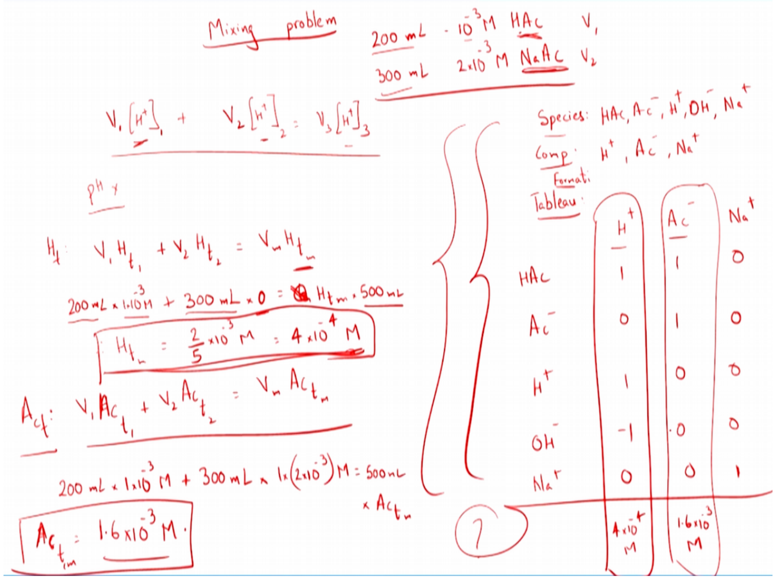

Mixing problem

200 mL · 10^{-3} M HAc V_1

300 mL 2×10^{-3} M NaAc V_2

$V_1[H^+]_1 + V_2[H^+]_2 = V_3[H^+]_3$

pH ✗

H_t: $V_1 H_{t_1} + V_2 H_{t_2} = V_m H_{t_m}$

$200\,mL \times 1\times10^{-3} M + 300\,mL \times 0 = H_{t_m} \times 500\,mL$

$\boxed{H_{t_m} = \frac{2}{5}\times10^{-3} M = 4\times10^{-4} M}$

Ac_t: $V_1 Ac_{t_1} + V_2 Ac_{t_2} = V_m Ac_{t_m}$

$200\,mL \times 1\times10^{-3} M + 300\,mL \times 1\times(2\times10^{-3}) M = 500\,mL \times Ac_{t_m}$

$\boxed{Ac_{t_m} = 1.6\times10^{-3} M.}$

Species: $HAc, Ac^-, H^+, OH^-, Na^+$

Comp: H^+, Ac^-, Na^+

Formati

Tableau:

	H^+	Ac^-	Na^+
HAc	1	1	0
Ac^-	0	1	0
H^+	1	0	0
OH^-	-1	0	0
Na^+	0	0	1
?	4×10^{-4} M	1.6×10^{-3} M	

So let us move on I guess let us look at the example that we have for today so we going to look at mixing problem and this mixing problem is that you have 200 ML or volume V1 and it is 10 power -3 molar HAC or acetic acid and the second one is 300ML and let us go with 2 into 10 power -3 molar NAAC sodium hesitate right unlike the earlier case where we were looking at individual what do we say solution right or independent solution.

Now we have a relatively complex case I mean not much more complex we look at it obviously and so we have two solutions and different consequence we are mixing them up and you want to know the PH relevant equilibrium concentration right so let us see how we go about that let us see.

The first aspect is that you know obviously all the other aspects such as species what are they obviously again HAC and what else please AC – H+ OH – and NA + they are going to say the same we looked at relevant example in the earlier classes and the components too I guess will be same and this case H+ AC- and NA + and then you are also going to look at the tableau right you are also going to look at the tableau and in general we will need to write the formation equation but once we have the relevant expertise let us say we can try to skip the formation equation.

But in general until you are relatively acquainted with the system or the process here we were discussing I would suggest that you continue with writing down or (()) (12:17) down the formation equations and then using that as a base to write your tableau or come with the tableau right because if you mess up your total component concentrations or balances pardon me if you mess up your total component balances you are going to mess up your whole system right.

So that is a key aspect that is one reason why I suggest that you take it easy their right so that tableau and such tableau again we know that is H+ AC- NA + I can skip NA + because did not list any other species other than NA+ itself that has NA+ skip that if I want because it plays no further role in particular system right and these are my species and we see that H+1 0 1 – 1 and 0 1 1 0 0 0 NA + has only NA+ and here the key though so what are the how do I come up with ,y recipe species now.

So keep in mind that unlike that one of the previous examples we did not have one simple solutions and two different compounds we have two different solutions of two different volumes and we are mixing them together right. So that is the whole aspect here so how do we go about that right so let us look at that now. So here we have V1 and V2 right volume two different volume right also obviously again the key is that you want to connect the balance right you want to look at the mixture but the case is that you need to look at variable that is conservative right.

So for example how can I connect the balance on H+ you know concentration of H+ + volume into concentration of H+ H+1 H+2 = volume 3 into concentration of H+ 3 no I am able to do that obviously you know i can do with all the aspects right if I can directly the convert the balance on H+ no why is that because we not adding just two solutions at different PH right we also have various acid and base conjugate acid and base species so they can either take up the acid I mean H+ or donate the H+ so you cannot do a balance on H+ it is not a conservative quantity right.

And same case you cannot do a balance on PH either right so obviously we need to go through the component balance base solutions. So what is the conservative quantity here so obviously I guess it depends upon the components or if you look at components they obviously where we choosing them their conservative quantity right so why do we mention now the H right the total H is going to stay the same it can stay in HAC it can stay H+ or we consume by OH –.

So the total H+ right or total H is always going to stay the same and same case with the estate ion I can either VN HAC or in the form of estate ion or let us say it can form a complex we are going to look that in later classes but still right eh total estate is going to stay the same right. So that is what we are looking at right obviously when we do the balance we are going to look at balancing a conservative quantity the key is that it needs to be a conservative quantity.

So here we are going to look at two balances one with respect to H total and then other with respect to estate total and H total what is that going to be I guess so V1 in H total 1 + V2 H total 2 will be equal to volume of mixture into the H total of the mixture and same case here V1 H not H pardon me now we are conducting the mass balance in the estate total 1 + V2 into estate total 2 is going to be equal to volume of the mixture into estate total of the mixture.

So I can calculate the total what do we say component in the mixture I can use that as my recipe species here and then I can proceed with the answer so obviously I need to conduct the mass balance here first with respect to just the mixtures. So let us see let us plug I the values and see what we have here and so V1 let us say this is my solutions 1 and this is my solution 2 V1 and V2.

So I have V1 has 200ML into what is the H total in particular volume 1 that is going to be equal to as you know 1 times 10 power -3 1 into 10 power -3 right so the units I am going to use the same units ML and molar we can come up with that is okay their +V2 is 300 ML right into H total. So the H total here the key is that there is no contribution right we are going to be 0 so NAAC there is not contribution the second particular solutions that we have here has just sodium hesitate so can I contribute to your H no that is why we are going to have H total in our second solution as being = 0 right.

So that is going to be equal to volume of mixture and H total of the mixture as we know volume of the mixture is going to be 500ML and therefore H total of the mixture is going to be equal to 2/5 into 10 power -3 molar right that is what we have here and that is going to be equal to 20/5, 4 into 10 power -4 molar right.

So that is the H total of the mixture here right and that is what you are going to balance it out here when you do the H total balance on your system right and so let us move on and we are also need obviously calculate the estate total right again that is a conservative quantity that we going to conduct the balance on conservative quantity again so here we have the balance with respect to estate total let us plug in the values please.

So the volume 1 is 200ML into so let us write down the units just to be on the safer side okay I messed it earlier so I am going to write down the units much more apparent this time so that people who trying to follow it can do so right. So here in the first earlier case I use the volume for the units where ML always so that will balance out and so the other two cases are molal concentration so that is why answer 2 is going to be in the units of molar units I guess right.

So again here we are doing to do the same with respect to estate so 200 ML into and what do I have here estate 1 estate here into 10 power -3 molar + what is this volume of the second solutions 300ML into and estate contribution again is 1 times 2 into 10 power – 3 molar that is going to be = 500 ML which is the total volume 200 + 300 into the estate total of the mixture right.

So let us see what is this can turn out to be estate total of the mixture will probably turn out to be I guess I have the key here to be 1.6 into 10 power -3 molar so that is what I have here so here now I have the estate total of the mixture and also have H total of the mixture. So again the key here is that you cannot just what do we say convert the balance with respect to H+ why is that H+ naught conservative right H+ on the proton can be either taken up by the estate ion or be release by the HAC because you do not know what is the final PH is going to be right.

So that is what reason why you cannot balance on H+ or PH obviously and then you know use that to calculate the relevant variable so that is going to be (()) (20:33) at least by now we should be able to understand that. So we are only going to do the balance on the conservative quantities which are H total and estate total and that plug that in in doing our mass balance can be component balance.

So let us now put this in and we have H total to be what now please we have that we just calculate that 4 into 10 power -4 molar and 1.6 into 10 power -3 molar. So let us go back to VMINTEQ right and I guess again to refresh your memory VMINTEQ is software can be used or you know free to download software. So if anyone has not done that yet strongly due to do so right it is free to download software again it is pretty user friendly too.

So we are going to go ahead with going to use VMINTEQ can able to solve it so bi-hand I guess you also going to look at how to solve that Bi-hand I believe we discussed in detail in the earlier classes we are just going to have the couple of minutes are that.

So if I move on to the particular case so I need to used show organic computer why is that because it is estate which is an organic compound estate and I believe the concentration was what is now 1.6 into 10 power 3 if I am not wrong and let me choose the milli molal to make it easier for me and so I am going to say concentration units here are 1.6 milli molal I am going to add that to that list so this is the key here.

And then the next aspect is to choose H total and H total and what did we calculate that as 4 into 10 power -4 molal I guess that is what we calculated so it is going to be 0.4 milli molal so 0.4 milli molal units here so here I am adjusting the units here add to list let me also add NA+ that is something we did not calculate it so let me calculate that so let us move on to a new slide so 1.6 and 4 into 10 power -4 we got that right.

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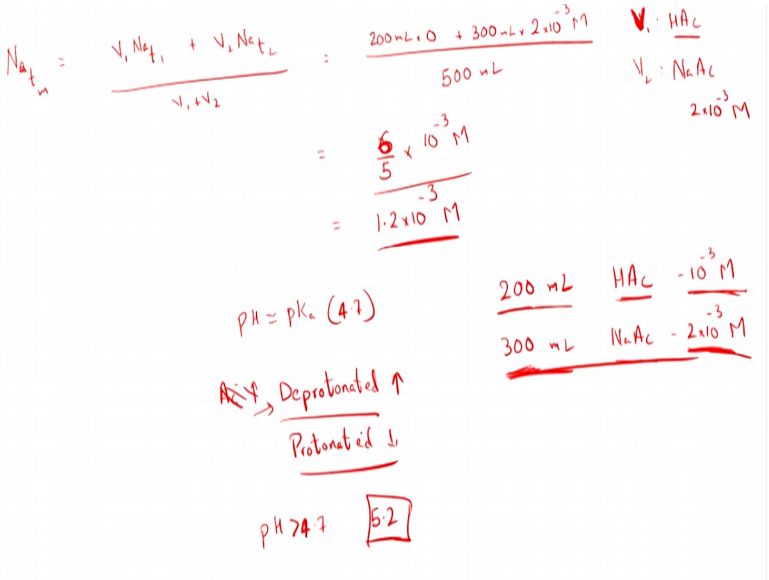

$$Na_{t_m} = \frac{V_1 Na_{t_1} + V_2 Na_{t_2}}{V_1 + V_2} = \frac{200\,mL \times 0 + 300\,mL \times 2\times10^{-3}\,M}{500\,mL}$$

$$= \frac{6}{5} \times 10^{-3}\,M$$

$$= \underline{1.2\times10^{-3}\,M}$$

V_1 : HAc

V_2 : NaAc

2×10^{-3} M

200 mL HAc - 10^{-3} M

300 mL NaAc - 2×10^{-3} M

pH ≃ pKa (4.7)

$\xrightarrow{}$ $\frac{\text{Deprotonated} \uparrow}{\text{Protonated} \downarrow}$

pH > 4.7 $\boxed{5.2}$

So we also need to plug in NA total right and that is going to be V1 into NA total 1 + V2 NA total / V1 / V2 right and whatever our solutions is they were HAC so the first case it is going to be 200 ML into 0 because volume 1 is HAC as no source of sodium in it right or is not a source for sodium and V2 looks like we had NAAC right and if my memory serves me right 2 into 10 power -3 molal units right so let us see if we are right track here 2 into 10 power – 3 molal +.

So that is going to be + volume 2 is 300 ML into NA total is going to be 2 into 10 power -3 molal by what is it here please 500 ML right so that is going to be equal to what now 3/5 into 6/5 pardon me into 10 power -3 molal units so 60 / 5 so let us say 1.2 into 10 power -3 molal units so hopefully my calculations are right you can correct me if I am wrong hopefully I am right though and let us go back plug in the relevant values here again.

So here we need to plug in the relevant values and where is my key here so it is 1.2 milli molal and I am going to add that in list and going to confirm that I put in the write values and I believe that 0.4 milli molal estate was 1.6 and NA + was 1.2 right so that is expected so because only in one solutions did we have the source of H or H+ that was in the first solution that too at the lower that is you see that H total is relatively less compared to estate total.

Estate was present in both volume 1 and volume 2 that is why you see that it has a higher value and again same case with sodium it is only present second solution I believe but that is it as a greater contribution because I believe the volume is greater and also the concentration of NAAC was also higher. So let us go back to the main menu and let us try to see if okay.

If PH calculate from mass balance ionic strength to be calculated and so on temperature is 25 let us run VWINTEQ right and now first look at PH and let us try to understand this later on PH is 5.2 will come back to that and what else do we have here please okay we see that relevant concentration here what are these concentration here again please so these page with respect to the page will give you an idea about what now the concentration of the species or the equilibrium concentration right of all the compounds that are present.

So believe we have been neglecting NAOH right and sodium estate and why is that in general they we would not be present in solutions at higher concentration so I guess that is what you see NAOH remarkably less 10 power -12 and this is 10 power -6 so what is that mean it is almost two order of magnitude less that almost or the compounds but compared to OH- sodium hesitate is relatively higher is maybe we can look at that later but that not going to affect your answer in general right.

So again as we go along I guess as you use VMINTEQ we will help you in developing your understanding about what species are going to be relatively important let us say for example I in general with my background I took the or I had the assumption went through the assumption that sodium estate is not going to be at significant concentration so that is I still stand for because 10 power -6 compare to estate at 10 power -3 concentration and the acetic acid the 10 power -4 level right.

So again let us come back to it and we have the PH and the relevant equilibrium concentration and obviously the activity and here we have the ionic strength here yes and obviously the charge difference is going to be 0 especially if you give a right what do we say component balance the charge difference needs to be 0 if it is not 0 what is that mean that you gave erroneous what so we say inputs right.

So anyway I will go back to looking at species distribution and here what will that give me an idea about for example I have the total estate let us say I want to know what fraction of it was not has which particular species let us say so that is what I am going to look at it here. So as we know and PKA what is it now 4.7 or is 4.7 for acetic acid and for this particular example or solutions we got our equilibrium PH to be 5.5 right.

So PKA was or is 4.7 PKA PH now was 5.5 so the PH is greater than the PKA what is that mean it means that most of your particular what do we say acid base system we are going to stay in its conjugate base or the deprotonated form so that is what you see here 75% of this particular estate is staying as estate or deprotonated form and only 25% is staying as deprotonated form and why is that because PH is greater than the PKA right and again minor fraction very minor or negligible fraction less than 0.1% is staying as sodium estate.

And again same case with sodium salt is staying as sodium itself 99.9% and the other particular species can be neglect right this is what we have. So let us go back to our particular case back to main output menu input menu back to input menu and so on. So here I guess pardon me I was trying to look at output file so PH is 5.2 so let us try to look at the system have an understanding about how this came about right.

So let us look at what we had we had 200 ML of your acid HAC and 300 ML and concentration I believe was 10 power -3 molal units and 300 ML of NAAC 2 into 10 power -3 molal units so the first aspect we need to look at is the relevant volume and the relevant concentration and so again what I am trying to do is I guess is that I should done earlier we should be able to come up with the good enough guess what the PH would be right we are trying to develop our intuition right so let us look at that.

This is a mixture of a compound unlike the earlier cases we just one particular solutions so anyway we now have two variables to look at not just the concentration but also the volumes of the relevant mixtures so if I look at it here volume is less volumes 2 is greater not huge difference but still considerable difference right and then the concentration of acid is less concentration of conjugate base is more.

So first keep in mind that if you using the same or the conjugate acid based pair and the concentration are similar what would you expect now so you have the acid and the base or the protonated and deprotonated forms or if their concentrations or equal what would that means. That mean the PH is going to be equal to PKA so but that is not the case here but we know that concentration or way to high or way to half or not way to different from each other.

So what does that mean we can still (()) (30:49) it is going to be around 4.7 or the PKA of or case but we now want to able to take all with respect to is going to be less than 4.7 or is the PH is going to be less than 4.7 or greater the 4.7 so how do we do that? We need to look at the relevant quantities of your acid or the conjugate deprotonated form right. So here obviously it is easier for us because 200 M of HAC that too it of lower concentration but here we have the 300ML of the deprotonated form and that to it higher concentration.

But the concentration are not way to far off and same case with volume so we can estimate that the PH is certainly going to be near PKA right which is 4.7 and because we have AC – being added in greater quantities let us say or the base being added in greater concentration concentrated to the acid or HAC of the protonated form right what are we having here we are saying that deprotonated form we are adding in a greater concentration compared to the protonated form right this is relatively lower right.

So those particular deprotonated form can take in H+ so what does it mean when the deprotonated form can take in H+ let us say or right or accept a proton now so if you remove H+ from solutions that mean your PH is going to increase so I guess we can take a call saying that I guess we do a slight calculation here back of the envelope calculation here but I am going to skip that so we can say that the PH is going to be greater than 4.7 and maybe without calculation say it is going to be around 5.2 or so.

And I believe the answer we had was okay 5.2 that is close to estimate at least greater than 4.7 or near 5 so the I need the answer turned out to be 5.22 I guess right so that is what we have here say again we will wrap up today's session with the very brief summary of what we discussed so here today's class we will looked a case where we have two different solutions right two different components so you want to mix them together and find the relevant concentration of the mixture now right.

But the case here is that you need to conduct the balance right with respect to mixture 1 and mixture 2 or solution 1 and solution 2 on a conservative quantity but is H+ conservative know it can transform right it can go into HAC right why AC- can take it up or HAC so it is in your solution can donate the proton and H+ can increase right so you want to choose a quantity that is conservative does not change right and what is that and those are the components are H total and estate total.

And that is why we looked at V1 into H total 1 + V2 into H total 2 = volume of the mixture into H total of the mixture and you can go ahead with that right so again with that I will end the today's session and I will look forward to meeting you again in next time I guess.