Environment Engineering: Chemical Processes

Prof.Dr. Bhanu Prakash Vellanki
Department of Civil Engineering
Indian Institute of Technology – Roorkee

Module No # 04
Lecture No # 20
Inverse Dose Problems

Hello everyone so welcome back to our latest lecture session so we have been looking into applying our component balance and also looking at how to at the same time apply VMINTEQ right to be able to solve out acid and base equilibrium question right so acid and base that is what we are going to look at again right because that is going to be a fundamental aspect environmental engineers.

And again why is that because PH is the master variable you know wherever or whichever aspect you look at or rarely will find the system at where PH is not worthwhile or you know PH is not important let us say especially if it is inorganics PH is certainly going to be important because you need to look at the charge right you need the same case with organics but not to a great extent though but we are going to come back to that later on.

So again we have been looking at issues with respect to I believe we started looking at I have one particular acid in a particular solution what is the PH and equilibrium solutions the second I think we looked at I have sodium estate or relevant conjugate base and what is going to the PH and the relevant equilibrium concentrations next I believe we looked at two mixtures right or two solutions pardon me I mean looked at what is going to be or has not the equilibrium concentration right what are they going to be for this mixtures.

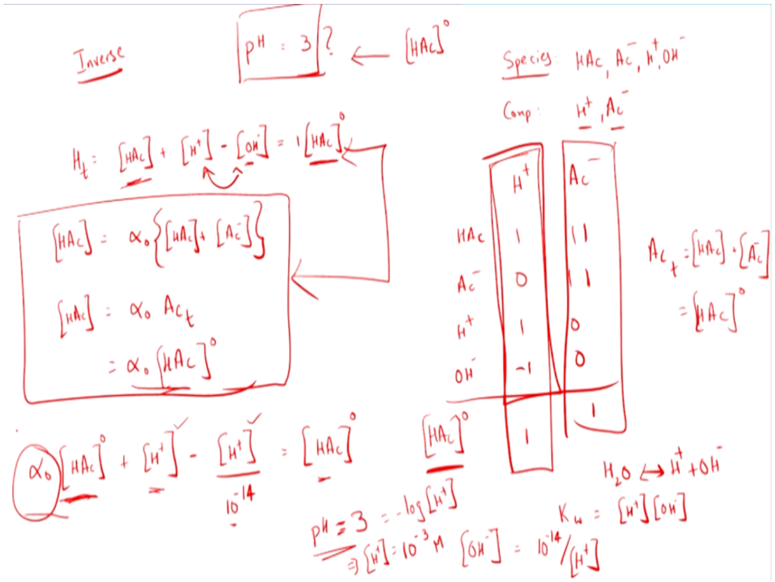
And more and more we are shifting towards the equilibrium but we always we need to have a basic understanding about fundamental process so that is why we are still trying to have a understanding about how to solve that by hand and how do we do that by looking at conservative quantities and what are these conservative quantities again please these are the component that we are define right so in this class we are going to look at inverse problem.

So for example let us say ask a student to what do we say this is the solutions right and I want to bring down a particular PH to a particular value let us say right let us say 3 or 4 let us say and this is the only acid that I have in my lab and let us say I do not have enough solutions you cannot do trial and error to get it out or you know to try it out let us say for example he can take 10 ML at the relevant volume look at proportionately and so on.

So let us say she or he does not have the particular flexibility because volume of sample is less so what can you do I guess looking at not guess you can may be some approximation with respect to the species present or the compounds present at the particular solutions use VMINTEQ to be able to relatively I guess relatively you know come up with precise relative I guess so it is because you do not know or you do not have complete information about your particular system you are going to make assumptions that certain compounds are present or absent or so on.

So in this case we are going to start looking at or today session we will start out looking at inverse problem right. So until now what do we look at I put in HAC or you know acetic acid what is the PH that I can expect or what is the equilibrium condition but here what am I asking now for PH to be a particular value how much HAC do I need to put it so that is what we are going to look at right.

(Refer Slide Time: 03:33)



So here are going to look at the inverse problems number 5 I guess the inverse problems right. So the setup again the components component balance and everything going to be the same but let us try to understand the system now so let us say let us take the example with respect to the PH this is supposed to be 3 we will see why we choose 3 okay so I want PH to be 3 and I want to know how much of HAC do I need to put in right initially to be able to get to a PH of 3 right.

What is the concentration of HAC that needs to be added initially right so how do we go about this now right. So again you might see the relatively more complex but it just issue of identifying the known and the unknowns. So earlier we need not have be concentration of the relevant variables at equilibrium but we had the concentration of the specific species or whatever it is we are adding initially right we had this or the initial concentration we need not have the equilibrium concentration.

But now we have equilibrium concentration if not concentrations why is that because I know that the PH at least one of these variables which is H+ PH is 3 i know one particular variable but I did not know the initial or the initial variable right and that is HAC naught so I am going to play around with this and we can solve it accordingly so it is going to be more or less same case so you are going to use what do we say define the same species right what is that species though at equilibrium you know HAC H- H+ and OH – right and components are going to be what now H+ and AC- and how do we choose this components now.

You choose them by saying that or look at the proton always the H+ and then choosing the most deprotonated form which is the estate ion in this particular case most deprotonated form right again component balance I am skipping the formation equation and we have these HAC AC- H+ and OH – so we will see that more or less the key is H+ just H+ balance so 1, 0, 1, -1, 1, 1, 0, 0, and if I the recipe species are HAC naught which is my unknown right this is my unknown now right.

And what do I have here that is going to be equal to unknowns I am going to leave it as it is so I am going to do the balance on H+ so an aspect that we need to consider where we doing the balance on H+ or H total and not your estate total or why is that because if you look at the H total and which are going to look at obviously I guess the equation you can see it is easier for you to transform it into an equation with just an single variable that we already have information about what is that the PH right.

So I am going to transform the equation once I write down the H total such that everything will just be in the form of PH or H+ and HAC naught and then I can solve for it right. So let us see how that goes about so let us see that here we have H total = concentration of HAC at equilibrium + concentration of H+ at equilibrium – the concentration of OH- right this is just the balance from here H total that is going to be equal to 1 times the HAC naught.

And what are my unknowns here this is the unknown variable that I am trying to find out and these two are inter related and these seems like an issue now HAC I do not know what is the concentration of the protonated form is right so how do I go about it so keep in mind that we can try to approximate that by using your ionization fractions so in this case what do we have here HAC is nothing but what is the HAC in terms of ionization fractions alpha naught into HAC concentration + AC – concentration right.

And as you know if you look at the balance with respect to the estate what is that now estate total = HAC + AC- right and so I am going to plug this in here so the concentration of HAC at equilibrium is going to be = alpha naught times AC total again estate total seems like we do not have the information but again going back to the relevant drawing let us say right what do we have we can again conduct the balance their and what is the source only the source of this estate I guess that is from the acetic acid is initially putting in or you are trying to put in anyway right.

So what is that equal to is going to equal to HAC naught which is again the unknown variable that you are trying to calculate right so that is what we have here. So that is going to be equal to alpha naught into HAC naught right so this is what we just derived and I am going to plug this in here right or plug this in this variable so alpha naught into HAC naught + H+ and what is this OH- I guess.

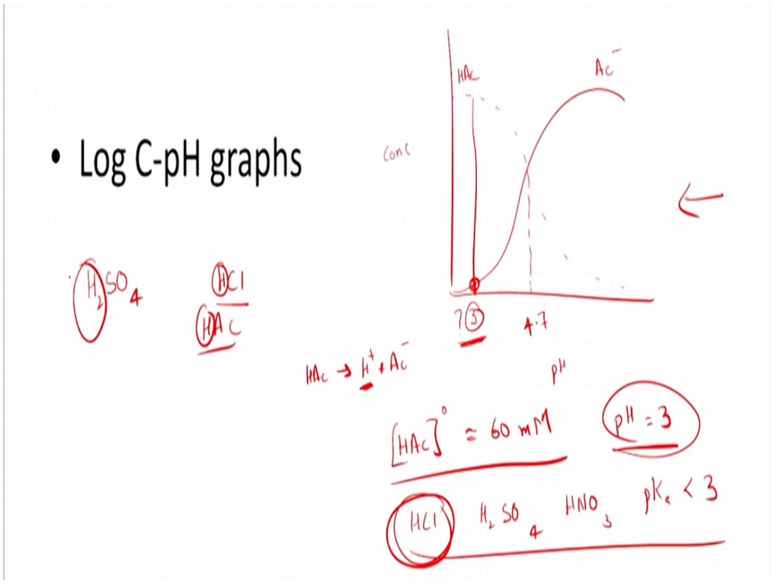
OH – how you write that we write that water can dissociate into H+ and OH – so the water dissociation constant W is concentration of H+ into OH- and again why do not we have H2O here the variable here because the reactant right it is and why is that again in general the dissociation constant or equilibrium constants are returned in the units of activities and activity of water right in this dilute system is going to be equal to 1 right.

So that is the reason we do not have denominator here right so anyway KW into H+ into OH – so OH – is going to be equal to KW is 10 power -14 I guess right by concentration of H+ so –H + / KW value is 10 power -14 right and that is equal to my unknown here HAC naught right alpha naught into HAC naught which is my unknown variable which I am trying to calculate H+ / 10 power – 14 which is KW = HAC naught.

So obviously here we have information with respect to H+ and why is that because I am trying to get to the what do we say now case where the PH is going to be 3 as in what is that mean it means activity or in this case H+ is going to be equal to what now PH = -log concentration of H+. So H+ is going to be equal to 10 power -3 molar units or molal let us say I am approximate with molar unit it is now right H+ is going to be equal to 10 -3 molal units.

So I can plug this in but looks like I still have an issue with alpha naught now how do I calculate alpha naught though.

(Refer Slide Time: 11:10)



- Log C-pH graphs

Let us move on to the okay next slide let me so it is alpha naught into HAC naught + H+ - H+ / 10 power -14 = your HAC naught and you already have the information that H+ is going to be equal to 10 power – 3 molar and why is that because you know that this is solutions that you want because you know that at equilibrium you know that PH you want is PH3. So from that we have concentration of H+ so that is the whole key here these are the inverse those problems I guess right.

So here we are going to plug in those problems right but the issue is that we need to be able to calculate alpha naught at what is alpha naught though right it is going to be function of PH or H+ and PKA or KA and we know the formula for this it should be aperient by now so HAC mono protic acid right so you have two ionization fraction alpha naught and alpha 1 and we know that alpha naught = concentration of H+ by concentration of H+ + KA so alpha naught is again H+ by concentration of H+ KA 1 right.

So you have the numerator H+ you know and KA1 because you know the PKA of acetic acid is what now 4.7 that is equal to – log KA so therefore KA is going to be equal to 10 to the power of -4.7. So alpha naught is the known value HAC naught is what you are trying to calculate H+ is the known is the known value H+ is known and so here now we have just left with an equation one equation and one variable right and thus you can calculate your HAC naught.

So what is HAC naught again and this case is the concentration of the acetic acid that you need add initially to your solutions right the relevant total concentration such that you will end up with a PH of 3. SO you can solve for that we are not going to do now but let us try to see how to do this by VMINTEQ though so that is something we need to look at for a second right.

So let me erase this so that is a bit of not an issue though so here we are going to buy go by trial and error right we can set the relevant what do we say component balances but here how do I go about that it has no way of back calculating it right so what can I do though I am going to say that I am going to change my estate total and H total until I come with PH of 3 right.

So that is what we are going to going to do here and what is my HAC total let us say let us go with that and here I am going to edit the list directly because we use this okay so let us say HAC where do I go here is so H total or estate total are going to be concentration so right that is going to be HAC naught so that is going to be let us say for the sake of my is I am going to use 1.6 mili molal again right and key here back to main menu error here 1.6.

So going back to the main menu so everything else I am going to run the MINTEQ and I know I have the PH of 3.7 or 3.8. So right again what are we trying to do here I am trying to use the

VMINTEQ by trial and error to be able to calculate my PH right so I want to estimate by trial and error how much HAC you should I dump initially to be able to do the value of PH3. So in general from intuition you should know that the PH in this case is much less than the PKA value right PH is less than the PKA value.

The PKA is 4.7 the PH I am trying to go to is 3 right so what does that mean now at PH3 most of the acid that you go into put in is going to stay as the protonated form so what does that in effect mean that you need to add a lot of acid right to be able to come up to your particular PH so that is what we are trying to look at here so let us see you know out values are good enough we will go back to input menu at the list may be take where do I edit that here.

So again we are going to try to increase the value let us say now what do we say 10 might be a bit high we are going to see why and then that to main menu and let me run the MINTEQ and hopefully now at least even now as you see right even at 10 milli molal concentration we are unable to get the value 3.3 only why again why is that so the issue is that concentration or let us say ionization factor in PH and here you have the speciation.

So this is HAC and this is HAC – and you know that the PKA value is 4.7 that the PH you want to go to is PH is 3 so this is your target right so what is that mean though so it mean that because again I am trying to use graphical representation to help you understand I guess right as you see here at graph at that particular PH you see that almost all of your acetic acid will stay in its protonated form or HAC right so very little is going to be dissociated as AC – and dissociated into AC- right.

So it is very little of it dissociates into H+ and AC- so there is very little source of your H+ so very little H+ is actually given out into the solution. So thus what you need to do the total what do we say concentration of your acid needs to be very high to be able achieve that PH why is that again because the PH is less than your PKA again let us go back to VMINTEQ and check that I guess so back to input menu and edit list here so it is logarithmic scale right I am going to run the MINTEQ now.

And now see that is relatively reaching PH3 but not yet so we will go with one more trail here so I am going to go back to the input menu edit the list so may be again go to 100 let us say so I am going to increase it further I probably do not need to implicit by this value that because logarithmic scale I am just trying to be on the safer side and back to main menu and I am going to run it so now I guess it is below what do we say PH3 so again one last trail before we stop this iteration let us see not iteration pardon me this is trial and error so I am going to go with 60 now but that might be a bit tied less.

So again as you see when you are trying to back calculate it is easier to do it by hand anyway 2.993 that is close enough you need to add lot of acid in this case what is it now I think 60 milli molal right so considerable amount of acid to be able to reach PH3 right. So in that let us say the session would be let us say or a better question could be so which acid would you choose if you want to get or choose minimum amount of acid to be able to come up with PH3.

So let us just discuss for a second please so the question is we saw that HAC naught was now act to be almost 60 milli molal right to be able to come to or get the solution PHS down to PH3 and why is that when we just looked at particular case here so the other question that we are going to have that is so which particular acid would you choose so that you can use a minimum quantity of acid so that you end up at PH3.

So which one you choose now right so the obviously the key is that your background you will try to choose a acid who whose PKA is less than the PH that you are looking the PH we are looking at is 3 so you want to choose a PKA less than PH3 so why is that so when the PH is greater than PKA what is that mean now it means that the acid whatever it that we add most of it will be in the deprotonated form what is that mean in a perfect mean it mean that the H+ is going to be donated right.

So when H+ is donated then the PH can drop out right not drop out pardon me it can drop are decrease so that is the reason you want to choose and acid whose PKA is less than the PH under question and so you can choose base acids so I guess HCL H2SO4 or HNO3 these are all strong acid with whose PKA is going to be less than 3 right. So when you choose these acid it is probably going to be such that you are going to end up with using minute concentration use to be able to come up with your particular to come up to PH3.

So again let us do that again on VMINTEQ so now we are going to look at HCL so let us see how much HCL do I need to add to be able to come up to PH3 right. So we are going to try that out so I am going to go back to excel and input menu so I am going to edit the list right so delete the estate back to main menu I do not need organic compound now and CL where is CL okay and add to list I am going to edit it here okay 60milli molal I guess right.

Again why are H total and CL total the same so we do not need to go back to over particular situation it is because you know they are source of H total CL total is only HCL right. So we are going to move on with that right so back to main menu so for the first run I am just trying to ask for a check let us say trying to use the concentration of acetic acid that we use earlier to get to PH3.

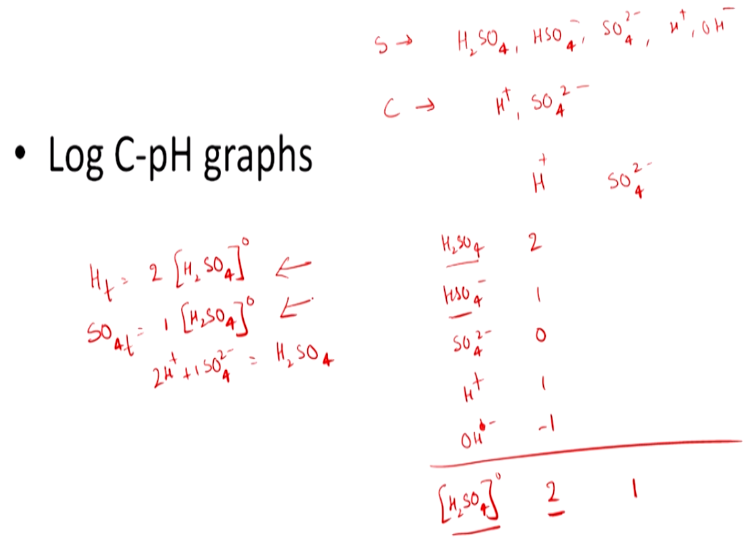
So let us see with this case what is the PH going to be as you see that PH is much lower 1.3 so at the same levels acetic acid that added earlier which was 60milli molal so earlier went to PH3 now it is drop down to 1.3 well it is not seems like a huge drop to you but keep in mind that PH is negative logarithm of H+. So we are looking at logarithmic scale right so that means each chain in unit of PH means there is 10 times change in H+ right so it is a magnitude of 1 right.

So again so it is how much hundred times lower the H+ concentration is hundred times higher pardon me. So we do not need that let us look at again input menu edit the list so let me go with maybe 1 60 times less let us say and we are going to go with 1 go back to main menu run MINTEQ and so now you see that now the PH is 3.016 and what is the explanation here because the PKA of your particular HCL right it is probably near 0 or less than 0 probably ah it is more or less going to dissociate more or less everything is going to dissociate are around PH3.

So while you add to add 60 milli molal of your particular acetic acid only one milli molal are 60 times less concentrating of your acid is going to be good enough to be able to achieve a PH of 3 right. So again same case let us try it out with HSNO4 and HNO3. So I am going to go back to main menu here and I am going to hit the list and it is not going to CL anymore back to menu HL2SO4 right so this one thing we need to look here so now I am adding H2SO4 how does it going to change.

So earlier we added HCL or HAC right they were all or they were both mono protic acid right only one proton but the key here is that H2SO4 it can give out how man now 2 protons so how will that particular speciation change let us look at that.

(Refer Slide Time: 24:30)



- Log C-pH graphs

$S \rightarrow H_2SO_4,\ HSO_4^-,\ SO_4^{2-},\ H^+, OH^-$

$C \rightarrow H^+,\ SO_4^{2-}$

	H^+	SO_4^{2-}
H_2SO_4	2	
HSO_4^-	1	
SO_4^{2-}	0	
H^+	1	
OH^-	-1	
$[H_2SO_4]^0$	2	1

$H_t = 2\,[H_2SO_4]^0 \leftarrow$

$SO_{4t} = 1\,[H_2SO_4]^0 \leftarrow$

$2H^+ + 1SO_4^{2-} = H_2SO_4$

So we have what are the species going to be in this case H2SO4 HSO4- SO42- and H+ and OH – and choosing H+ and SO42- as my components these are my species these are the component I am choosing so if am choosing an H+ rather getting that done on a HSO42-. So H2SO4 HS04- SO42- H+ and OH- and my source is initial H2SO4 that I am adding to the solution right.

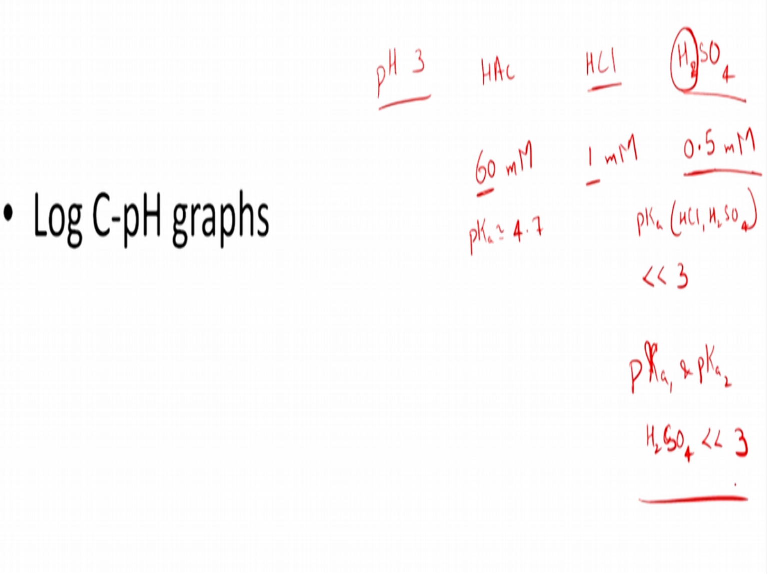
So here it is going to be how many H you need to form H2SO4 you need 2 how many H you need to add HSO4 1, 0, 1 and -1. So the key here is that H total is going to be twice the concentration of your particular H2SO4 that is the reason we just looked at this component balance. So H total is going to be two the initial concentration of your H2SO4 initial but about SO4 is going to 1 because you only need.

So for example H2SO4 let me write down the formation equation right how do I form that I need to 2H+ +1HO4 2 – right that is where we are getting it from 2SO4 total is going to be 1 times H2SO4 naught right again this is the key here. So let us try to go back to our trial and error so again try to look at how much H2SO4 needs to be added if I want to achieve a PH of 3 and I am going virtual error the reason we looked at the component balance just now was unlike the case of HCL or HAC right the H total or CL total are not going to be our similar earlier but this though H total and HO4 total are not going to same why is that?

Because H2SO4 is diprotic acid right so it can give out two protons that is what we just looked at so H total is going to twice that of HO4 total. So let us look at that I guess so we have H so H total is 1 milli molal what does SO4 total need to be where is SO4 here please I guess this is SO4 another other cases right that is SO4 where is that again miss that again this is oxidation state sulphur and oxidation state 4 0 and -2 as sulphur I mean sulphate pardon me and we just mention that needs to be half of what it is with respect to H total and what is that mean it is going to be equal to 0.5 right and that adds to the list as 0.5 right.

And I am going to go back to the main menu and run VMINTEQ and I see that now again the balance out to be right. So the PH is again around 3.305 so how much acid I need to put in H2SO4 I only need to put in 0.5 milli molal right so how do I know that coming back to input menu in the edit list so it is equal to the SO4 total right H total is equal to twice the initial acid and SO4 total = 1 time the initial acid so that is why the acid that we need to put in initially is going to be just SO4 total why it is just to be 0.5 milli molal.

(Refer Slide Time: 28:22)



- Log C-pH graphs

pH 3

HAc

HCl

H_2SO_4

60 mM

$pK_a = 4.7$

1 mM

0.5 mM

pK_a (HCl, H_2SO_4) $<< 3$

pK_{a_1} & pK_{a_2}

$H_2SO_4 << 3$

So let us compare what we looked at until now so get to PH3 how much HAC did we need to add how much HCL and how much H2SO4 HAC we have put in 60 milli molal right and that is what we looked in earlier approximately it is PH3 for HCL it was around 1 milli mollal right and for H2SO4 it is 0.5 milli molal and what is the reason I guess the PKA or HAC is around 4.7 but for PKA of these particular acids of HCL and H2SO4 is for lesser than 3.

I believe it is around 0 right so that is the reason why you see here considerable difference in the amount of acid required to be able to come up to your particular required PH and again we further see we only need half the concentration of H2SO4 when compared to HCL to be able to get the PH3 why is that because H2SO4 is diprotic acid and it will give out 2 protons so looks like the PKA 1 and PKA2 of your H2SO4 are much lesser than PKA which is 3 right.

So again what do we look at here today we looked at the relevant we first try to look at calculating the amount of acid required to be able to achieve a certain PH so these are the inverse dose or dose problem right so how much acid do I need to put in to get to my particular PH rather than doing trial and error in lab you can just plug it in right and then the second case we looked at is we wanted to compare the relative strength and weaknesses is or not weaknesses pardon me relative strength or a relative strength of the particular acid.

So in this case we looked at three acids acetic acid, hydrochloric acid and sulphuric acid right so we looked at HAC HCL and H2SO4 and we saw that because PKA of HAC is relatively high which means a weak acid that is the reason why had to put in almost 60 times here right we put in 60 times trail concentration of your particular acetic acid but with hydrochloric acid and sulphuric acid.

We just put in one milli molal and 0.5 milli molal because it is PKA value is much less than what it is that you wanted and here the reason why because these two acids has being strong acids right again this so the take home message we must need to look at the component balance plug them in and get your solutions and I guess with that I will end the today’s lecture session and thank you.