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Lecture - 30 Acidity and its Applications

Hello everyone, so welcome back to our latest lecture session so again we will have our brief summary of what we discussed in the last lecture class right. So we are talking about alkalinity and we looked at it in terms of the acid neutralizing capacity and in general because the natural systems only contain or usually not only contain I guess the predominant acid base system is the carbonate system.

We usually define the theoretical alkalinity in terms of the carbonates species and calculate the amount of acid that would take to neutralize the relevant deprotonated forms of your particular carbonate system right and that is why we end up titrating it to or we end up titrating it to 4.5 and when would your theoretical definition of alkalinity be at odds with what you would measure practically by titrating with the acid in the lab I guess right.

When you have other relevant acid-base systems, you know with pKa values greater than 4.5 right which can again consume or you know neutralize some of your acid yes in that case again we looked at the relevant aspects in detail. So we would not go into that further and then we started discussing about acidity right. So alkalinity is about the acid neutralizing capacity of your particular solution and acidity will obviously give you an idea about the base neutralizing capacity of solution.

Anyway acidity is not rarely I guess less widely used or applicable when compared to alkalinity which is used everywhere in almost all your relevant calculations. So again we are going to go through and look at acidity right now right.

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So acidity right we started discussing about that that we say is equal to or similar to the base neutralizing capacity yes that is something we discussed and I believe in the last class we also talked about that unlike alkalinity we have you know 3 kinds of acidity that people look at, one is the one which you would look at the mineral acidity right and next we look at phenolphthalein acidity.

And this I believe is also called methyl orange acidity right based on its you know the type of indicator that you are using, again phenolphthalein acidity based on the type of indicator that you are using and then total acidity and depending on the textbooks that we or you are going to look at let us say you know people sometimes think of phenol acidity too as total acidity but you know there are 3 distinct kinds of acidities right and we are going to look at the each of them in greater detail right.

So again acidity is nothing but base neutralizing capacity right so you are let us say in the lab how would you measure that. You know you are going to take a base of known concentration in your particular burette and keep titrating that against your solution until you reach an equivalence point right and what is this equivalence point about? When the amount of base in this case added is equivalent to the amount of acid initially present in your solution.

But obviously if it is diprotic or triprotic system, you are going to have multiple equivalence points right. So again here looks like we are going to look at 3 equivalence points. So let us look at what they are in greater detail right.

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So first case is when we look at mineral acidity or methyl orange, so the equivalence point we look at is 3.7 and we will see why 3.7, we will go back to that soon right and what else here, so here what are we trying to measure, what are we trying to measure here right. It measures the strong acids present in the solution right, it will give you an idea about only the strong acids present in the solution.

So the key here is that strong acid, so H2CO3 with the pKa of 6.3 and the pKa 2 of around what is it now 10.3 you know we do not call that a strong acid but HCL, HNO3 and so on we look at them in terms of strong acids because of their low pKa values and ability to donate the proton or deprotonate even at low pH values right. So this particular mineral acidity or methyl orange acidity is only trying to calculate or measure the amount of the strong acids present in your solution right.

So let us look at why pH is 3.7 now right, the key is that it only wants to measure the strong acids and not the H2CO3 that is present in your system right. (Refer Slide Time: 05:12)



Let us look at obviously the relevant carbonate speciation system, so this is something that we looked at previously too right. I believe we looked at this with respect to VMINTEQ and developing it for alkalinity. So I believe the total concentration we have is 0.01 molar and we have a figure where x axis is pH and y axis is concentration. So now I only want to measure the strong acids right.

Obviously, the key is then the pKa is going to be low and obviously I do not want to measure the amount of H2CO3 present right. So what is that now? So as we see it was around 3.7, what was it? The equivalence point right and as you can see from here at 3.7 let us say at pH of 3.7 what do you see here? You know H2CO3 does not start dissociating yet or any base you know if any base is added to your solution, well H2CO3 be able to neutralize that until pH of 3.7 or in this region.

No, why is that as you see in this entire region until 3.7 you know H2CO3 does not dissociate into H+ and HCO3- right. So obviously if I am not trying to measure H2CO3 but only trying to measure the strong acids until what pH will I titrate to, until that pH when H2CO3 is not going to dissociate and that as you see is around 3.7.

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And that is the reason we end up measuring or having an equivalence point is 3.7 for your mineral acidity right. So that is the key here that we are not trying to measure the H2CO3 but only the strong acids, that is one particular case yes.

So let us move on to the next particular aspect and here again one way to understand this is your reference is H2CO3 right so looks like I missed writing down the relevant equation, will come back to that, so keep in mind that if you are trying to write down the component balance and understand it in terms of H total. If you have the reference or you know your one of the components as H2CO3 you will be able to write the relevant equation.

So obviously I missed writing the relevant equation so we are going to go back to that right so we understood how.

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And so here in this case acidity is going to be equal to what now. First you are going to write down all the acids present so only strong acids so it will be one in the form of H+ in this case right and then again the case we are considering is when we have only the carbonate system here and obviously any other strong acids present are going to dissociate right. So we are going to have H+ and we obviously need to subtract all these bases here right. So it is going to be obviously OH- here right -.





And what are the bases do we look at here. We obviously look at CO3 2-, you know in this region this is CO3 2- and HCO3- and obviously HCO3- can consume one proton. So you know we are going to have a coefficient of 1 for it, CO3 2- can consume what do we say 2

protons right and the reference is with respect to H2CO3 yes and that is why we are going to have coefficient of 2 here.

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So it is going to be –HCO3- -2 times of CO3 2- right and obviously what are the units here because we already looked at the relevant coefficients here right. The units are not equivalence per liter but moles per liter yes. Again the units for these particular variables 1, 2, 3, 4 are moles per liter and you will end up with acidity in terms of equivalence per liter right. Again you know to understand this we mention that we can look at the system with respect to H+ and H2CO3 as our components.

So what is you know relatively unique aspect here? Usually if you remember whenever we analyze the system we take H+ and the most deprotonated form which is CO3 2- as our components but because our reference right we are trying to not measure H2CO3 and the reference here is H2CO3 so we are going to try to look at the system in terms of H2CO3 and not CO3 2-.

So if that is case and I write down H total right or let me just plug this in here not plug this in write it down in the form of Tableau, so what are the species that you would expect H+, OH-. We are not going to write H2CO3 because that is not something we are measuring here right, HCO3- or even if I write that let us see why do we do not need that H2CO3 and here again H2CO3 total, H2CO3 is then CO3 2-, so how many H+ do I need?

So I am going to have 1 and how many OH- -1, HCO3- how do I form that by H2CO3-H+ right and that is the reason why we end up with – here again and how do you form H2CO3 by 0 and 1 and CO3 how do you form that by 1 H2CO3 and -2H+ right and more or less if you look at it that is H total and that is similar to your acidity right, when is that now H total is equal to acidity when you choose H+ and H2CO3 among your components right.

So that is for the sake of your understanding here, so again what we are measuring here, we are only measuring the strong acids which will be in the form H+ and obviously we need to subtract the other bases which in this case we are only assuming HCO3- and CO3 2- and why do we take the coefficient of 1 and 2 here because CO3 2- can neutralize 2 protons before you know moving on to its protonate state which is H2CO3 and HCO3- can take 1 proton so that is the case we have the relevant coefficients here.

So until now we looked at mineral acidity and obviously pH 3.7.

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So let us move on to the next case I guess right. So next case obviously is phenolphthalein acidity again based on the indicator that we look at. So obviously the pH we are looking at is 8.3 and again let us see why? So in this case what are we trying to measure with this particular acidity I guess, when you titrate the system with the base until you achieve a pH of or reach a pH of 8.3.

So why is that now? The acidity I guess we are going to obviously develop the equation later. So again in the earlier particular what is it now mineral acidity we only try to look at the strong acids present and which certainly would have to rule out H2CO3. In this case, phenolphthalein acidity right we are going to go a bit further, we are obviously going to measure all the strong acids present. We are also going to measure H2CO3 right.

We are going to measure H2CO3 but obviously not HCO3-, so in this case we are going to look at all the strong acids right and then H2CO3 and thus we need to come up with an end point that will help us you know measure that when we titrate your solution or our solution against a base right. Let us look at what it is. So here we are trying to measure what do we say strong acids obviously and H2CO3. So this is what we are trying to measure right.





So let us just look at the relevant graph once and let us see how we can do that. So H2CO3 right as you see this is the profile for H2CO3 and this is the profile for HCO3- and this is the profile for CO3 2- right. So let us look at this here and you see H2CO3 is still in considerable quantities until around this point. So if I want to measure all the H2CO3-, I titrate until this particular what do we say pH with the base right.

I keep adding a base until I reach which point now, this particular point and why is this point because you want to exhaust all the H2CO3 present in the solution because you are trying to measure H2CO3. So obviously in this region what am I measuring? I am measuring all the H2CO3 present and obviously if there are any other strong acids present, they are going to be titrated here in this region, in this region as in in this pH right.

So now the key is that if you look at this particular equivalence point, your H2CO3 is not the reference anymore but HCO3- is the reference right. So when we looked at your what is it now mineral acidity we chose our reference as H2CO3 but in this case it is not H2CO3 anymore, we are trying to also measure H2CO3 you can think of the reference when you choose your components or try to understand the equation with respect to your acidity that you are going to have the reference as HCO3-.

So let us look at what the relevant equation will turn out to be right.

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So let us go back here and now acidity so obviously you need to measure all the strong acids so that is why I am using H+2 understand them because all the strong acids are going to deprotonate and I am also going to measure the concentration of H2CO3 right. These are the acids that I am going to look at right. These are the acids and I need to subtract the bases, so bases are going to be certainly OH-.

Because if the pH is high you need to look at the relevant acidity right or the effect of high pH on acidity that is why you are obviously going to subtract the base and obviously any other what is it now bases and then this carbonate system what are the other bases that are present?

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So obviously CO3 2- not HCO3- why that the reference here in this case is HCO3- with respect HCO3- you are trying to understand the system right.

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So here you are going to have OH- -CO3 2- so those people who are following it keenly you might ask you know the question might arise in their minds. So if you look at the equation for mineral acidity we looked at I think -2 times CO3 2- but were not we looking at you know why do not we have a coefficient of -2 and only why do we have a coefficient of only -1 here in this particular phenolphthalein acidity right.

So the key is that earlier the reference was H2CO3, so CO3 2- can take 2 protons right but in this case the reference is only HCO3- so let us say if we think of it in terms of difference right, it is not a too difference obviously. HCO3- and CO3 2- differ by only one proton right.

So earlier H2CO3 and CO3 2- they differ by 2 protons. So that is the reason here because the reference is HCO3- we look at the coefficients from that point of view.

So same case here with respect to H2CO3 because H2CO3 can only give out 1 proton before transforming into HCO3- which is our reference right or CO3 2- can only take one proton before transforming into HCO3- which is our reference right. So this is where our coefficients come from I know 1 H+ for H2CO3 because it can donate one and -1 here because CO3 2- can take 1 H+.

So that is the relevant equation here H+ +H2CO3-OH- and -CO3 2- and most people end up using or trying to calculate phenolphthalein acidity why is that? Again most people end up looking at this particular acidity when you know people talk about acidity, why is that because you know we are trying to measure all the H2CO3 and the strong acids present which in effect means you are titrating to a value which is 8.3 here obviously, it is slightly higher than pH 7 but around or you know still near by the pH 7 right.

So that is the reason people usually look at let us say this phenolphthalein acidity because it gives an idea again about the natural systems you know their ability to neutralize a base if you go till around pH 7 or in this case obviously pH 8.3 but obviously with our background let us say with our fundamental background we know there is one more level right.

And that is going to be the total acidity and why is that because you still have CO3 2- present or you know HCO3- present. So in the next case we are going to look at which is the total acidity, we are going to look at CO3 2- as the reference and also measure HCO3- and H2CO3 right. Again before we go further just to understand the system, we set the reference was what now HCO3-.

Let us try to look that up not look that up pardon me try to understand how we arrive at this right and what are the different species H+, OH- and what else CO3 2-, HCO3- and H2CO3 and how many H+ do I need to form 1 H+1 and obviously 0 here and here it is going to be -1 and 0 and how can I form HCO3- by 1 HCO3- and -1 and thus you see you know that particular coefficient here -1.

And how can I form HCO3- just 1 HCO3- and no role for H+ right that is why we have no term here with respect to HCO3-. Again the key is that HCO3- is the reference here and why is it that we are looking at HCO3- as the reference because the equivalence point needs to be around 8.3 so that we end up measuring all the H2CO3, so you know they are interlinked obviously.

And how do I end up measuring H2CO3 in terms of the components or expressing H2CO3 in terms of the components here. So 1 HCO3- and 1 H+ and that is what you see here when you are writing it as where is this now H2CO3 and so obviously H total in this case will be what now? H+ -OH- -CO3 2- +H2CO3 right and again thus in this case is going to be similar to this equation as you can see and obviously only when you choose HCO3- as your component right.

So that is the key you know earlier we chose H2CO3 as the component and then the relevant equations are going to be different and HCO3- here is our component of the reference and that is why your H total equation is going to be different right.



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So next up so here we are going to measure total acidity right and the pH is 10.5 so obviously we need to understand why we are going to look at 10.5 right that is obviously the key here. So we are going to go back to that so again keep in mind that some people also think of phenolphthalein acidity as total acidity but that is not strictly speaking not strictly speaking it is not true, so there is something else called total acidity right.

Again acidity we are look at base neutralizing capacity, so what is that mean? We want to sum up all the acids that can neutralize a base. So earlier we looked at strong acids, the next aspect we looked at was strong acids and H2CO3 and next aspect which we are going to consider now obviously is you know by logical you know understanding our analysis we see that it is going to be strong acids H2CO3 and also HCO3-.

So what do we end up measuring here right we end up measuring strong acids or we want to measure the strong acids, we want to measure H2CO3 and we also want to measure HCO3-right and this is what the total acidity gives you an idea about. So let us now go back to the figure and see why pH of 10.5 is necessary right but the key obviously is you want to also measure HCO3- right.

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So earlier when we are trying to measure H2CO3 right, we end up titrating until that point or until that pH when all the H2CO3 would be consumed which approximately turns out to be 8.3 but obviously if I am also trying to measure HCO3-, so what do I need to go to so obviously 10.5 I guess right or 10.7 right, around this particular value what was the value given okay 10.5.

So people end up measuring or going to 10.5 right, so you know again keep in mind that we are not measuring all the HCO3 by – but more or less most of it right. So anyway that is the key here and that is the reason we end up choosing what do we say 10.5 I guess right pardon me here it is not here it is somewhere out here I guess right and obviously the reference here is that it is going to be CO3 2- right.

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Let us look at the relevant equation there, so the reference is going to be CO3 2- right and what next please we are trying to write down the equation here acidity and that is going to be equal to all the sum of the acids so it is going to be H+ +2 times H2CO3 and why is that, the reference now is CO3 2- and obviously 1 times HCO3- right and -OH- and obviously what is this as you can see is the total acidity right.

So let us try to understand this in terms of our components once, so what is the reference here, it is CO3 2- now and H+ obviously is always our component. So let us try to understand the system from that point of view. So what do we have here please, we have the relevant species, they are H+, OH-, H2CO3, HCO3- and CO3 2- right and H+ is 0 and 1, 0 and -1 and how do I come to H2CO3 1 and 2.

Because you know 2H+ +1 CO3 2- would end up as H2CO3 and that is what you see here and obviously the key is that. Now the reference or the component is CO3 2- but with HCO3-what do you see, it is going to be 1 here and 1 here and here obviously it is going to be 1 and 0. So obviously H total in this case is concentration of H+ -OH- so you are just summing up this here H total right +2 times of H2CO3+HCO3- right.

So that is the case we look at yes so thus in this case obviously as you see this equation when you write up H total with the components of CO3 2- and H+ you will end up with H total that is similar or you know the same as total acidity right. So again we looked at 3 aspects, one for

strong acids, one for strong acids and H2CO3 and the last one for strong acids, H2CO3 and HCO3- right.

Again why HCO3- because it can also neutralize a base by donating one proton and you know transforming into CO3 2- which is its deprotonated form right.





So let us move on, I believe you are going to look at the effects of addition of acids and bases. So we looked at this in the context of what is it now our alkalinity. So here let us look at a particular equation let us say and then try to understand that. So let us say you know we are going to add let us say first an acid right and the second we are going to see a case of adding a base and then third case we are going to look at addition of carbon dioxide right.

So one of the equations I guess let us see if it changes with different cases. It strictly speaking should not so let us take total acidity for now H+ right, what is total acidity, let us work it out for one case, total acidity=what now H+ and what are the other acids present 2 times of H2CO3+ HCO3- pardon me right –OH- right. So if we add an acid right, if I add one equivalent per liter of acid right how is that going to transform the equations?

So I am going to end up increasing my H+, so that means when I add acid it is going to end up increasing my acidity right by 1 equivalent per liter. So now let us move on to our particular case of the base and what we are looking at here. So base we are adding if I add 1 equivalent per liter of base to my solution. So what is the total acidity or acidity how is it going to change?

So here by adding a base, I am going to increase the OH- concentration, so in effect what is that mean I am bringing down the value of the total acidity right. So that is what it means so when I increase the concentration of the base present here or you know add a base to the solution, so the initial acidity will come down right or will decrease and how I guess if I add 1 equivalent per liter of base, I am going to have 1 equivalent per liter of my particular acid right, so that is the case.

Again you know we need to understand that you know acidity is nothing but base neutralizing capacity right. So if you end up increasing the concentration of your acid what is that mean? You have more compounds that can neutralize your base but obviously if you are adding a base right and extra load on your system so thus you are decreasing the acidity or the ability to neutralize the base in your particular case right.

So let us see with respect to CO2, let just try to apply that in this case. So obviously we know that CO2 can dissociate into H2CO3 right in the gaseous to aqueous right and H2CO3 we know can either go to what is it now H+ +HCO3- or it can also dissociate to 2H+ and CO3 2-right. So let us say if I add you know 1 equivalent per liter let us see what the effect is going to be so? Let us consider this case first right.

So H+ is going to increase and HCO3- is going to increase yes and so in this case for 1 equivalent per liter let us say increase the total acidity. The total acidity is going to increase by what is it please units of 2 right 2 equivalence per liter why is that? So if it is just H2CO3 you see there are 2 units here and if it is dissociating into H+ and HCO3- you see that they are H and HCO3- 2 units so that 2 equivalence per liter.

But obviously if you look at the equation for let us say phenolphthalein acidity and what was that equation, let me remember that or try to just analyze that here. The reference is HCO3-right so it is going to be the first the acids present. Reference is HCO3- H2CO3 right- the base is present which are OH- and CO3 2- but for phenolphthalein acidity how would your particular system change right.

This is phenolphthalein acidity not total acidity right, how would the system change when you add carbon dioxide right. We know the total acidity changes by 2 equivalence per liter, so

CO2 can dissociate into H2CO3 right. So obviously if I am adding more CO2 what does that mean?

The phenolphthalein acidity would change by or increase by 1 equivalent per liter. So when I increase CO2 right by 1 equivalent per liter, the total acidity changes or increases by 2 equivalence per liter but the phenolphthalein acidity would only increase by 1 equivalent per liter. Again so we looked at various aspects right until now, the three kinds of acidities and then we started discussing about the effects of acids and bases.

Just to refresh your memory right if you look at if you remember that with respect to alkalinity which looks at the acid neutralizing capacity right. We saw that when we bubble carbon dioxide through the solution, the acidity does not change right and why is that? The key was that with respect to alkalinity we had a particular set of definitions that we try to understand right.

As in you know when we put in H2CO3, it dissociates into either H+ or HCO3- which in that alkalinity equation cancel each other out or can further dissociate into 2H+ and CO3 2- and again cancel each other out because we need to look at the equivalence and CO3 2- has a equation there and let me write this down here. Where can I write this down okay I will just try to do.



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What did we have with respect to alkalinity? The definition was OH- right+HCO3- so all the bases+2 times of CO3 2- -H+. So when we bubbled carbon dioxide through it, what did we

see? Carbon dioxide can go to H2CO3 right which can dissociate into HCO3- +H+ and also further to H+ and CO3 2- right. So if it stops at this step you see H+ and HCO3- they cancel each other out even though they are produced yes.

And if it goes to complete dissociation, you see the 2H+ are given out right -2 there and CO3 2- 1 but you have a coefficient here so again they cancel out, so whenever you increase carbon dioxide concentration or bubble it through your water there is no effect on alkalinity right. It is still a constant but that is not the case here when we look at acidity and why is that?

Obviously you know we have different cases here again, one for what is it now, the total acidity and one for phenolphthalein and so on. So obviously for total acidity when we look at the relevant variables you see that when you add carbon dioxide, we notice that it increases by 2 equivalence per liter, when carbon dioxide increases 1 equivalent per liter.

But for phenolphthalein acidity if you should look at the relevant variables you see that it only increases by 1 equivalent per liter right. So we are done with discussing alkalinity and acidity which are remarkably important aspects in natural and engineered systems. So in the next class, we are going to look at the applications right. So again we are going to heavily look at using VMINTEQ again and with that I will end today's lecture session and thank you.