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

Module No # 04
Lecture No # 16
Ionization Fractions

Hello everyone welcome back to our session with respect to acid and basis in the context of our chemical process so quickly review what we have been discuss in the last session or lecture session anyway and then move on to the relevant application so I guess right.

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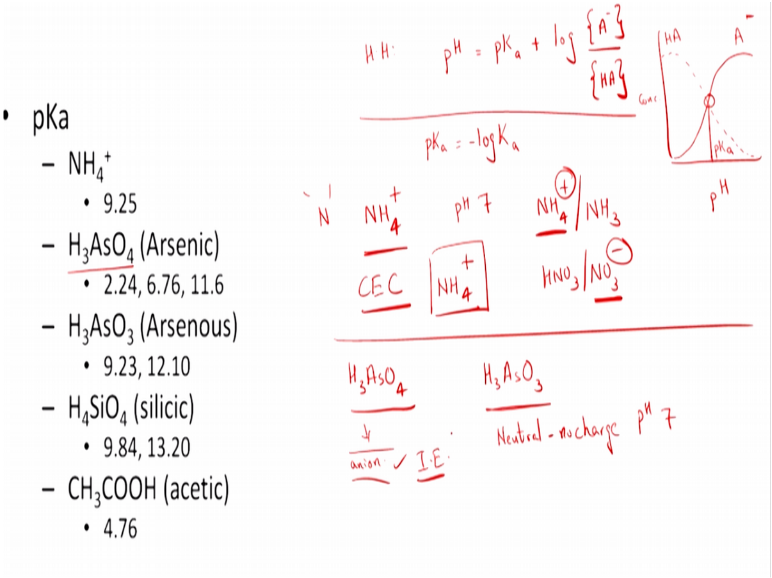

- pKa
  - NH_4^+
    - 9.25
  - H_3AsO_4 (Arsenic)
    - 2.24, 6.76, 11.6
  - H_3AsO_3 (Arsenous)
    - 9.23, 12.10
  - H_4SiO_4 (silicic)
    - 9.84, 13.20
  - CH_3COOH (acetic)
    - 4.76

I believe we looked at primarily deriving the Henderson Haselbach equation and that gives us an idea of the relationship between PH and PKA and the relative concentrations of the deprotonated and protonated form right.

So looking at those or looking at that equation we can get the relevant graphs PH and concentration here and you see that the as the protonated form decreases in concentration that deprotonated form is going increase in concentration pardon me this is a negative symbol here and this where the concentration or both of them are equal that is going to be the PKA value right. And what is PKA?

PKA is the negative logarithm of the acid dissociation constant right and this is what we discussed and I believe we also discussed examples with respect to application of nitrogen and we saw that the former would be better of if we applies nitrogen in the form of ammonia why is that because at neutral PH right NH4 will stay as H4+ not as an NH3 but while HNO3 and NO3 – HNO3 would stay as NO3 – that PH7 and NHO would stay as an NH4+ right PH7.

So this is an cation this is anion and because the soil as cation exchange capacity or it can dissolve cation the former is better of applying nitrogen in the form of ammonia now right or ammonium. So and then we also looked at the example of removal of arsenic so there are two forms H3ASO4 that is here and H3AS O3 and this is more oxidized form obviously right.

And we saw that this particular form is neutral or has no charge at natural PH or around PH 7 but this more or less believe in deprotonated forms right and so this as or this in the form of anion and this can be removed as by the ionic exchange process right this is what we were discussing earlier. So let us move on to the other sets of examples that we have here so believe we are also going to look at silisic acid.

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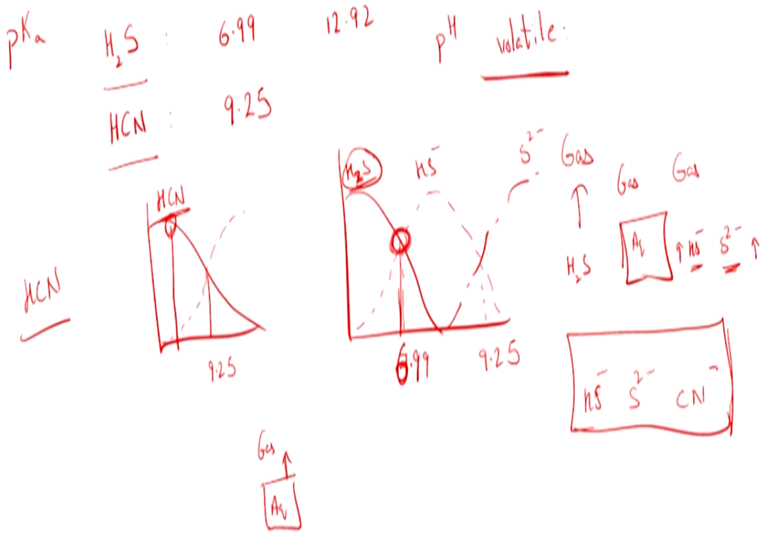

If somebody would want to remove silica let us say from your water let us say if it is an issue and you know that the PKA 1 I am talking about H4SIO4 here and if I want to remove silica the ionic change let us say electro-dialysis and PKA1 is 9.84 PKA2 is 13.2 right. So let us look at that again and what is this mean this is HOSO4 and the next deprotonated and again the next deprotonated form that is label then H4SIO4 H3SIO4 – H2SIO4 2- and the PKS values are 9.8 and 13.2.

So at PH7 everything is going to stay as H4SIO4 which does not have a charge and thus it is obviously cannot be removed by ionic change process at the natural PH right. So let us see the other examples so CS3COOH we are going to look at that in greater detail later but in general the issue is that acetic acid will be produced in anaerobic digesters now right. And the issue that as you see the PKA is not relatively low it is around 4.76 right.

So that means acetic acid is not a strong acid yes but the key here is that when acetic acid is produced in your anaerobic digester the PH can fall to let u say anaerobic digestion process so that is the reason why we need to look at acetic acid in greater detail even though it is not a strong acid as you see it is PKS is 4.76 right.

So anyway we will come back to this again let us look at the other example I guess one example that we have here is respect to toxic gases hydrogen sulphide and hydrogen cyanide and in general with respect to gases we want to see at which particular PH would there be Volatile and which particular PH would their not be I guess Volatile right as you see here with respect to H2S let us say this is H2S HS – S2- this is around 7 or 6.99 and this is 9.25.

And what do we see here so at PH7 right there is considerable amount of H2S present or the neutral molecule let us say or the protonated form which is neutral and so it can be volatile or be stripped out of your solution now what is this mean now? so let us say if this is the aqueous phase and this is the gaseous phase if it is in the form of HS – or S2 – you know being negatively charged and water being polar compound that will be relatively difficult for this two compounds to escape into the gaseous phase not escape pardon me change phase into gaseous phase.

But if it is in the form of H2S which it can be around PH7 as you see here right so it can change phase into gaseous phase. So same case with hydrogen cyanide right and so what do we have here again this are not two scales so please keep this in mind the PKA is 9.25 this is for hydrogen cyanide right and PH7 somewhere here so you see almost all of it will be protonated form with no charge so this can change phase from the aqueous phase to the gaseous phase because there is charge on it right.

Anyway charge compounds like HS – S2- and CN- you know and water being polar and they would want to stay in the aqueous phase anyway here we see some application of where PH would effect your natural or even engineering systems so we are going to look what do we say the mono parotic diprotic acid and tri-protric acid and what they are about in greater detail now.

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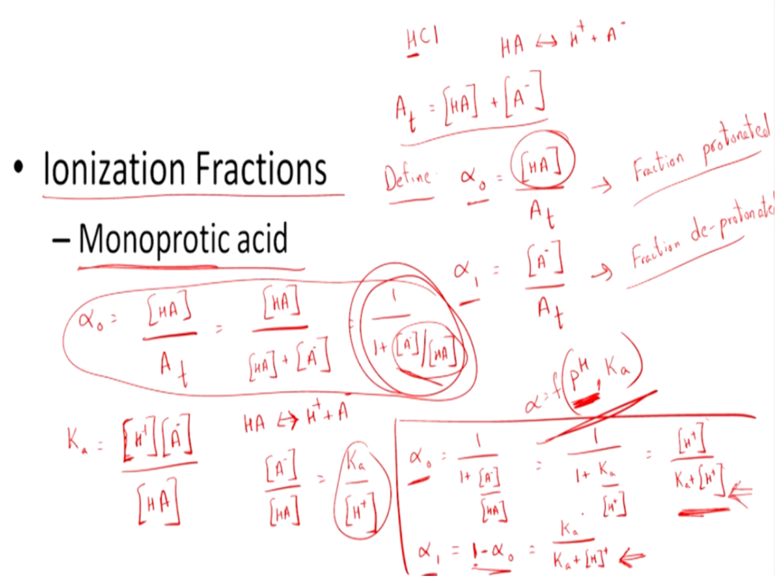

- Ionization Fractions
  - Monoprotic acid

HCl

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

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

Define $\alpha_0 = \frac{[HA]}{A_t}$ → Fraction protonated

$\alpha_1 = \frac{[A^-]}{A_t}$ → Fraction de-protonated

$\alpha_0 = \frac{[HA]}{A_t} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + [A^-]/[HA]}$

$\alpha = f(pH, K_a)$

$K_a = \frac{[H^+][A^-]}{[HA]}$ $\quad HA \leftrightarrow H^+ + A$ $\quad \frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$

$\alpha_0 = \frac{1}{1 + \frac{[A^-]}{[HA]}} = \frac{1}{1 + \frac{K_a}{[H^+]}} = \frac{[H^+]}{K_a + [H^+]}$ ⇐

$\alpha_1 = 1 - \alpha_0 = \frac{K_a}{K_a + [H^+]}$ ⇐

So let us move on why waste time please so here we are going to come with new term called ionization fractions. So let us look at or let us define what they are so in that context we need to look at monoprotic acid and example is HCL I guess right it is only single proton to donate this monoprotic acid so the usual example we are looking at is HA dissociating into H+ and A –.

And so let us say if I define total acid as being = HA + A – right I will now define ionization fraction such that you will have two ionization fraction for monoprotic acid alpha naught that is going to be equal to the protonated form concentration of protonated form by the total acid and second ionization fraction alpha one is going to be concentration of deprotonated form by the total acid concentration right and this is how we define the ionization fractions.

And do we use them I guess so let us say if we know the PH of your solutions let us say right and you want to calculate what is the fraction of the deprotonated form or protonated form of your own or various purposes let us say rather than going to through the calculations just looking at the ionization fraction for that particular chemical or that particular acid or base would give an idea about what is the fraction of your acid or total acid pardon me that is going to be in the protonated form or it is going to be in the protonated form right.

So let us look at how to calculate these aspects I guess right so what do we have here we have alpha naught = concentration of HA / A total and that is = concentration of HA so again if it not yet clear what is alpha not give an idea about the fraction that present as fraction that is present as the protonated form right that is what we see here in the numerator protonated form right and what does this give you as give an idea about fraction that has deprotonated let us say right.

That is what we get an idea about so anyway moving on so we have alpha naught HA / 8 total and A total you know is the total acid it is HA + A – so divided by HA let us say 1 / 1 + A – by HA right so I guess we want to represented in terms of what now PH because we usually look at what is it how is the ionization fraction changing as a function of PH and some other constant the constant usually that we use in your acid and base is obviously the acid dissociation constant so let us look at the acid dissociation constant for a second here.

So KA of this reaction and let me rewrite the reaction here HA goes to H+ A – or dissociates 2 I guess right and KA is activity or concentration let us go with the concentration here in general as you know it is going to activity but approximating activity by concentration here / HA and the fraction that I am looking at is A – HA so that particular fraction deprotonated form by HA is going to be equal to KA / H+ right and this is what I have.

And so I am looking at this particular equation here right and I am going substitute this variable A – by HA KA / H+. So more or less Alpha naught which was earlier 1 + A - / HA concentration of A- in HA obviously is going to be equal to 1 / 1 + KA / H+ and that is going to be equal to concentration of H+ / KA + H+. So as you now see alpha naught to the function of PH or H+ and a constant KA. So for a given compound or monprotic acid you can calculate alpha naught.

So similarly alpha 1 what is that going to be it is nothing that look at the definition that the way define it is going to 1 – alpha naught right and that is going to end up being KA / KA + H+ I mean we can do the derivation again but obviously we do the alpha naught + alpha 1 fraction to be equal to the sum of the fraction to = 1 so we can always calculate alpha 1 / 1 – alpha naught that is equal to KA + H +.

So keep in mind that there are two aspects here so it is like denominator here going to be the same right that is obvious and the numerator 2 is H+ here in case and KA in this case right.

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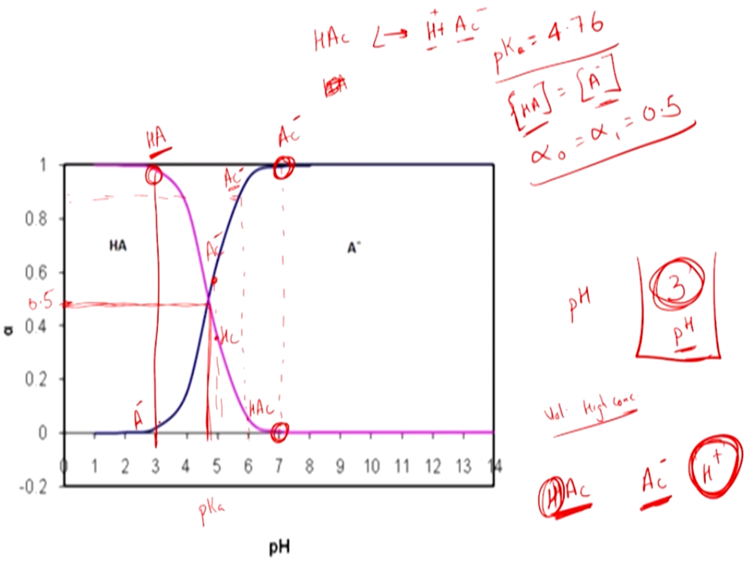

So I believe let us look at one example here and here I have figure and believe this is for acetic acid so I think the PKA is around 4.76 so here on the X axis you have the ionization fraction relevant ionization fractions so HA will be given by HA naught and A – alpha 1 so looks like this figure is to scale so let us use this to understand what it is that we have talked in the past right.

So ionization fractions and the Y axis and PH on the X axis so as you see at PH 4.7 which is PKA value right what do we see there we see that the concentration of both the fractions right so here the example for the acetic acid dissociating into H+ and a state ion though they are representing H / HA right anyhow we know that the PKA value for estate acetic acid is 4.7 or 2.76 I guess right.

And at PKA value you know that activity or concentration of your protonated form should be equal to the activity of your protonated form so that is what you get from you Henderson Haselbach equation or even when you look at the figure right and when I look at this figure what do I see at the PKA value obviously the ionization factor is going to be 0.5 right because when we say HA = A – that is only feasible when there is alpha naught = alpha 1 = 0.5 right so that is what you understand here.

So because this is to scale let us see let us try to look at some of the concepts we looked at earlier so PH7 let us say if I am going to look at PH7 and if there is any acetic acid added at PH9, 8 or 7 as you see it is dissociate into H+ KC – and the deprotonated form AC – is going to predominate and we have (()) (15:35) of your actual acetic acid HAC or the deprotonate form.

But as you move towards the PKA value let us say we will have a look at PH6 and what do you see I guess now the fraction changes I guess it is going to be 90% let us say around 90 I guess we can calculate that from the Henderson Haselbach equation again right till AC – is going to predominate and now though you are going to have some form of the acetic acid in equilibrium a state ion.

And as you move further towards your PKA at PH5 you will see is that the fraction changes factor of HAC here yes and now the trend is going to reverse as you decrease the PH beyond the PKA and obviously at PH3 what do we see here that almost all of your acid is present in deprotonated pardon me the protonated form and let you to none of it is present as the deprotonated form so what is that mean if I had acetic acid to a solution at PH7.

You know assume that there I beaker here and the PH is 7 not 7 pardon me 3 here they current what do we say concentration of your H+ if I look and the PH is 3 of your solution now and I add some acetic acid relatively low concentration low volume that let us say higher concentration let us say. It might change the PH little to none why is that because ah PH3 you see that almost all of it stay as or acetic acid and thus it would not release the proton right.

Where in literal or if minute fraction of will stay as AC – or will be in the form of AC – and thus little H+ will be released so there is little to be change in PH at PH3 right.

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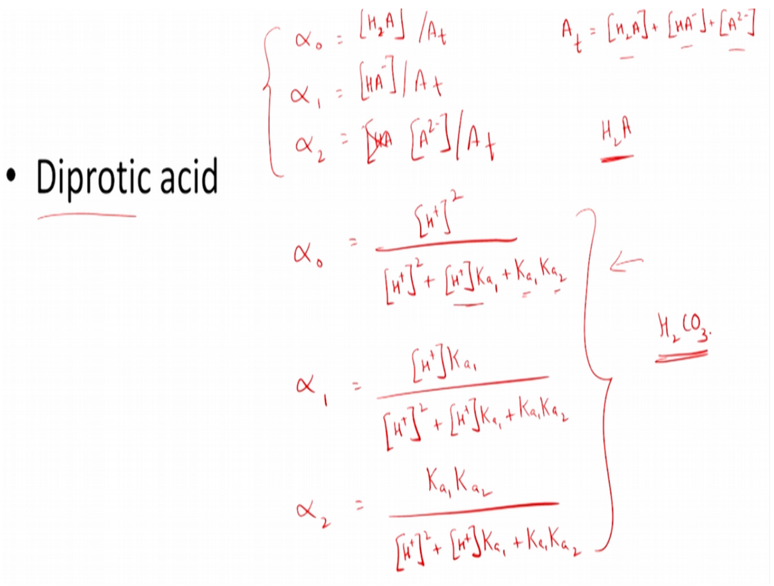

- Diprotic acid

$$\alpha_0 = [H_2A]/A_t$$

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

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

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

H_2A

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

$$\alpha_1 = \frac{[H^+]K_{a_1}}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

$$\alpha_2 = \frac{K_{a_1}K_{a_2}}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

H_2CO_3.

So that is what we see here so let us move on and i guess we are going to move on to diprotic acid in the same case we can come across I mean develop ionization fractions. So for diprotic acid now we are going to have three ionization fraction let us see how what they are I guess right.

So the first one will be diprotic acid and I am going to say it is going to say H2A the protonated form by the total acid and what is the total acid in this case obviously it is going to be equal to sum of H2A + concentration of HA - + concentrating of A2 – and in this case HA - / A total and again we can have HA pardon me it is going to be A2- / A total right and this is what we have diprotic acid we are obviously going to have 3 fraction H2A HA - A2- and thus we are going to have three ionization fraction right.

And we can go through the derivation and more or less it is relatively intuitive let us see if you can let that right here so alpha naught is going to be equal to first I am going to write the denominator here. So it is going to be equal to H+ square + concentration of H+ into by the first acid dissociation constant + the part of KA 1 and KA2 right KA1 an dKA2 acid dissociation constants for your diprotic acid and the numerator is then going to be H+ square and similarly though alpha 1 is going to be H+ into KA 1 by the same denominator which is H+ square + H+ into KA1 + KA1 KA2.

Please notice the similarity with respect to the equation or the fraction that we derived for the monoprotic acid with respect to the denominator and how you can approximate your particular numerator 2 right. Anyway we can derive this but this I a straight forward equations here so KA1 / KA2 / H+ square is H + into KA 1 + KA1 KA2 right so these are the three ionization fraction that we have and examples of diprotic acid H2CO3 carbonic acid which is widely present in nature and we will see and later on anyway.

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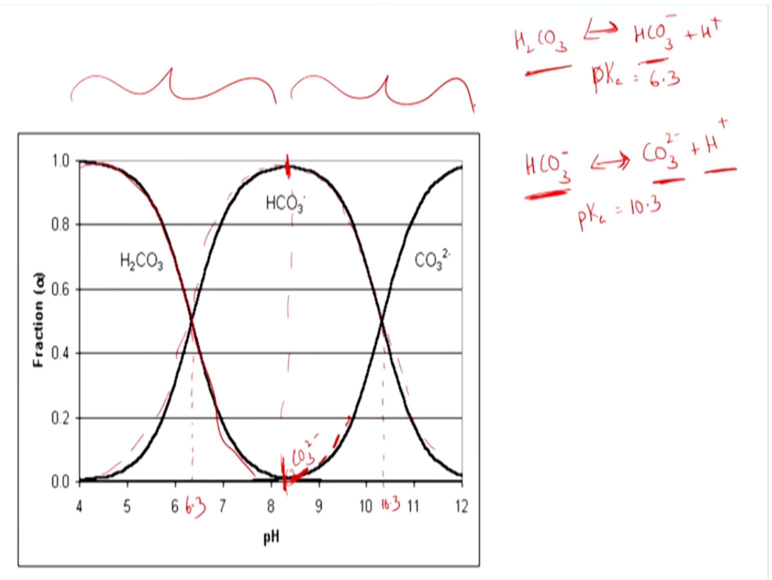

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$pK_a = 6.3$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

$pK_a = 10.3$

So I believe here I have the ionization fraction but that and believe the PKA values are going to be 6.3 and 10.3 right. So here you see ionization fraction on the Y axis and PH 1 the X axis so as H2CO3 initially right here there is starting the graph on PH4 so make sense because PH4 is going to stay only as H2CO3 or equilibrium with carbon di oxide obviously if there is gaseous phase.

So initially it is present as H2CO3 as I keep approaching the PKA H2CO3 start dissociating and forming HCO3 – that is what you see here let us say if I am PH5 what do I see there so most of it still as H203 but now I see that there is some release of H+ and thus formation of HCO3 – right and this is the graph for HCO3 – obviously right and as I keep moving towards the PKA I see that the ionization fact decreases or the concentration of H2OC3 decreases while the concentration of HCO3 – increases and once I am passed PKA or at PH7.

So once I am at PH7 what do is see here I see that most of it now in the form of SCO3- and fraction of it may be 0.15 or so I guess HCO3 is in the form of H2CO3 right and so as I move further at around PH what is it now 8.3 may be 8.3 looks like everything is going to be HCO3 – at around 8.3 and then as I move further away from or increase the PH and move to towards PKA 2 I am now going to have so initially H2CO3 was dissociating into HCO3 – and H+ right that is what we see here I mean pardon me here let me high light that again please.

So initially H2CO3 was dissociating into HCO3 – and H+ and that is what you see here as H2CO3 decreases right at the same time HCO3 – is increases and here at a particular point you have no H2CO3 at all I guess at 8.3 and here at 8.3 everything in the form of HCO3 – right and then as I keep what is that KA or PKA for this particular equation it is 6.3 and that is what we see here 6.3 and then you have the other acid dissociation HC3 – dissociation it is going to be = CO3 – and H+ dissociation and what is PKS for this case that is equal to 10.3 and that is what you see here.

So 10.3 and 6.3 so as you now see everything is SCO3 – 8.3 PH and there is no more H2CO3 as I keep increasing the PH now HCO3 – further dissociating in CO3 2 – and H + here and that is what you see here as HCO3 – is decreasing you now start having the deprotonated form here and that is what you see here right which is CO3 2- form right. So now again this repeat itself this as this particular (()) (23:56) graph because diprotic again repeat itself here right.

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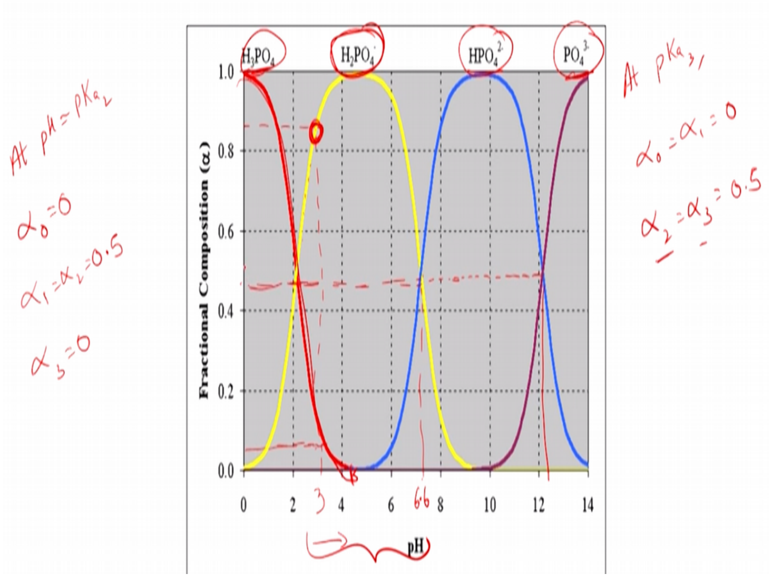

So this is what we see here anyway let us move on now we are going to have a tripotic acid is an example I guess is phosphoric acid and I believe we are going to look at that in greater detail in the next slide so here what are dissociation reaction H3A can go to H+ and H2A – and so on and you will have PKA 1 you will have PKA 2 and PKA 3 and we let me try them down so that people who have some trouble understanding are it is clear for them I guess right okay.

So H3A is going to dissociate into H+ and H2A – and again this H2A – going to further dissociate into H+ and HA2- and HA2- is again going to dissociate into H+ and 3- so again because we have what do we say 3 protons we are going to have four ionization fractions alpha naught alpha 1, alpha2 and alpha 3 and obviously each one would be equal to what now the concentration this will be H3A by A total.

And what is A total in this stage please it is going to be equal to total acid in all its form + H2A - + HA2 - + A3- right that is what we have here and the second ionization factor is going to be ratio of H2A – concentration by A total and the other one is going to HA 2 – concentration / A total the other one is going to be HA3 – concentration pardon me not A3 – HA3 – A3 – / A total and now again let us try to first approximate this equation now I am going to have H+ cube + H + square into KA1 + H+ into KA1 KA2 + KA1 KA2 and KA3 and this is what we have and the numerator is going to be H+ cube.

And same here alpha 1 is going to be H+ square into KA1 / same denominator as above alpha 2 into KA 1 KA2 by the same denominator and what is alpha 3 is going to be it is going to be equal to KA1 KA2 KA3 / the same denominator as above so again what will these fractions give an idea about let us look at that I guess for example we are going to look at is phosphoric acid H3 PO4 I guess right and it has 4 species that exist at equilibrium H32O4 the most protonated all the way to PO43- by the most protonated form right.

And so in general it has 3PKA value one is around 2.3 you can correct me later and other is I think around 6.3 or 6.6 I guess or 7.2 I am not sure let me go with 6.6 for now so as an approximate value and this is going to be 12.1 guess right so 3 PKA values. So again let understand this figure and will be done for this session so initially at 0 everything is going to stay as H3PO4 right so at PH1 let us say where will be PH1 now.

So at PH1 let us say if I had H3 PO2 PH3PO4 to water so I have beaker and a solution at PH1 and I had H3PO4 right there will be little 2 no change in PH why is that most of it going to stay in the protonated form as H32O4 and little to none of it will dissociate into H2PO4 – and H+ right so no H+ is being listen and little H+.

So as in keep increasing the PH around 2.3 I guess which is the PKA you see that alpha 1 or alpha naught = alpha 1 right and that is what you see here and that is going to be equal to .5 there and obviously alpha 2 = alpha 3 = 0 at this stage PKA 1 at PKA 1 right. So if I keep moving further though and let me erase this and now let us say if I keep moving further down and this particular range and what do I see and now see that H3PO4 will dissociate into H3PO4 – and H+.

And as now you see that let us say at around PH3 right what do I see any acid that added to the solution will dissociate into H2PO4 – most of it around what do we say 90 % let us 0.9 or 0.85 and very little of it will be present as the protonated form which is H3PO4 right and again if I move further down the line to the PKA 2 value what is the 7 or 6.6 something like that and what is the case their at PH = PKA2 what do I see I guess I see that alpha naught or H3PO4 there is no H3PO4 represent at 6.6 right there is H3PO4 is done here about 4.3 hertz.

If alpha naught is going to be 0 and alpha 1 = alpha 2 = 0.5 right and alpha 3 = 0 in the same case as we move further to the PKA at PKA 3 what do we see it going to be present as a HPO4 2- and PO4 3 – so alpha naught = alpha 1 = 0 and alpha 2 and alpha 3 are the concentration of HPO4 2- and PO4 3 – are going to be the same that is given by alpha 2 = alpha 3 = 0.5 and that is what you would see here in this graph right so this is at the 0.5 let us say right.

And so the ionization fraction here will give you an idea about the fraction of that particular species which were talking about in the context I guess so in today’s class we have discussed mostly about ionization fractions right and I guess at this stage you should be able to once you look at the PH and the alpha naught values to be able to figure out which acid you want to use let us say if you want to bring down the PH or the fraction of that particular to protonated or deprotonated form at that particular PH where particular acid right. So I guess with that will end today’s session and thank you