Environment Engineering: Chemical Processes
Prof.Dr. Bhanu Prakash Vellanki
Department of Civil Engineering
Indian Institute of Technology – Roorkee

Module No # 05
Lecture No # 21
logC –pH Diagram

Hello everyone so welcome back to our latest session so in the recent lecture session we have been discussing the application with respect to the component balance and the same time looking at how to intact to be able to understand the system and solve the system so by this stage you should be conversant with PH PKA at the deprotonated form protonated form acid and how to use VMINTEQ to set up your particular system as in component balance right.

So now we are going to today we are going to move on to looking at you know summarizing information let us say right so for example you can always use VMINTEX for sometimes you want to look at a summary let us say you want to present the information to a layman let us say right and for this particular people in general out there in the field look at log C PH diagrams right.

So on the Y axis you have log C and on the X axis you are going to have PH so again why log C because PH is negative logarithm of H+ to able to scale it I guess for the scaling purposes we take log C on the Y axis and PH on the X axis and what is this or what these graph in general typically useful they used for providing the snapshot of what your system is like or how your system is going to change with PH right. So today we are going to discuss that initially so let us look at an example graph here.

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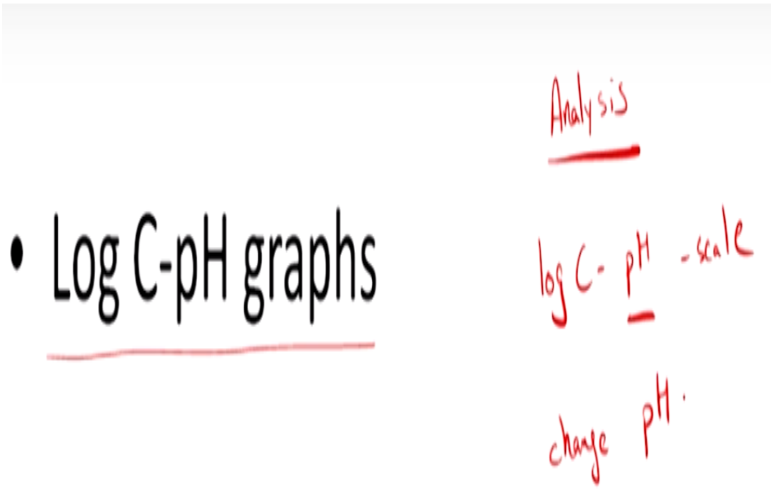

- Log C-pH graphs

Analysis

log C- pH -scale

change pH.

So today we are going to look at log CPH graphs right so again what are the useful they are useful analysis again analysis so earlier such mathematical tools or matlab and such matlab is way to hammer in this case I guess at least excel and VMINTEQ you can get your relevant information relative easily but in the past let us say we did not have the assistance of the computer tools right.

So you like mostly on log CPA diagrams to be able to get an idea about system right but people still use that in India considerably at least if you are looking at the scores hopefully the next time someone brings up a log CPH diagram hopefully you will be able to talk about VMINTEQ and such right anyway hopefully so again we look at log CPH diagram keep in mind that you know this been used in the past or you still in use in mostly right so what else do we have here.

Again we do the log C versus PH why to be able to scale it so what can we see we see the changes with PH how does the system change with PH right. So let us look at one example I think the example are example graph I guess that has obviously H+ and OH- and also I believe NHO+ and NH3 and also the acetic acid and protonated and deprotonated form. So let us look at that graph here.

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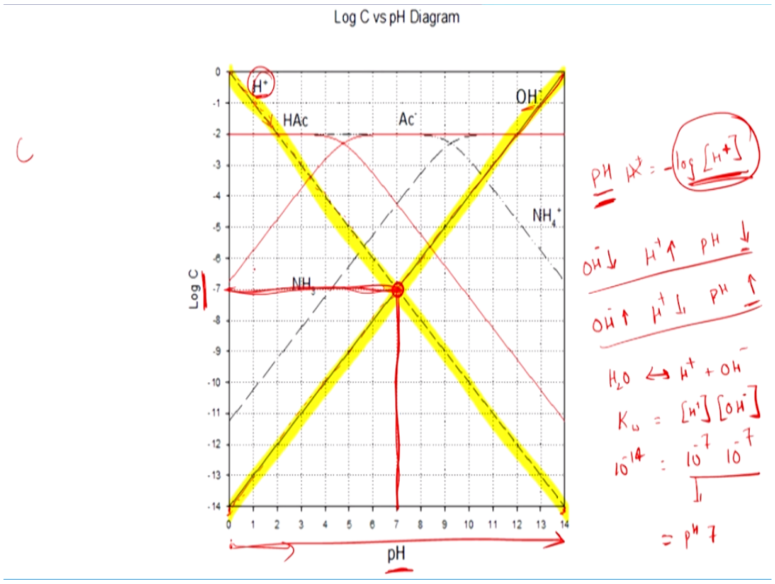

So here let us try to take a few minutes to be able to understand our system so here on the X axis we have PH and on the Y axis we have log C right and log C I guess C total depends on the C total in this case the particular graph for particular C so and here the acid is from 0 to -14 and here is 02 14 PH is from 0 to PH14. So first let us try to analyze H+ and OH- I guess so what are you looking at here?

We are looking at H+ and we are also looking at H- initially right so again what is H+? H+ = -log pardon me not H+ PH – log concentrating of H+ right so what happens as you increase the concentration of your H+ the PH will decrease as we increase H+ concentration PH will decrease as you decrease H+ concentration the PH is going to increase or similarly as you decrease the OH – concentration the PH is going to decrease as you increase the OH – concentration the PH is going to increase and more of less the same aspect mentioned lower.

So let us see how it changes so we are going to look at H+ initially and at PH 0 you see that log C the concentrating is higher and as you keep increasing the PH right what is C here just see that the concentration decreases and here since we are looking log C that is why it is linear looking at log C here log C this is what we are looking at negative that is why the slope is negative here. So PH log P versus PH and so that is why you see linear decrease here so from 0 to 14 here so that is what you see here 10 power -14 pardon me 0 to 10 power 14 and same case PH 0 to PH14.

So at the same time what would you expect as H+ concentration decreases that means the OH- concentration increase and that is what you see here OH- concentration is increasing from ahh 10 power -14 to 10 power 0 right and that is what you see here again that is what you would expect here right. So we will look at how to we will also try to look at ahh simple example I guess with monoprotic acid later on and also look at H+ and OH- but we will come back to that later about how to go about that right.

So for now we still try to understand the log CPH diagrams in better manner so obviously if you look at the point of intersection that is going to KW value and then should be 7 PH 7 right and what is that mean at that particular case the concentration of both H+ and OH- are going to be the same and we know that H2O dissociates into H+ and OH- and the dissociation constant is concentrating of H+ into concentration of OH- so that is 10 power -14 right and when they are equal both 10 power -7 and 10 power -7 so that means at PH7 anyway.

So that translates to PH7 so at PH7 you see that both the concentration are equal and that is 10 power -7 again you that relatively easy to understand.

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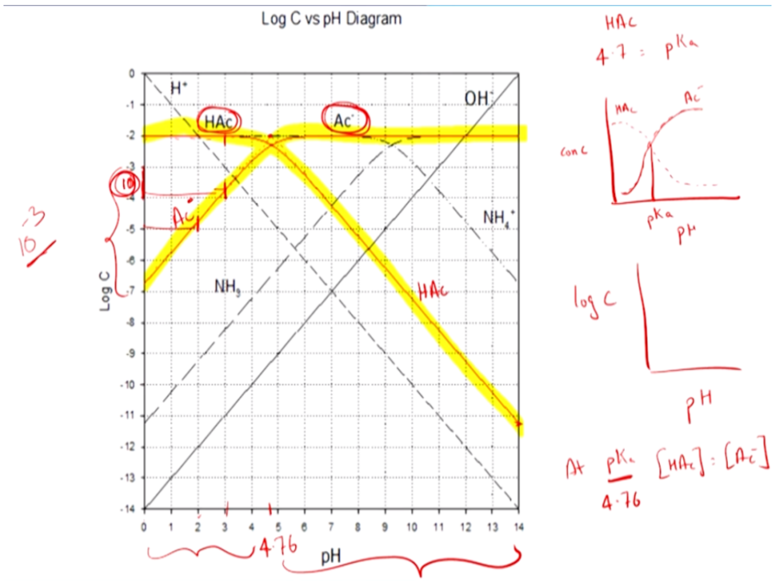

So let us move to the next particular aspect let us look at acetic acid something we have looked at until now right so acetic acid you now that the PKA is 4.7 right we have a PKA of 4.7 so now we are trying to look at acetic acid the PKA is 4.7 right and with your background you know that the PH is less than PKA what is that mean the deprotonated form is going to predominate right and when the PH is greater than PKA we know that protonated form is predominant.

So you know earlier we looked at this speciation diagram where we looked at concentration versus PH right that is not normalize and this is what we looked it earlier and this was HAC and AC – and this was PKA right and so now obviously if you now taking a log C rather than concentration versus PH you know the shape is going to be relatively different s let us highlight the relevant particular graph we are trying to look at it is the red graph here I believe right so this is HAC and this is AC- right.

So again let us try to understand the system here so here the PKA you know it is not going to insertion of this point but if you draw the slope here and also the slope here the intersection of those slope should be equal to your PKA and that should be 4.7 or I think gets 4.76 right. So the PKA of that particular system HAC and AC – is going to be or the PKA of the acetic acid is 4.76 that is what we just plot it here and so let us try to analyze the system now.

So when you are in this zone right when PH is less than PKA what would you expect you would expect that the deprotonated form is going to predominate so HAC is going to predominate so that is what you see as you move from PH0 to PH3 almost all of it is going to stay at HAC right at least in the lower concentration so as you keep increasing the concentration though there is a slight increase and increase in AC-.

So though it looks like considerable increase keep that it is log C and negative here so the change is 10 power -3 or so on which is relatively minimum right so again HAC most of it is an HAC and AC – keeps increasing and then at PKA right at around at PKA you will have that particular concentration to be equal that is what you know right so for particular concentration that PKA the concentration of HAC at PKA you know that the concentration of HAC will always be equal to concentration of AC-.

PKA for particular acetic acid is 44.6 and that is what you see here and again you move further out and as in this region now right what do we see here we see that as we more away from the PKA we say that most of it is now going to go as estate ion or the deprotonated form and there is going to be a rapid decrease concentration of your protonated form this is your HAC right and this is your AC- that is what you see here.

Again this will give an easy idea about that right this is logarithmic scale right keep in mind that it means it is 10 times difference in the concentration right so magnitude order of 1 right. So thus in general PH3 is the concentration and at PH2 the AC- concentration is here and it of by unit of 1 that means it is of by it is 10 times lesser I can neglect that.

So in this case keep in mind that it means log C versus PH logarithm graph if one your variable is less than by the other by variable by unit of 1 that means you can more or less neglect it one or two times change translates to 10 times or hundred times being lesser or greater so you can accordingly you now neglect or use those particular values.

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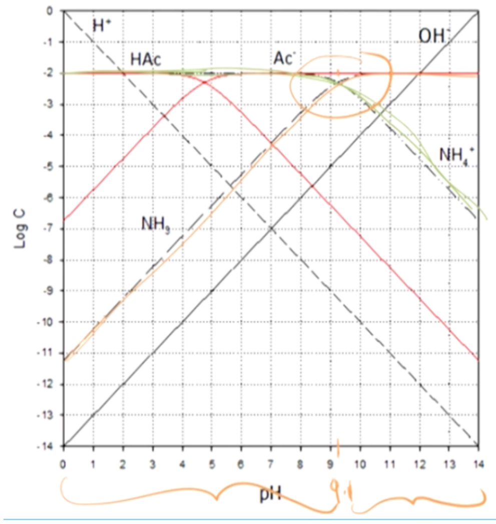
Log C vs pH Diagram



$NH_4^+ \leftrightarrow NH_3 + H^+$

$NH_4^+ \downarrow\downarrow$ $NH_3 \uparrow$

So let us now move on to what we have here or we look at the other system here so we are now going to look at ammonia here and H3 okay and hopefully I got that right and NH4 + right so that is what we have here and now we are talking about NH3 and NH4 + and looks like PKA is going to be around 9.1 it is approximate has 9.1 from this graph PKA is going to be intersection of this scope and it is going to be 9.1 let us say and assuming that as 9.1 that is good enough assumption for now.

So again we are going to apply our basic knowledge in PH or less than PKA look that how the system is and PH greater than PKA look at how the system various. And this region when the PS is less than PKA what would you expect right you would expect protonated form to predominates so let us look at that so this is the NH4+ let me try to use the difference highlighter probably.

So this is your NH4+ and your particular NH3 is that now is out here right and the PKA value is 9.1 so what do we see here so you see that where the range is PH 0 PKA value what is going to predominate it is going to be NH4 + and that is what you see here in this region and is approaching the PKA value which is here right

What do we see? You see that it is going to be changing or shift in speciation fromNH4 + going to NH3 so this transformation you see in this zone right and as you keep moving further away from it you see that now NH4+ is going to decrease further NH4+ is going to decrease much further and you are going to have an increase in your NH3 right.

So again we will at holistic view here so this more or less the log CPH background will give you an idea about you know the summary I guess it is snapshot of what you are looking at. So again use in the past widely but now with your computer tools such as excel or your VMINTEQ you can done this easily again with respect to VMINTEQ.

One aspect is that all those data files that we were able to generate in the previous lecture sessions you can easily output them or you now save them as in the excel format and once you save them in excel format you can you know do the relevant what do we say modifications or such in a presentable manner if you (()) (14:32) so right. So let us look at how to we look at one particular example here right and we will see we look at one particular example and how we can go about analyzing it here.

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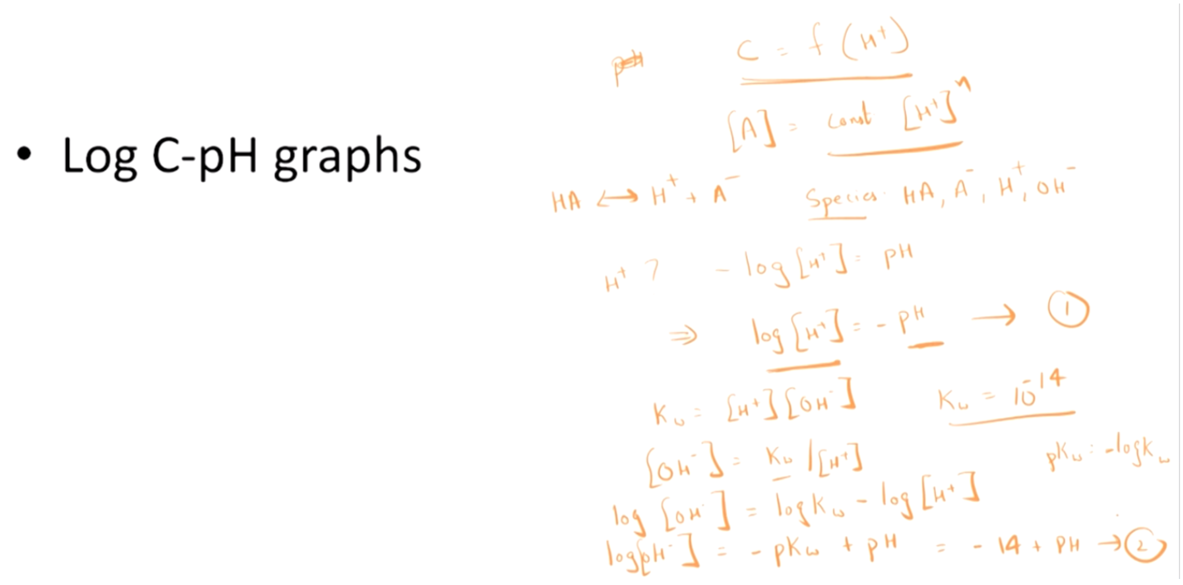

- Log C-pH graphs

~~pH~~

$$\underline{C = f(H^+)}$$

$$[A] = \underline{\text{Const}\,[H^+]^n}$$

$HA \longleftrightarrow H^+ + A^-$ $\quad$ $\underline{\text{Species}}$: HA, A^-, H^+, OH^-

H^+ ? $\quad -\log[H^+] = pH$

$$\Rightarrow \underline{\log[H^+]} = \underline{-pH} \rightarrow ①$$

$K_w = [H^+][OH^-]$ $\qquad$ $\underline{K_w = 10^{-14}}$

$[OH^-] = \underline{K_w} / [H^+]$ $\qquad$ $pK_w = -\log K_w$

$\log[OH^-] = \log K_w - \log[H^+]$

$\log[pH^-] = -pK_w + pH \quad = -14 + PH \rightarrow ②$

So what is the key here we are going to express everything right let me change the color to red okay anyway never mind we are going to have to express all the concentration are the function of H+ this is what we are trying to do right you want to do everything because we are trying to draw log C PH graph right you want in terms of H+ so more or less you will have to make some assumption as especially at the boundaries so we are going to see what they are I guess.

So the first aspect is that we need to express everything as H+ or you can so that you can concentration as constant let us say into H+ to the power of N and so on. So that is the usual form that you would look at let us say so let us look at one example I think again we are going to look at the usual monoprotic example that we are looking at so let us say HA dissociates into H+ and A- so what are your species obviously there HA the deprotonated form is A- and obviously you will always have H+ and H – right.

So before we go further just look at the simplest case which is H+ and how do we go about that and we know that negative logarithm of H+ is PH so what is that mean it means log concentration of H+ = -PH so that is one equation already right so you have log C versus PH so that is equation 1 so that is obviously relatively similar that is what you see here I guess what do we see as PH increases you see that log C decrease that is what we just looked at in the graph.

Right as PH increase here you see there log C keeps decreasing anyway again OH- but for that we know KW = H+ times the OH- concentration so the OH – concentration is than going to be equal to KW / H+ right and what is KW I guess water dissociation constant anyway you know again it is a constant similar to the equilibrium constant and we know that the value is 10 power -14 right.

And then let us move on again we take the logarithm on both the side so log of OH- will be equal to the log of over this value here KW – the log of what is it here H+ right so log OH- is going to be equal to log KW I guess that as –PKW right where PKW = - log of KW think of it as PKA right and +PH right and what is this particular value going to be = it is going to be equal to -14 + PH.

So this is my equation number 2 so what do I have here? I have OH - = -PKW and PKW that value is going to -14 1PKAW is -14 +PH let us look at the graph now and as you see -14 starts from -14 right -14 + PH these are log OH – concentration right PH-14 it starts from -14 when PH is 0 and as you see it keep increasing until it keep increasing the maximum of 0. So that is what you see from this particular graph right so let us move on I will move on to another fresh slide here.

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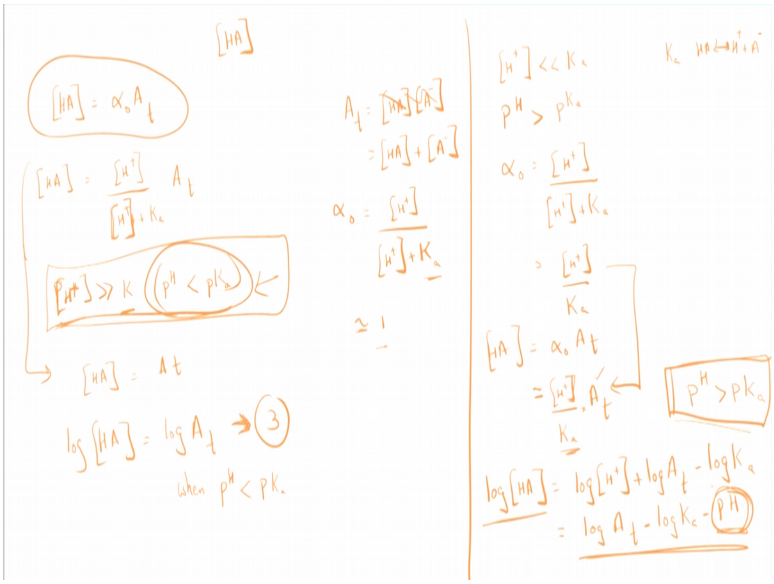

$[HA]$

$\boxed{[HA] = \alpha_0 A_t}$

$[HA] = \frac{[H^+]}{[H^+] + K_a} A_t$

$\boxed{[H^+] \gg K \quad (pH < pK_a)}$

$[HA] = A_t$

$\log [HA] = \log A_t \rightarrow ③$

when $pH < pK_a$

$A_t = \cancel{[HA]}\cancel{[A^-]}$

$= [HA] + [A^-]$

$\alpha_0 = \frac{[H^+]}{[H^+] + K_a}$

$\simeq 1$

$K_a \quad HA \leftrightarrow H^+ + A^-$

$[H^+] \ll K_a$

$pH > pK_a$

$\alpha_0 = \frac{[H^+]}{[H^+] + K_a}$

$\simeq \frac{[H^+]}{K_a}$

$[HA] = \alpha_0 A_t$

$\simeq \frac{[H^+]}{K_a} \cdot A_t$

$\boxed{pH > pK_a}$

$\log [HA] = \log [H^+] + \log A_t - \log K_a$

$= \log A_t - \log K_a - \boxed{pH}$

So next aspect is we need to be able to come up with approximating HA concentration of HA and what else please approximating concentration of A-. So we are now into HA and A- and other two species and so let us look again what we are trying to do so here let us say (()) (19:01) PH graph so you need to be able to look at some approximations so we are going to divide into two phase and I guess the reference here is going to be PKA right.

So we are going to consider two cases one the PH is less than PKA and the other PH is going to be greater than PKA and look at the relevant assumption that you can make and we are going to go through is that. So right and in general we know that HA the concentration of HA = alpha naught into A total and again what is A total A total = HA into A – again the concentration of protonated to be expressed as alpha naught that is the first ionization fraction right into A total is I know how did we define this ionization fraction?

It give us idea about at least alpha naught we define that as the protonated form the fraction or protonated form of the total acid and that is what we have here and so obviously this is not the problem but the summation here right that is the total acid so here let us say and what do I know alpha naught = we know that alpha naught = the concentration of H+ / H+ + K and right what is K or KA.

KA is the answer acid dissociation constant for reaction HA dissociating into H+ and A- so that is what we have here. So let us plug this in here so HA = alpha naught is H+ / H++ KA into A total. So now as we mentioned we are going to look at two cases what were they one when the PH is less than PKA and the other one the PH is greater than PKA so we will consider the first case when H+ is far greater than K what is that mean so H+ far greater than mean is nothing but PH being less than PK right.

So let us try to understand this system so the variable we are going to look at is simply is going to be alpha naught then H+ is far greater than K right what is that alpha naught is transform into it transforms into 1 more or less what is that mean now so when PH is less than PKA or far less than anyway what is that mean it mean that almost all the particular acid is going to stay in it is protonated for that is what alpha naught = 1 means right.

So again when PH is far less than PKA what is that we know that two from our background that all of your particular acid is going to stay in its particular form and so that is what you see here is at PH is less than PKA or H+ is far greater than K we see that and here I am writing that from here HA is going to be equal to A total or log HA = log of your total acid and that is my equation 3 right and that is for one particular case where is that when PH is less than PKA when PH is less than PKA.

So let us try to look at our graph and see if that makes sense and here I am going to look at HAC let us say so PKA is 4.7 so as you see when PH is less than PKA what do you see here? You see here it approximate saying that all the particular acid is going to say as its protonated form that is what you see here. So let us move on and look at the other case so we are going to look at the other case when now H+ is far lesser that KA or what does it mean?

It means PH is greater and just referring to this particular what do we say the assumption that we looked at case so it means the PH is greater than PKA right so what is that transform into again so alpha naught again as we know is H+ / H++ KA right so because H+ is far lesser than KA I am going to approximate at H+ / KA right and so where is my fundamental equation here HA I am looking at this particular equation here HA = alpha naught into A total and that now is going to be equal to substituting that here H+ / KA into A total right.

So more or less let us look at A total is your particular total acid that is more or less constant for particular scenario right and the denominator KA and acid association constant for that particular acid is obviously a constant and so the only variable is your H+. So obviously log concentration of HA = log H+ + log A total – log KA and that is equal to log A total – log KA – PH right. So again this is the case that would be applicable when PH is greater than PKA right.

So that is what we just derived please keep in mind that we are making strong assumption here is what does it mean PH is greater than PKA as you keep increasing the PH what happens to log HA it keeps decreasing so let us look at the graph here again as we are increasing the PH and are talking about this zone now the PH is greater than PKA as we are increasing the PKA in this direction we see that log HA is decreasing so that is what we just derived now so let us look now for the deprotonated form though right.

So now until now we looked at protonated form same case we are going to look at the deprotonated form.

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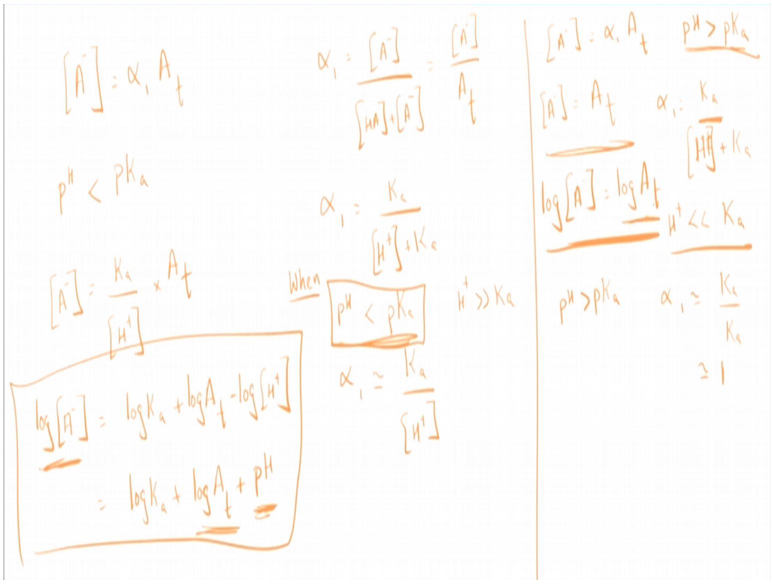

$[A^-] = \alpha_1 A_t$

$pH < pK_a$

$[A^-] = \frac{K_a}{[H^+]} \times A_t$

$$\boxed{\begin{aligned} \log[A^-] &= \log K_a + \log A_t - \log[H^+] \\ &= \log K_a + \log A_t + pH \end{aligned}}$$

$\alpha_1 = \frac{[A^-]}{[HA]+[A^-]} = \frac{[A^-]}{A_t}$

$\alpha_1 = \frac{K_a}{[H^+]+K_a}$

When $\boxed{pH < pK_a}$ $H^+ \gg K_a$

$\alpha_1 \simeq \frac{K_a}{[H^+]}$

$[A^-] = \alpha_1 A_t$ $pH > pK_a$

$[A^-] = A_t$ $\alpha_1 = \frac{K_a}{[H^+]+K_a}$

$\log[A^-] = \log A_t$ $H^+ \ll K_a$

$pH > pK_a$ $\alpha_1 \simeq \frac{K_a}{K_a} \simeq 1$

So deprotonated form again that is A- concentration = alpha 1 into A total and again where is this from we know that alpha 1 is defined as concentration of A- by concentration of HA + concentration of A- that is equal to the concentration of A- by total acid that is where we have that from and first case is that we are going to consider is PH being less than PKA so what does this particular alpha 1 transform into we know that alpha 1 = KA / H++ KA so when PH is less than PKA so when PH is less than PKA the alpha 1 will be similar to PH is less than PKA means H+ is greater than KA right.

So I am going to say it is going to be equal to KA / concentration of H+ right so if I plug that particular value in concentration of A- is going to be equal to KA / H+ KA / concentration of H+ into the total acid. So now again what do we have the equation to be we have A- = the function of H+ and the constant so that is what we want to have right. So let us write that down now talking the logarithm on both hands and both sides log A – or log C = log KA + log A total log H+.

So what is it mean it means it is going to be equal to log KA + log total acid + PH again let us understand this equation please. So we are looking at log C and obviously as you see the deprotonated form concentration increases with PH right the deprotonated form increases with PH in which zone now the PH is less than PKA right you see that that is the case and what do you see here it also depends on the total acid what does it mean.

So the greater the concentration of your total acid right also the concentration of your particular protonated or deprotonated form in this case it is going to be higher. So again we looked a one particular case and what was what PH is less than PKA and let us try to understand this with respect to graph so the log A – should increase with PH and let us see what we here in this particular zone with respect to acetic acid this is 4.76 when PH is less than PKA right we see that deprotonated form AC- is now increasing with your particular PH and that is what we just look at in our particular graph right.

So let us move on to the other scenario and what is that other scenario please the other scenario is for A- = alpha 1 into A total when the PH is greater than PKA right that is the case we need to derive and once we have done with that we will be done with this lecture session. So again we know that alpha 1 = KA / what now H+ concentration H++ KA and when PH is greater than KA what is that mean it means H+ is much lesser than KA right.

So if that is the case alpha 1 will be equal to KA/ KA or meaning alpha 1 is going to be 1 so more or less A- is going to be equal to A total again let us understand the system here. What does it means when PH is greater than PKA we know from our background I guess at this stage but almost all of it is going to hit as in total acid is going to stay as the deprotonated and that is what we see here right when the PH is greater than PKA we can say that deprotonated concentration you know that species is going to be equal to total acid concentration.

So again just taking the logarithm it is going to be equal to log of A – is going to be log of the total acid so that means the total constant when PH is greater than PKA and the constant is going to be equal to the log of the total concentration let us look at the graph again okay and this region as in when the PH is greater than PKA what do we see here we see that deprotonated concentration right the deprotonated concentration.

Concentration of the deprotonated form which is AC – constant and what is the constant = it is going to be equal to your log A total so these are the log CPA diagram is usually come across and usually understand them again keep in mind that let us say if I am trying to come to the value let us say. You know I am going to compare ah PH 7 the AC- concentration and then the HAC concentration right this is what I am trying to compare and I see that it is both of them differ by unit of 2.

But because it is log C what can I say? I can say that I can confidently say that I can neglect the HAC concentration and only AC- concentration is relevant why is that? Because it is logarithmic scale and you know it is different by unit of 2 right so the order differs by 2 okay. So with that I will do for this lecture session and thank you.