Environment Engineering: Chemical Processes
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Module No # 06
Lecture No # 27
Buffer Intensity: Monoprotic And Diprotic Acid

Hello everyone, so welcome back to our latest lecture session. So we have started discussing about buffer intensity and without further a due wastage of time. Let us go through, so we are talking about buffers.

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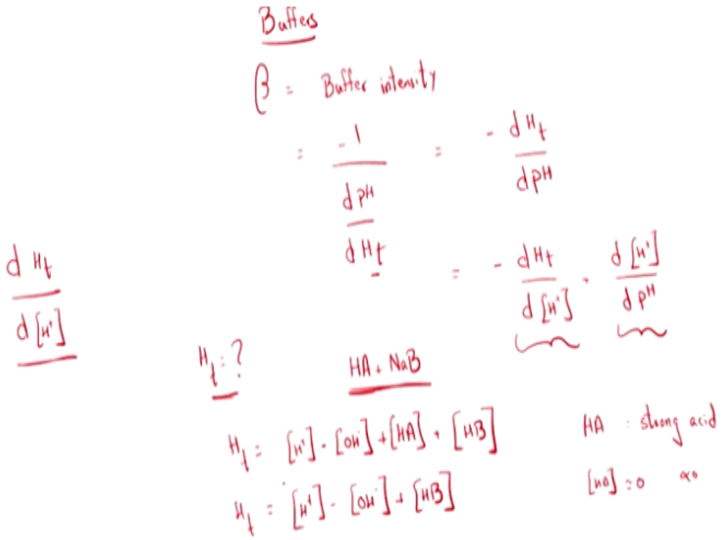

Buffers

β = Buffer intensity

$$= \frac{-1}{\frac{d\,pH}{d\,H_t}} = -\frac{d\,H_t}{d\,pH}$$

$$= -\underbrace{\frac{d\,H_t}{d[H^+]}} \cdot \underbrace{\frac{d[H^+]}{d\,pH}}$$

$$\frac{d\,H_t}{d[H^+]}$$

H_t : ?

HA + NaB

$H_t = [H^+] - [OH^-] + [HA] + [HB]$

$H_t = [H^+] - [OH^-] + [HB]$

HA : strong acid

$[HA] \simeq 0$ α_0

We discuss the relevant aspect in detail. Buffer intensity we know that is going to be universally proportional to change in PH. When you add an acid or base, since of H + we are going to have derivative with respect H total. So that is going to be = - DH total D PH. So by chain row that is going to be = - DH total by derivative of H total with respect to H + into derivative of H + with respect to PH.

I guess by the chain row. So this is what we have, so we are going to look at the two variables here, two sets of derivatives. So first we are going to look at DH T derivative of H total with respect to H +. So derivative of H total with respect to H +. But first we need to express, What H is total? For that we need to be able to look at one particular scenario. So that is the scenario where we have strong acid HA and relatively a base.

So this is the situation we are considering. We have these two in our particular system, so from now our background we know that H total is going to be equal to concentration of H + - the concentration of OH - and the protnate form of acids. So let us see A and HB, keep in mind that these weak acids were H as a strong acid. Because we are assuming that what is it now?

HA is a strong acid, so we know that when it is a strong acid it will disassociate at almost all PH ranges. We can assume that the HA concentration or we know that the alpha not is going to be negligible. So we are going to assume that it is going to be 0. So that H total is now going to be equal to the concentration of H + - concentration of OH + -. Now potent form of B, so now we need to calculate the derivative of the H total with respect H +. Let us work that out in next set here.

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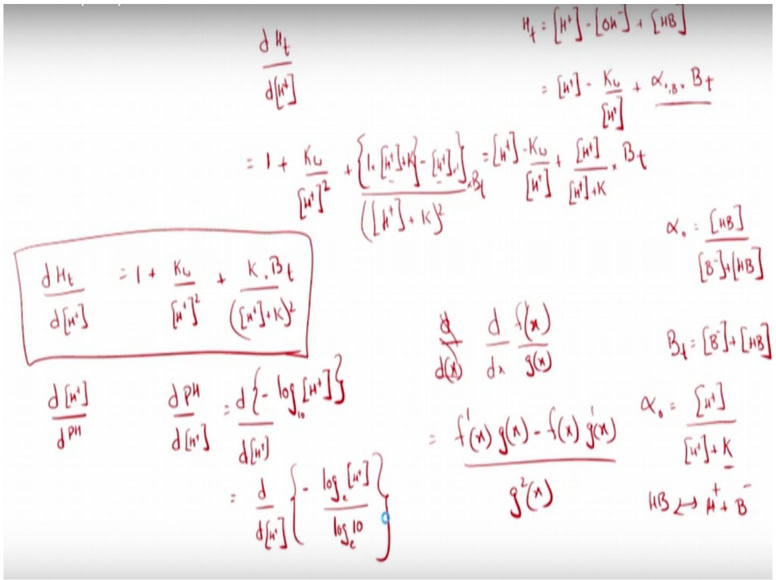

$$H_t = [H^+] - [OH^-] + [HB]$$

$$= [H^+] - \frac{K_w}{[H^+]} + \underline{\alpha_{0,B} \times B_t}$$

$$\frac{dH_t}{d[H^+]}$$

$$= 1 + \frac{K_w}{[H^+]^2} + \frac{\{1 \times ([H^+]+K) - [H^+] \times 1\}}{([H^+]+K)^2} \times B_t$$

$$= [H^+] - \frac{K_w}{[H^+]} + \frac{[H^+]}{[H^+]+K} \times B_t$$

$$\alpha_0 = \frac{[HB]}{[B^-]+[HB]}$$

$$\boxed{\frac{dH_t}{d[H^+]} = 1 + \frac{K_w}{[H^+]^2} + \frac{K \cdot B_t}{([H^+]+K)^2}}$$

$$B_t = [B^-] + [HB]$$

$$\cancel{\frac{d}{d(x)}} \quad \frac{d}{dx}\frac{f(x)}{g(x)} = \frac{f'(x)\,g(x) - f(x)\,g'(x)}{g^2(x)}$$

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

$$HB \rightleftarrows H^+ + B^-$$

$$\frac{d[H^+]}{dpH}$$

$$\frac{dpH}{d[H^+]} = \frac{d\{-\log_{10}[H^+]\}}{d[H^+]} = \frac{d}{d[H^+]}\left\{-\frac{\log_e[H^+]}{\log_e 10}\right\}$$

So we have DH total by D derivative of H +. What is H total? Just for my memory, I am going to write down here it, H + - OH - + HB. Let us try to simplify that it is going to be equal to as you know H + - KW by H + + the protonate form. So alpha not B into B total. Again we know that alpha not will give us an idea about HB by the deprotonate form and the protonate form.

The total acid that is what we have here and that is what we are using it and we know that B total is going to be equal to HB and that is how we end up here and obviously, we also know that alpha not can be expressed as H + by H + +, K being the acid disassociation constant for HB. HB disassociating to H + and B - and the relevant acid disassociation constant is K.

So, let us plug here H total = H + Concentration - KW by Concentration of H + + where this alpha not is Concentration of H+ / H + + K into B total. Now the derivative of that particular equation is what we are going to look at here, that is going to be = 1 - KW / H + where is it going to be +. Now we have F of X by G of X, so if we are going to look at that particular case, how do we go with that D of DX function of X GX?

How do we think it is going to be equal to first derivative function of X into G of X - F of X into the first derivative of G of X by square of G of X. This is what we have, so let us try to plug that here. So F of X derivative which is H + here. So let say that is going to be equal to one into G of X is H + + K and negative symbol here and that of X. So let us have this brackets that of X is now G of X derivative is again equal to one and the denominator is now equal to H + + K whole square into B total.

So let us try to simplify this here and now we are going to have 1+ KW / H + square + K K. K because H + and H + K / H + square H + + K whole square into B total. So this is what we end up here, so that is one equation we need to refer to later on. The other aspect I believe that we have to calculate with. Now DH + / D PH, so derivative of H + with respect PH.

So for that I am going to look at calculating the derivative of PH with H +. What is that going to be equal to that PH is - log H +? So that derivative is what we are trying to look at here. But we know that the integrals and derivatives, we cannot look at log at base time. So we need to transform this to natural logarithms. So how do that we are going to look at D / DH + - log H + to the base E which is the natural logarithm by log 10 to the base E. Here log means log 10, this is what we have and let me try to continue this in next particular sheet. So we have trying to calculate D PH.

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$$\underline{\frac{dpH}{d[H^+]}} = \frac{d}{d[H^+]}\left\{\frac{-\log_e[H^+]}{\log_e 10}\right\} = \frac{d}{d[H^+]}\,\frac{-\ln[H^+]}{2.303}$$

$$= \frac{-1}{2.303}\cdot\frac{1}{[H^+]}$$

$$\underline{-\frac{d[H^+]}{dpH}} = 2.303\,[H^+] \qquad \beta = \frac{-1}{\frac{dpH}{dH_t}} = -\underline{\frac{dH_t}{d[H^+]}}\cdot\frac{d[H^+]}{dpH}$$

$$= 2.303\,[H^+]\left\{1+\frac{K_w}{[H^+]^2}+\frac{B_t K}{\left([H^+]+K\right)^2}\right\} \qquad \begin{array}{l}\alpha_0\\ \alpha_1\end{array}$$

$$= 2.303\left[[H^+]+\frac{K_w}{[H^+]}+B_t\times\frac{[H^+]}{\underbrace{[H^+]+K}_{}}\times\frac{K}{\underbrace{[H^+]+K}_{}}\right]$$

D PH by a derivative of PH with respect to H + and we believe end up with D by DH. So this is what we ended up with. Let me just double check that now that is going to be equal to derivative with respect to H + - natural algorithm of H + / 2.303. So that is going to be = - 1 /2.303 into 1 /H +. So that is what we have here, but keep in mind we are trying to calculate - the derivative of H+ by with respect to PH the derivative of H+ with respect to PH.

So now is going to be equal 2.303 into H +. So these is what we have but again keep in mind what we are trying to calculate this particular variable. So let us try to plug that up the buffer intensity. I guess beta be equal to - one by the derivative of Ph with respect to H total. This is what we had and we express this as - D H total with respect to H + and the derivative of H + with respect to PH.

This is what we expressed it as, so now let us try to plug the relevant values here and this particular value is 2.303 into H +. What is this particular variable here? I think we have that written down somewhere, I think it was one + KW by H + square + B total into K by H + + K whole square. So let me just check that out please and one + KW by H + square + K into B total by H + + B square.

We are on the track, so taking this here it is going to be equal to two point three zero three into concentration of H + + KW by concentration of H + + B total. Now I am going to express this into in terms that we are going to be able to simplify later by H + by H + + K into by H + + K and obviously as you see here, this particular setup variable will be equal to alpha not and this particular setup variable will be equal to alpha one. So let us just simplify what we have here. We now have buffer intensity.

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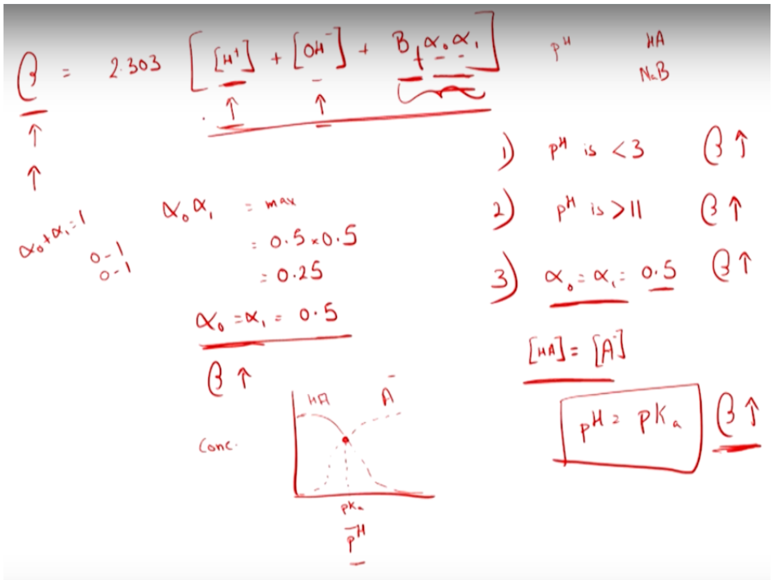

Beta is equal to 2.303 into the concentration of H + + KW by H + would be now OH - concentration + B total into alpha not into alpha 1. This is the take home message, so buffer intensity is going to obviously depend upon four variables. What are they H + OH -? The total base present alpha not and alpha one and again the assumption here. Obviously look at was HA was an strong acid and we looked at HA was an strong acid.

We looked at NJP where base is strong acid HP is weak acid. So that is something we looked at so we need to look at what we are going to analyze the system for it. But we are going to consider three aspects here or the three regions which we are going to have good buffer intensity. So what are these regions, we are going to try to identify them? So what are the variables here H + OH - and alpha not and alpha 1 and obviously B total.

So think of this now, when H + concentration is high B the buffer intensity is going to be high. So when H + concentration is high buffer intensity is going to be high. So what does that mean? So the PH is less those regions is very less, say less than 3. So you are going to have high buffer intensity that is what you see and we are trying to understand that later. The other aspect is - concentration is high.

You again see that the buffer intensity is going to be high. So again let us say PH here is greater than, let us say eleven that the buffer intensity is going to be high. So we are trying to understand this but just plug them in now and this is the critical aspect where you know the role of your particular acid or base that you are going to plug in will come into play.

So let us say for a particular system control B total and that is going to stay same, but that particular system alpha not and alpha one that they will change with PH. So we need to look at in which case will the product of alpha not and alpha one be the maximum and we know that alpha not can go from 0 to 1 and again alpha not can go to 0 to 1. We know that alpha not + alpha one is equal to 1.

If you look at it is going to be maximum only when it is 0.5 into 0.5 which will be equal to 0.25. So whole alpha not equal to alpha 1 = 0.5 where we have the maximum value here. So whole even alpha not equal to alpha 1 = 0.5 where we have buffer intensity to be maximum. So what is that about we will try to understand that the buffer intensity high.

We know the ionization facts will give an idea about the concentrations of the relevant acid and base into the protonate and deprotonate form. So we know that when alpha not and alpha 1 are equal and equal to 0.5. What does that mean? It means obviously that the concentration of your protonate form going to be equal to the concentration of deprotonate form, obviously it means that when you have equal amounts of acid or base present or (()) (15:06) and add any additional or base.

The system can consume proton or release a proton to be able to resist the changes in the Ph. So for that you obviously need to have acid or the base and that particular scenario will be relevant to having a higher buffer intensity and that obviously is the case when PKA, PH = PKA so what is this about when alpha not is equal to alpha 1 HA equal to a - that from our species diagram.

If this is PH and the concentration, we know that this is the behavior of HA. Let us say the behavior of your A - and when are they equal. PH is equal to PKA, so what does this mean? So when the PH = PKA for that particular compound or the conjure acid or base, the buffer intensity will be the maximum. So this is the take home message that we have from this particular equation here. So now we are going to plug this into two system.

So one case would be for the monoprotic acid. Let us say acetic acid and then we are going to look at the buffer intensity for a particular scenario and then we are also going to look at the diprotic acid. Let us say the carbonated system and look at the buffer intensity and how it changes with PH. So again initially we are going to look at how the buffer intensity changes with PH. So for that I believe I already have the relevant sheet to save upon time here. So let us go back to here, so here I have

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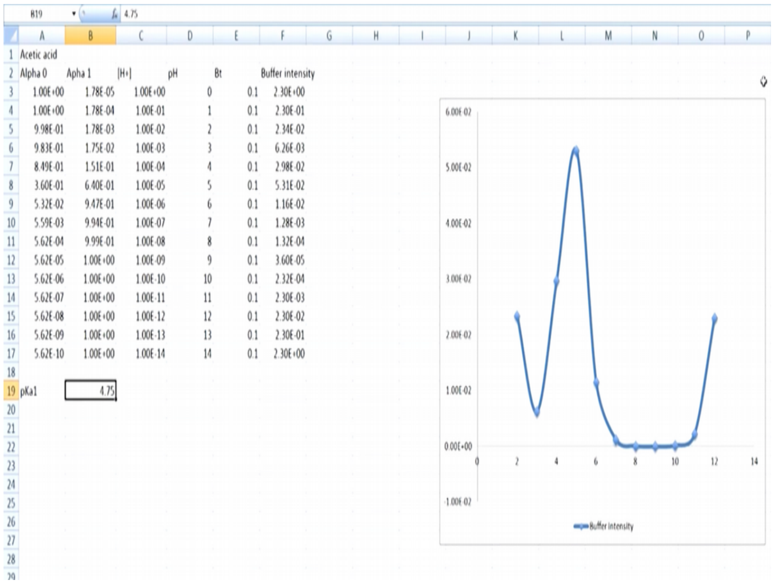

Acetic acid

Alpha 0	Apha 1	[H+]	pH	Bt	Buffer intensity
1.00E+00	1.78E-05	1.00E+00	0	0.1	2.30E+00
1.00E+00	1.78E-04	1.00E-01	1	0.1	2.30E-01
9.98E-01	1.78E-03	1.00E-02	2	0.1	2.34E-02
9.83E-01	1.75E-02	1.00E-03	3	0.1	6.26E-03
8.49E-01	1.51E-01	1.00E-04	4	0.1	2.98E-02
3.60E-01	6.40E-01	1.00E-05	5	0.1	5.31E-02
5.32E-02	9.47E-01	1.00E-06	6	0.1	1.16E-02
5.59E-03	9.94E-01	1.00E-07	7	0.1	1.28E-03
5.62E-04	9.99E-01	1.00E-08	8	0.1	1.32E-04
5.62E-05	1.00E+00	1.00E-09	9	0.1	3.60E-05
5.62E-06	1.00E+00	1.00E-10	10	0.1	2.32E-04
5.62E-07	1.00E+00	1.00E-11	11	0.1	2.30E-03
5.62E-08	1.00E+00	1.00E-12	12	0.1	2.30E-02
5.62E-09	1.00E+00	1.00E-13	13	0.1	2.30E-01
5.62E-10	1.00E+00	1.00E-14	14	0.1	2.30E+00

pKa1 4.75

Acetic acid here and we know that the PKA is 4.75. So I plugged in the relevant formula for alpha not which is the concentration of H + which is here, H + / H + + tender power of - P PKA which is k. So that is what you have here and I have PH here and total buffer I am taking it to be 0.1 molar and this buffer intensity have been calculated here.

So we are trying to calculate the buffer intensity and how it changes with what we say PH for system. Now we have acetic acid and the total base or the total acid present is 0.1 molar. So here I already set it up, so we can save up on time, so the PH is from 0 to fourteen the total acid or the base is obviously going to stay the same and the PKA for the acetic acid is going to be equal to 4.75 or 4.76.

So I am taking into consideration 4.75. So here we have alpha not, alpha 1, H +, PH, B total and buffer intensity. This has the relevant equation which we just derived, two point three zero three into concentration of H + concentration of OH - into B total + B total into alpha not into alpha one. So that is what we have here, so let us try to plug in the relevant values and alpha not is H by H + + K alpha 1 is K by H + + K.

So that is what we have here. So let us try to plug the relevant values here. So I was able to get hang up that now finally and alpha not and alpha 1 and finally the buffer intensity. We looked at alpha not alpha 1 and now we are trying to get buffer intensity. So I am just trying to calculate get the formula. So I already plugged in the relevant data here, so we have graph here and first try to analyze the data.

So alpha not obviously at the lowest PH is going to be one. What does that mean? All the particular total acid or base is going to be in the protonate form, so that is what we have there and alpha 1. The highest Ph fourteen, we know that alpha 1 is a - by HA + A -. What does that mean now? Alpha one is equal to 1 that means that all the acid or the base present only in the deprotonate form that is what you see here. As PH is increasing alpha not is decreasing and as PH is increasing you see that alpha one is decreasing.

So based on that we calculate the buffer intensity here and so obviously it is varying and here we have a graph where we have the Y axis is buffer intensity and on the X axis we have the PH. So graph showing from PH 2 to PH 12. So what do you see here? We see that PKA is 4.75 and from our equation we know that let us have a quick look at our equation. What do we know? It should be high at alpha not is equal to alpha 1 which is this third aspect alpha not is equal to alpha 1, means PH is when PH = PKA.

You are going to have high buffering intensity. So let us see if you are able to observe that here. So you know PKA = 4.75. So let us say I am assuming somewhere here and you see that the buffer intensity is maximum at you know high. I would not say maximum is high at when the PH = PKA. Again why is that at this particular point when PH = PKA.

You observe that alpha not and alpha one are the same or you have the same concentration of HA and A - or the CH 3 COH and CH three and COO -. So let us say when acid is added, so let us just cancel this case. So you have equal qualities of CH 3 COOH and CH 3 COO - and when you add an acid, what does that mean? You are putting in H +, so your estate ion CH 3 COO - can take the proton and go into the deep protonate form.

But now there is no change in Ph, but if you add a base. Let us say you are putting OH -, the acid which is CH 3 COOH can release its proton and that can take care of the base that you are putting it in the system. So again we are going to look at it later. So that is the explanation here, that is what is happening here. But the other key aspect is to notice that low PH or at high PH we again see an increase in buffer intensity. Why is that so? What does this mean?

Ph we know is - log H + and what does this mean? Now for any change in H + to occur you need to put in a lot of acid or you know lot of H + to be able to change the PH or similarly add full amount of base, may be able to change the PH. Why is that? Keep in mind PH means logarithm scale. So here at this particular extreme you need to add a lot of acid or lot of base to be able to change your PH.

So again the same case here higher PH when it is around twelve or higher than 12 it is going to go up like this until 14. So again its logarithm scale, like that particular point PH is 13. Let us say OH - Concentration is very high, so you need to add lot of H + or lot of OH - to be able to make any further change in the OH - concentration or the PH. So this is what we looked at so let us just try to understand that once again you know in our system here.

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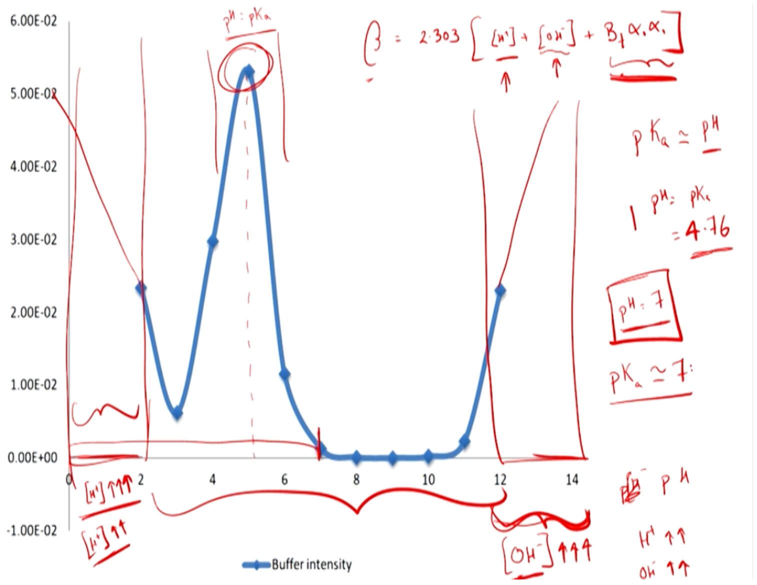

I believe I have graph here, so this is the graph here. So again this is the point where let us find out the buffer intensity equation here which I believe was equal to 2.303 into the concentration of H + + the concentration of OH - +. B total into alpha not into alpha 1, so this particular region.

What is this relevant to it is relevant to this particular set of variables here where the PH = PKA that is when you have the maximum buffer capacity or intensity part, if you go to the other extreme. Let us say in this particular region you again see that the buffer intensity is going to be maximum. Why is that that? It is because of that particular variable where you see that H + concentration is high.

So in this particular case or the regions you know that H + concentration is very high already. So to be able to make any change in further in H +, you should still need to add lot of H +. So that is why you see that the buffer intensity is relatively high in this region. But obviously it is in the extreme regions of 0 to 2 or so. PH at same case here but 12 to 14, 11 to 14 let us see again the buffer intensity is going to be high in this region.

Why that is because of this variable OH -. Concentration is high in this particular region, the OH - concentration is very high and the PH is between 12 o 14 or 11 to 14. So to be able to make it further change in your PH, what do you need to do? You need to add a lot of H + or a lot of OH-. So that means that the system is a good buffer in this particular region.

But obviously rarely you would try to have system that is well buffered in either in low PH or high PH ranges. You usually do look at ranges from 2 to 12. So what is the key here? You need to be able to choose a buffer whose PKA is almost same as the PH where you want to have a good buffer. So for example in which region will this particular system act as a good buffer in the usual regions of PH.

Only when PH = PKA which is in this case acetic acid. So this case was 4.75 or 4.76. So that is what you see here, but let us say if I want good buffering around PH7. Let us say I wanted good buffering at PH7 would this work? So let us look at where PH7 is here? So you see that the buffer intensity is very less at this particular PH7. So acetic acid is obviously not a good choice when you are going to have a system that is well buffered PH7.

So what do you need to do we need to obviously look for acid base system whose PK will be nearer or equivalent to 7 or near 7, so that is the take home message here again. So we need to choose your buffer based on where the PKA value is so let us also look at the multi protic acid. Let us choose the carbonate system because we have looked at that in great detail and once we have done with that we can wrap up todays session.

So let us see where we are, we will go back to excel again and here I have the relevant aspect carbonate system. So what do we have here? We have alpha not, alpha 1, alpha 2 because it is multi protic or diprotic that is why we have three ionization fraction. Again same case as earlier H + PH and B total that is what we already had earlier and buffer intensity. Now the formula is going to be relatively different. Let me try to write that down here for a multi protic system.

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$$\beta = 2.303\left[[H^+] + [OH^-] + B_t\underbrace{\left(\alpha_0\alpha_1 + \boxed{4\alpha_0\alpha_2} + \alpha_1\alpha_2\right)}\right]$$

1) $\alpha_0 = \alpha_1 = 0.5$

$[H_2A] = [HA^-] \Rightarrow pH = pK_{a_1}$

2) $\alpha_1 = \alpha_2 = 0.5$

$[HA^-] = [A^{2-}] \Rightarrow pH = pK_{a_2}$

$\alpha_0 = [H_2A]/A_t$

$\alpha_1 = [HA^-]/A_t$

$\alpha_2 = [A^{2-}]/A_t$

$A_t = [H_2A] + [HA^-] + [A^{2-}]$

Diprotic system let me try to 2.303 into concentration of H + + concentration OH -. Same case as earlier + H B total into alpha not alpha 1 + 4 times of alpha not alpha 2 + alpha 1 alpha 2. So again let us try to identify or understand this particular system. So we have already talked about these two variables where PH is in the extreme. So we are concerned with this particular system.

So again we know that alpha not alpha 1 and alpha 2 are the ionization fractions which give you relative concentration of H 2 A HA - and A 2 -. There are relevant concentrations with respect to the total acid here. What is the total acid? In this case you know which is B total which different nomenclature here. But that is fine, so that is equal to as you know H 2 A + H A - + A two - anyway.

It is giving you an idea about which particular form predominates. So again keep this in mind when we look at this data and without background, we can eliminate this variable. Why is that, whenever H 2 A is at higher concentration H 2 - will be at remarkably at low concentration? So again H try to think of this variable 4 alpha not into alpha 2 alpha not gives us an idea about the fraction present as the most protonate form.

Alpha two gives us an idea about the most deprotonate form which is H A 2 - and also the other case alpha not refers to H 2 A. So when 1 is high other one would be almost 0 and vice versa. So we can more or less end up neglecting this particular set of variables here. So what are we left with? We are left with B total into alpha not alpha 1 and alpha 1 alpha 2. So again this is the same case as earlier.

So you will see maximum buffering intensity at two cases and what are they when alpha not equal to alpha 1 = 0.5 or what does that mean when H 2 A concentration is equal to HA - concentration. So that is one case and what is the second case, when alpha 1 = alpha 2 = 0.5 which more or less translates to the concentration HA - being equal to the concentration of the most deprotonate form.

So this is what we have, so when does this occur? This occurs obviously when the PH = first PKA 1 and this occurs when PH = PKA 2. So let us try to understand this with respect to the graph. So where do we have that here? So PKA1 is 6.3 PKA 2 is 10.3, I think they are approximate value is for the carbonate system. So you can let us go with that and I have plugged in the relevant formula.

So let us try to go through, now we are able to calculate alpha not alpha 1 and alpha 2 as you can see with the increasing PH or you know increase your lessening concentration of H +. What do you see? You see that alpha not decreases and you see that alpha 1 increases to certain point till time. But you know point respect to PH and again decrease alpha 2 keeps on increasing to its maximum of Alpha 1.

So again let us calculate the buffer intensity here and now we have a graph and let us try to understand and look at this graph. So X axis is the PH, Y axis is the buffer intensity. So what do we see here at the extremes PH less than 3. We know that again system is well buffered. Why is that? Because the H + concentration is high and same case PH greater than 12. This is going to go up again, so let use this graph we came up with, I think I have that in my particular slides.

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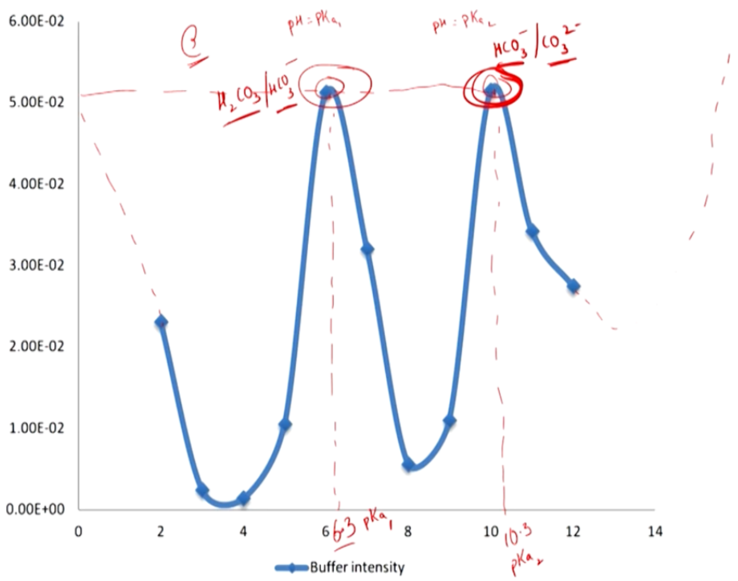

Let us go back to the slide. So this is again going up like this and this two will again go up like this till 14. So again what are the cases we are going to look at where PH = PKA 1 and also when PH = PKA 2. So obviously we see that buffer intensity is going to be maximum at those cases. But we see that these are the two relevant points here and when I look at where that goes to I see that that is more or less should be 6.3 which is PKA.

One of your carbonate system and here if here if you look at that it should be 10.3 which is PKA 2 carbonate system. So more or less the take home message is that the diprotic acid act like as if you have two different buffers in this system. So one is with respect to H 2 CO3 and H CO3 - and the other is with respect to H CO 3 and H CO 3 2-.

So in this particular you know, at this particular PH which forms predominantes you know that H 2 CO 3 and H CO 3 - predominates. So this will act as the acid when required. This will act as the base when required and at this point, what are the relevant Conjugate species?

There is going to be H CO 3 - and CO 2 -. So at this particular point CO 3 - will add as the act as the acid if required and CO 3 2 - will act as the base of required. So thus you will have high buffer intensity which you see here when the PH = the PKA. So I guess with that we will end up today's session and we will continue this forward in the next session, thank you.