Environment Engineering: Chemical Processes
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Module No # 03
Lecture No # 15
Acid Dissociation Constant, Strength of Acid

Hello everyone welcome back to the latest lecture session so I believe we have been discussing acids and basis right and we also discussed kinetics in relation to acids and basis and what did we see we looked at the characteristic time we look at with respect to acid systems and then looked at the usual half times.

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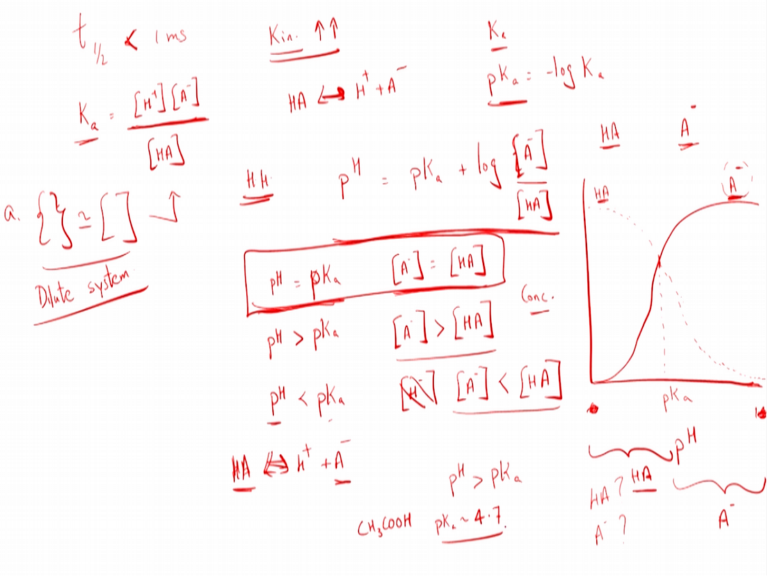

And believe the half times we said around or less than 1 milli second let us say right and thus invention that he kinetics of these acids and basis reaction are pretty fast and thus what do we what can we from this particular information we see that most of our systems the kinetics is so fast that we end up reaching equilibrium by the time we look at sample or such or we analyze the sample

So we are going to be looking at only equilibrium with respect to acid and base systems right and then we moved to discussing the relevant aspects so the first major aspect is going to be acid dissociation constant so for HA dissociating into H+ and A – it is going to be activity or here in this case I am going to switch over to concentration by HA and introduce a new term to as dissociation constant K and then PKA = - log KA and these are constant the specific acid right.

So we are going to go into that in greater detail and then we started looking at we derived the Henderson Haselbach equation and what is that? It gives us relationship between PH PKA and the relative concentration of the deprotonated form and the pertained form. So keep in mind that whenever we talk about equilibrium constant we need to express them in terms of activities but if we assume that the activity as relatively equal to concentration.

So that is what we have and this obviously will work out only in dilute systems I guess and this is something we already discussed in our equilibrium fundamental class right. So we are trying to understand this system better so in that context what have you looked at so we looked PH = PKA we consider PH is greater than PKA and we consider PH is less than PKA and the three cases more or less relate to A – B being to HA in concentration right and then A – A greater than HA in concentration yes and then obviously A – being less than HA concentration.

So what is this mean I guess and for this particular case so for any concentration for this obviously is independent upon independent of the model concentration of your acid that you are have initially let us say right. So let us try to drag this down in terms of a graph and then look at how to interpret the graph. So this is something that important again or remarkably important so we have PH and we have concentration here right and I want to be able to plot HA and A – on this graph now right.

And so keep in mind that this is our equation this is the PH of the solution or water or 0 to 14 let us say or in any other scale this is the concentration of your particular species and the species are HA and A- and take a moment and try to think of how the graph is going to be would be linear right or what shape it would take now right and if they are going to intercept it which point of the intersect and so on. And so first obviously the fundamental aspect is going to be depend upon PH = PKA + log A- HA.

So obviously it is always a ratio so as you see HA everything that PH 0 is going to stay as HA so as you increase the PH it can dissociate further and HA concentration keeps decreasing right and that is what you see here as you keep increasing the PH right the HA concentration keeps decreasing and let me try to get the better figure here again is the key is that as the PH increases HA will dissociate H + and A – it is equilibrium it is end balance here it depends upon the PH of the particular system and obviously the PKS we are going to look at that I guess right.

So it going to decrease and inflation point let us say and then again take this out and inflation point let us say and then again tape out and this let us say graph for HA right at the same time what is going to be behavior of your conjugate base or A – right so as HA or when mole of it dissociates of your going to have formation of 1 mole of your conjugate base. So the same case we are going to have this particular system okay again pardon my poor drawing skills so this is going to be A9.

So what is this mean so as the concentration of HA in your solution is decreasing the concentration of your A – is going to decrease right and obviously there is going to be a point at which both of them are going to be same right and again A – when as A – increases HA concentration decreases right said the highest PH what is going to or what do we notice that everything is going to be or all the acid is going to be of or it is going to dissociate right.

All the acid that we had initially is going to dissociate or it is going to be only in the form of A- and it lower PH VC that it is going to predominate as HA so we just use generic terms over PH higher PH and so on but we need to look at the reference right and what is the difference here we look at the point of intersection or where we have equal concentrations or as we just looked at it earlier and that case is PH = PKA and in that case we notice that A- = concentration of HA so this is the influence here PKA.

So let us try to understand this figure so when PH is greater than PKA right so when PH is greater than PKA so in this particular region let us say which form is predominating now is it the acid HA or the base so as you see the form that is predominating here from this graph as you see the conjugate base or A –or the deprotonated form so when PH is greater than PKA the deprotonated form predominates.

But what about it in this particular zone let us say when PH is less than PKA so what form predominates now it is going to the protonated form PHA or what does it mean now in practical so let us say if I take a particular acid let us take the example of acetic acid CH3COOH right and

I know PH PKA is around 4.7 I believe so do not take my word on that let us go with that particular value for now right.

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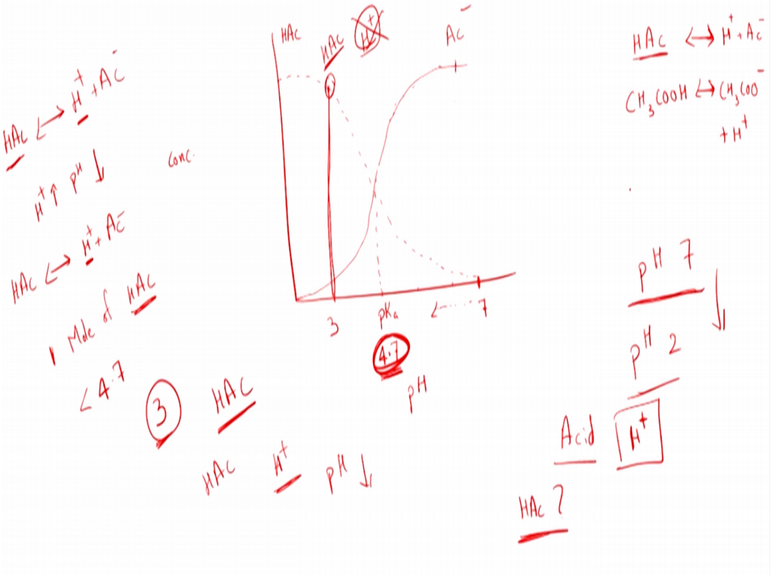

So take this example let us draw a figure and try to look at that particular case so what do we have here we have PH and we have concentration and so acetic acid I am going to what we say use the form of HAC and going to use that represent acetic acid so that can dissociate into H+ and is state on right this is what you can have so I want to draw this figure here and try to look at the conclusion you do in the previous slide right.

So here I am going to have the generic figure out here by this is HAC and obviously this is going to be AC – or state ion and this the value of what which both HAC and AC – equal concentration that is going to be the PK value and the PK as we just mention was 4.7 believe right so this is what we have so now think of this.

Now let us I say if I want to or have a solution at PH7 and I want to let us say get to PH 2 for example right I need to add and acid that we are aware of or I need a source of H+ that is what I mean right more or less if I want to decrease the PH from 7 to 2 I need the source of H+ so let us see if the choice of acetic acid is that a good choice can I use acetic acid to do so what happens to acetic acid as I what do I dump it at PH7 let us say or add acetic acid to solution at PH7.

So PH 7 is somewhere 4.7 let us say 5.7, 6.7 let us say PH around 7 here let us say right the PH is around 7 here let us say so PH 7 we see that HAC that add to your solution here at PH7 will dissociate into H+ and AC – or at PH7 estate is going to donate the proton right but as you keep adding H+ right what is going to happen to the PH the PH is going to decrease so from here let us say example this is PH7 I am moving to my left now right.

So what is that mean now as I keep decreasing the PH the ability of the acetic acid to donate the proton cubes decreasing and that is what you see here right so as you come here for 1 mole of your HAC you see that lesser number of moles of protons are going to be given out right so that is that is what you see here at this particular point in space and this is for 4.7 so below 4.7 or let us say if I need to go to 2 or let us say PH3 and let us say this is PH3 right.

And if it is PH3 I had acetic acid to particular solution will be able to bring down the PH not in the usual cases unless you dumb a lot of it even you dump a lot of probably not why is that because any HAC that you add at PH3 as you see that PH3 is less than the PKA right and what is that mean it means that HAC would prefer to stay as HAC and will no donate the proton here right it will not donate the proton is not dissociating right so thus you have no more of H+ right and thus the PH would not drop further so that is what we need to understand here.

Say again same case here right so when the PH is greater than PKA the acid and dissociate and act as a source of your protons right but then PH is less than PKA what do we see the predominant form is the pertained form or you will have a lesser ability of the acid to donate its proton or let us say ability as its layman term we can calculate that obviously right so the number of moles available of proton would be less and as you move far away to the left from your PKA it is mostly going to stay as its pertained form and it would not give out its proton.

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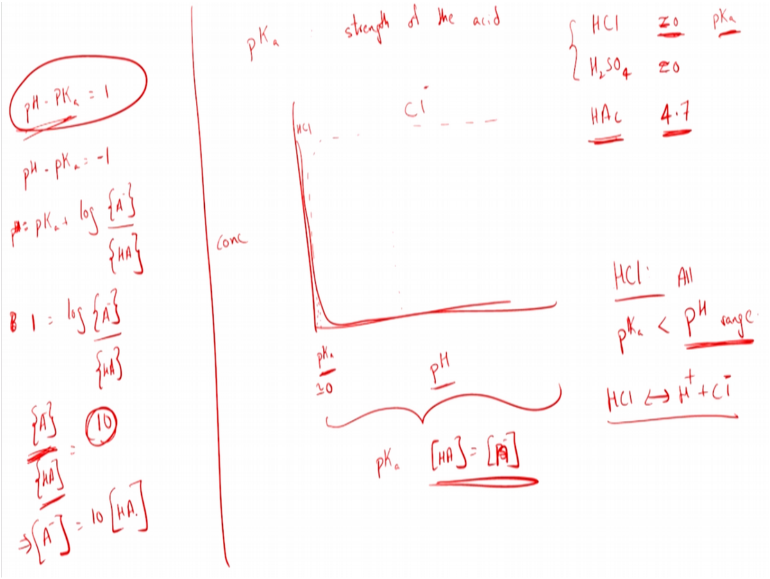

So that is what we understand from here so from here I guess obviously we see that PKA gives us an idea about the strength of the acid. So many people would have mentioned about okay HCL the strong acid H2SO4 is the strong acid and may be acetic acid not such a strong acid and so on.

So why is that if I look at a PK value CL and so on I think 0 or such or equal to 0 or near about 0 right for acetic acid we see that it was around 4.7 or 4.3 I am not sure so based on this you know what do I know that when the PKA of my particular acid is very low what is that means let us again draw that for HCL let us say so it means that at any PH is going to dissociate.

So this is my HCL right and this is the conjugate base which is going to be CL – because the PKA value is very less almost = 0 I believe right an this is with respect to your PH and this is the concentration so I am drawing HCL so compare that with the acetic acid the PK of the acetic acid is somewhere on 0.7 right and so here though with respect to HCL we can see that in normal range of PH because PKA of that particular HCL is always less than for HCL what do we see PKA is almost less than all the PH all PH range I guess it is always less than PH range that we come across.

So HCL will always end up donating its proton which is not the case with the other acid especially with acetic acid or (()) (15:02) acid and so on which we looked at so again PK will give an idea about the strength of the acid and this is what we just discussed. And at PKA we have conjugate acid and conjugate base at equal concentration so let us see what else we can think about let us say distribution with respect to PKA and so on so one aspect I guess I want to quantify that if PH –PKA = 1 and PH – PKA = -1.

So let us see what is the scenario or what can we understand from this let us see so we know that = PKA + log deprotonated form by the protonated form right this is what we have yes PH = PKA and so on but when the first case I am considering the first case PH – PKA is 1 = root log K – HA right so what does this mean concentration of activity of HA is going to be = 10 to the power 1 or 10 so when PH is greater than PKA by just 1 unit.

So because it is logarithmic unit I guess it means that the concentrating of A – is going to be 10 times is concentration of HA right so what does it mean. It means that concentration of A - = 10 times to concentration of HA right so let us look at another example I guess right.

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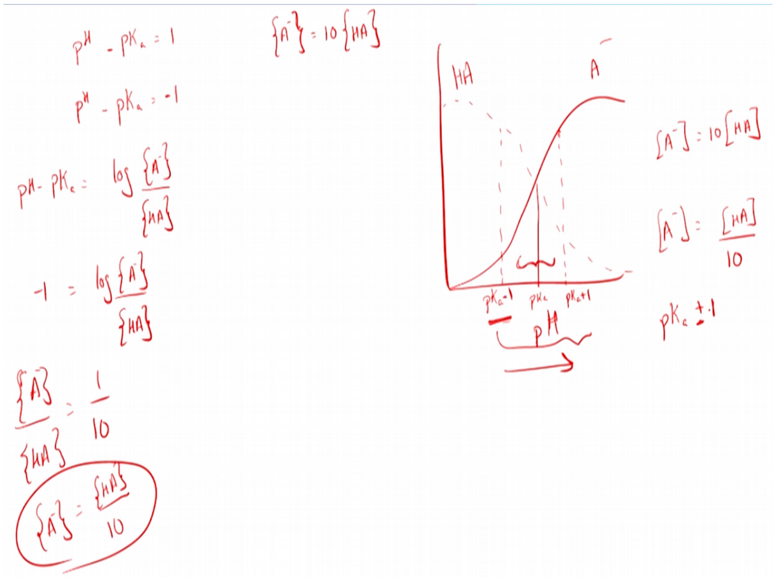

So one example we looked at was when PH – PKA = 1 and we see that activity of A - or the concentration is going to be 10 times the activity of HA right and when the other aspect PH – PKA = - 1 what is it going to be so we have PH – PKA = log activity of A – activity of HA so – 1 = log activity of A – by activity of HA so what does it means it means that 1/10 what is it mean now?

So it means that it is a tenth of the concentration of HA right so what do we understand from this now right. So again this is my PH and this is my HA and this is my A- and this is my PKA and this is the graph X axis to PH. SO within 1 unit from PK + 1 PKA + 1 and 1 unit to left is PKA – 1 so what do we observe?

We observe that there is 10 fold increase or decrease in relevant speciation so as in at this particular point what do we see we see that A- concentration is almost 10 times of HA obviously the graph is not scale that is why you are unable to you know understand here I guess and in other case in PKA at PKA – 1 let us say we see that A – is going to be HA / 10 so more or less effective region with respect to accept in proton or donating to proton is PKA + or – 1 so that is take home message for us right.

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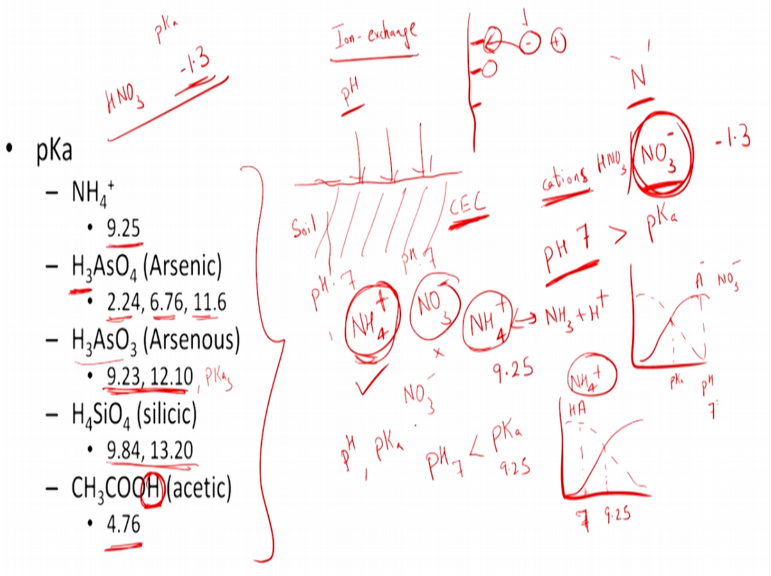

- pKa
  - NH_4^+
    - 9.25
  - H_3AsO_4 (Arsenic)
    - 2.24, 6.76, 11.6
  - H_3AsO_3 (Arsenous)
    - 9.23, 12.10
  - H_4SiO_4 (silicic)
    - 9.84, 13.20
  - CH_3COOH (acetic)
    - 4.76

So now I believe I have some practical examples let us look at them and try to understand those particular aspects in relation to what we see in nature. So let us say in general people look at ionic change this is something we need to talk about now ion-exchange process indicates you know we have let us say different binding sites your particular ion here depending on Anion on cation I guess and reason here they can be exchange with particular anion or cation on this particular binding site right.

So it is ion exchange process so we will see how PH will place a role we look at a specific example. So before going further here or some of the data for ammonium looks like the PK value is 9.25 or arsenic projects it has the ability to donate three protons we have 3 PKA values PKA 1, PKA 2 and PKA 3 right and that is what we see here 2.2, 6.7 and 11.6 and for Arsenous again I believe I am missing one value here but I believe I am missing PKA 3 value here but that is fine the effective range is only these two PKA values.

So again we have 9.23 and 12.1 right and for acetic silicic acid we have the 2 PK 1 and 2 and we are missing 3 and 4 that is not required now. For acetic acid respect donating this particular proton this PKA is 4.76 so we are going to look at a few examples with relevant to these particular values. So keep them in mind or background I guess the first example is with respect to ammonium I guess so background information that I am going to give you is that let us say this is your soil surface let us say sub surface or this is a soil here okay.

So soil in general has cation exchange capacity or what does it mean it means soil as ability to hold on to cation now right it has the ability to hold on to cation and I believe we also need to give the PKF for HNO3 or nitric acid it looks like – 1.3 right PKF for nitric acid is 1.3 so again we are coming back to our examples soil as an cation exchange capacity right and more or less that means soil can hold on to cation right.

And so let us say particular format you know as two option for adding to his side right you can either add it form of nitrate right or in the form of ammonia. So which one would you choose and which one would you suggest and why let us say right so here the key is PH so it is fertilizer soil needs nitrogen right you can add their IIT in the form of nitrate or ammonium now. So the key is that add it in the form of nitrate or NO3 – let us say and as you see the PKA value for HNO3 and NO3 is – 1.3.

So our effective soil range let us say around PH7 and we see that the PH is greater than PKA right so what is that mean now. So this is the PKA and so this is the PH and PKA so PH is greater than PKA right so what it mean the pertained form or what is the case NO3 – predominant. So NO3 – predominate at PH7 that is something that you understand I guess but with respect to ammonia let us say ammonium NH4 can dissociate into and H3 and H4 right and that is what we have here right.

But the PKA value for this particular case seems to be 9.25 the PK one value is 9.25 so for this case though right PKA is 9.25 and PH is going to be 7 PH is 7 so here we see that which is 7 is less than PKA which is 9.25 right this is what we see in this graph here. So this is the PH of the soil so at that particular PH which form predominates we see that pertained form or NH4 would predominate right.

S NH4 + would predominate at PH7 and NO3 – will predominate at PH7 so this is the take home message though but the issue is that the soil has cation exchange ability or hold on to cation how so it can hold on to NH4 + but not hold to NO3 -. So whenever there is rain let us say what happens now NO3 – can be reached away right to the ground but in general to the rough surface but NH4 + in general can be hold to by the cation exchange capacity of the soil.

So thus the forward would the better of what do we say dosing NH4 + rather than dosing NHO+ so what is the key here again we looked at PH and PKA right.

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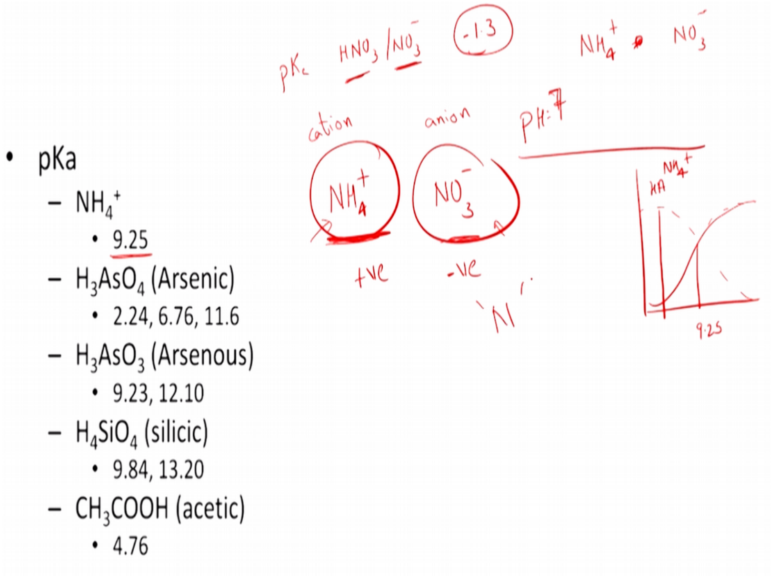

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So again we will summarize what we just discussed right now and the example that we are looking at was also had to have the information for PKA for HNO3 and NO3 – and that was I think – 1.3 and we are trying to see which one would be a better option and H4 + or HNO3 or NO3 – which one would be better and we know that soil exist solution at around PH7 not exist in solutions at around PH 7 not exist in solution pardon me.

The soil PH assuming is PHO7 right and then we looked at appreciation graphs this is the appreciation I guess right for both the cases so one is for ammonium PKA is 9.25 and we see that PH 7 most of it stays as HA or NH4 + and what does it mean it is going to it as H4+ as a positive charge right but we know that as PH7 HNO3 is not going to predominate but NO3 – because PH is greater than PKA so we are going to have an anion but with NH4 + we are going to stay as a cation right and negative charge.

So does it mean the soil can hold to NH4 + but not on to NO3 – right so in general the former would be better of applying ammonia rather than nitrate for is source of nitrate so that is what we have just observed I guess right.

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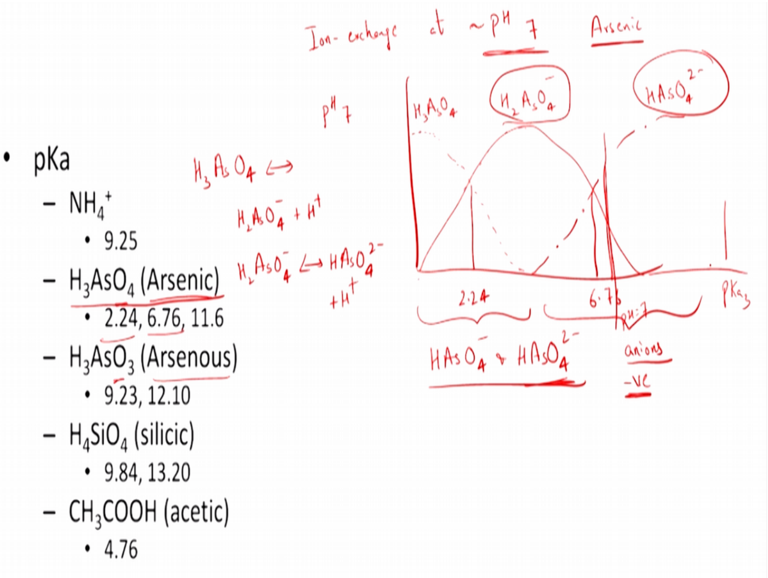

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    - 4.76

So let us move on the next example here please and the example here is let us say by ion-exchange right ion-exchange at let us say around PH7 you are trying to remove arsenic right arsenic by ionic change around PH7 let us say so in which form would you rate have your arsenic we have not talked about form set I believe the oxidation states are different in both these cases.

So would you wanted to be in the form of arsenic or arsenous arsenic acid or arsenous acid so here let us say at PH7 right at PH7 if I look at H3 SO4 what is this appreciation going to be here so let me draw the figure here right we never looked at the tripotic acid before so it going to decrease again and this so it is going to be H3KO4 H2AS O4 – HASO4 2 – and so on we still need to look at deprotonated form but let us limit other to here and what are the PK values they are 2.24 and 6.76 right.

So what is this mean at PH7 right which is our key and where is PH7 so somewhere here so the species are going to be are the form that predominant are going to be HASO4 – and more important HASO4 2 – so what is mean I guess they have charge or we have anions predominating or we have a charge negative charge in general it is going to be HASO4 2- that is what we see here right this is PH7 PH =7.

So what is this graph about this is for a (()) (28:20) acid I have not drawn the PK value for the third case or PKA3 and just limited myself to 2 myself to 2.24 and 6.76 so H3ASO4 as keep decreasing HAS24 – keeps increasing and as that again further increases you are now going to have HASO4 2 –.

So what are the relevant equation obviously H3AS04 right would go to H2A4O4 - + H+ this is one relevant reaction relevant to this particular region right and other is the other dissociation the next dissociation I guess dissociating into HASO4 2- and H+ and this is what we see here and this particular region right.

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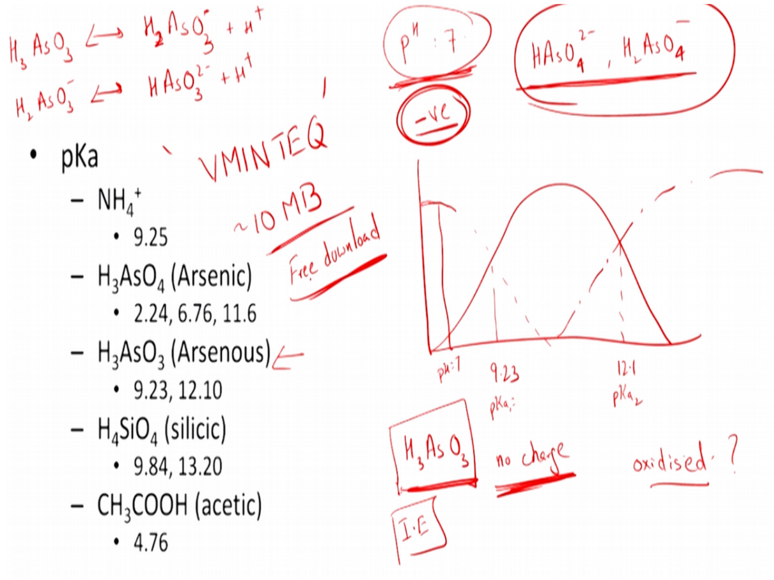

$H_3AsO_3 \rightleftarrows H_2AsO_3^- + H^+$

$H_2AsO_3^- \rightleftarrows HAsO_3^{2-} + H^+$

- pKa
  - NH_4^+
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So again we will try to erase this and try to get back to a better format so we that PH7 what were predominating I guess HASO4 2 – and H2SO4 – more or less take home message is we have negative charge on the relevant species so total Arsenic will be present in HASO4 2 – H2SO4 – but if come back to Arsenous and if I look at our particular so if I draw the diagram obviously this is not a scale that is the reason of anyone having an issue.

So I am going to draw the 2 PKS values here so H3SO3 what can that H3ASO3 can dissociate into H3 pardon me H3OSO3 - + H+ and again H2ASO3 – can further dissociate into H ASO32 – and again another H+ so that is what we have here and so the PKS value that though are 9.23 and 12.1 so here are only looking at PK1 and 2 but for our PH range which is 7 so that is going to be somewhere here.

So as we see like PH = 7 which form predominates now it is the protonated form than that is H3ASO3 I guess right so what is this mean now it means that this has no charge no charge right and this oxidation state of arsenic there is no charge at the usual range of PH7 is so can you use ionic change to remove a compound with no charge at least especially with this case at PH7.

So in which form should arsenic be present if it wants to be or if you want to remove it by ionic exchange it needs to be in the oxidized form oxidized form and why is that only because of oxidized form you see that it has negative charge only it can be removed by ionic exchange process. SO I guess with that I will end my session for today and we continue the other example in the next lecture session and I also request that you try to install a software called VMINTEQ you can Google this VMINTEQ.

So we are going to start discussing the application I think it is not a greater file size may be 10 MB or 20 MB at best you can Google in visual MINTEQ VMINTEQ with the first search such result itself gives a free download option so please have this load for this next session I guess. Again please try to look up visual MINTEQ or VMINTEQ it is software we use to model or you know model equilibrium I guess and we are going to use that throughout the class.

So it is a free to use software free to download free to use software so with that I will end my class today and thank you.