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Lecture - 29 Alkalinity: Theoretical and Practical Definition

Hello everyone. Welcome back to the latest lecture session. So again as discussed with me let us look at what we have talked about in the previous session or let us rather try to summarize that. So we in general looked at how we spend most of the time with respect to looking at designing the buffers right and then we also looked at alkalinity right and that is something that is always present in natural systems and that is one of the reason you would consider it.

Again also because that is important why because it will resist decrease in pH, yes that is one of the aspects. So then we end up looking at how to calculate the theoretical definition of alkalinity and we also looked at how to calculate the practical definition pardon me not practical definition the practical value as in when you do that in the lab what would you measure that right.

So the theoretical definition where did we get that from, we set H2CO3 as your reference point and again theoretical definition is valid only when only the carbonate system is the predominate system right and then we end up looking at all the bases present and in this case they are going to be CO3 2- and HCO3- and OH- right and subtract the other acids present already you know it is slowly now going to be H+ CO2 right. So that is how we end up with the theoretical definition.

Practical definition tries to mirror the theoretical definition as in you are trying to add acid or enough acid so that you titrate the solution to that particular end point of H2CO3 and as we calculate that it is around 4.4 for a particular CO3 total but standard methods looks at 4.5, why is that because you want to also look at the carbon dioxide loss into the gaseous phase during your titration set such.

So you are in your practical definition trying to look at how much acid am I titrating or need to be able to bring down the pH to 4.5 right then more or less that is the practical definition. So first today we are going to look at those cases. Let us say when your practical definitions

are not going to match what it is that you would calculate when you look at the theoretical definition right. So let us look at what we have here.

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So I believe this our particular figure and let me write down the particular alkalinity theoretical equation and what was that OH- and what are the other bases HCO3- +2 times CO3 2-. Why is that 2 times? As I go from let us say here to 4.5 right let say my initial pH is 13 you know the CO3 2- can take 1 H+ here and then be transformed to HCO3- which can again further take one more H+ and be transformed to H2CO3.

So that is the reason why we are going to have 2CO3 2- here and –H+ obviously, again this in theoretical definition right. So what was the practical definition again? We just look at the amount of acid required to be added to the solution so that you decrease the pH from your initial pH which in my example here we are assuming 13 to come down to 4.5 right which is the standard method defined equivalence point for H2CO3 yes and so that is the case.

So obviously when the practical definition let us say alkalinity calculated due to practical definition not be equal to the alkalinity from your theoretical definition. So the obvious case is when the carbonate system is not the only predominant acid-base system right. So in general we look at natural waters right and there is a reason we more or less can get by with assuming that the carbonate system predominates you know any other acid-base systems present in the solution.

So even if there are any other acid-base what we say systems present or species present pardon me right the carbonate system concentrations are the relevant species, concentrations of these species of the carbonate system would be remarkably high compared to these particular other acid-base systems. So in those cases we can get by with our particular theoretical definition of alkalinity right.

But obviously if you have other acids and bases that let us say have equivalent concentrations or you know in that particular ballpark range as your carbonate system concentrations, so then what is going to happen let us look at that I guess but the theoretical definition alkalinity is still going to the same yes but what is your practical definition going to look at. So let us look at that I guess. For that I ended up we are going to look at one particular example.

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So in that particular example let us say I have H3PO4 0 at let us say 0.01 molar and also H2CO3 0 at 0.01 molar right. The previous figure that we looked at was when I believe we use VMINTEQ to be able to come up with that and we considered I believe only H2CO3 to be present in the system and at 0.01 molar if my memory serves me right but now we are going to look at system when there is another acid-base system present.

In this case, the phosphoric acid at concentrations that are similar to your particular carbonate system.

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Let us go back to VMINTEQ now right, so how do I get that done?

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Let me first identify the relevant species here right, so what are the species here and there going to be H3PO4, H2PO4-, HPO4 2-, PO4 3- and then the carbonate system this is from the phosphoric acid-base conjugate acid-base systems, H3H2H and PO4 and the relevant charge obviously right and here now we have H2CO3, HCO3- and CO3 2- and we are obviously always going to have our H+ and OH- right.

So in this case, the components that we usually end up choosing what are they? They are going to be H+ and the most deprotonated form CO3 2- and PO4 3- right. So what is H total going to be? So it is going to be due to these two particular solutions initially so that is going

to be 3 times H3PO4 0 why is that? You know from Tableau and component balance you can look at that.

But 3H3 right I mean 3 protons here and again 2 times of H2CO3 0, again this is from the formation equations of the component balance equations you can come up with that because we have had considerable practice in that regard I am skipping those steps. So the H total is now going to be 0.05 molar right and same case now CO3 total what is that going to be equal to H2CO3 0 meaning that is equal to 0.01 molar and PO4 which is the last component total, what is that equal to?

The only contribution is due to H3PO4 so that is equal to H3PO4 0 and that is equal to 0.01 molar. So what do I need to plug in I need to plug in H total, 0.05, CO3 total, 0.01, P4 total and 0.01. Again here my particular what we say objective is to be able to calculate or you know come up with graph where I have pH on the x axis and all the concentrations on this what do we say y axis right.

I am trying to get this speciation system, so how do I do that? I can look at the titrations tab right in my VMINTEQ or you know because you are just looking at pH I can also look at the sweep option right and I am going to look at the sweep option and let us look at how to get this done.



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And let us go back to VMINTEQ here right, so what do we have here? I am going to choose H, where is H here please, okay H and now we need to plug in that it is 0.05 right and what is

the value here 0.05 and now I am going to add that to the list and now next I am going to look at CO3 total and that is that that is here and that we know is 0.01 right and I am going to add that to the list and the last component was PO4 and that is that here okay that is here and again that is equivalent concentration to 0.01 so I am going add that to the list.

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To be on the safer side, I am going to check what I have here. As we see here, we have H total is 0.05, CO3 total is 0.01 and which is similar in concentration to the PO4 total right. (Refer Slide Time: 09:27)

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I am going back to the main menu, so I am going to go to the multi-problem or sweep menu here right and now I am going to use sweep where one parameter is varied, so here you have different parameters which can be varied but for now I am only going to look at pH. So I need to calculate the number of problems, so let us calculate that. Start value I know I am going to have 0 right.

And increment between values to have you know relatively continuous distribution of the relevant data points. I am going to look at 0.25 right. So I need to calculate number of problems.

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So let us just try to do a minor calculation here and let us say you know so 0.25 meaning there are going to be 4 pH, 4*14=56 and that should also include your 0 so 57 equations I guess right.

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So number of problems I am stating that as 57 to go from pH 0 to pH 14 with an increment of 0.25 each time and what do I need here. So the present selection is already pH which is going to be my x axis later on. Now I am going to choose CO3 2-, I am also going to choose PO4 3- so I am going to choose all the relevant conjugate acids and bases right. So I am just going by the relevant list that popped up here when I choose those components.

How did we get this list because you chose those components here H2PO4-, H3PO4, HCO3and HPO4 2-. Let me check if we have all the relevant aspects with 3+47 right diprotic and triprotic acids so 3 species CO3 2- okay 1, 2, 3, 4, 5, 6, and 7 so I am done with that. So save and back.



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And now let us run VMINTEQ. So the first aspect is obviously going to be at pH=0 and so here I can individually choose right and this particular option what is this? Select problem number so that is 57 so 57 if our calculation was right it should end up with pH 14 that is what we see here right. So we have different values right, pH let us say let choose a random value of 3 you would expect most of it to be present as H2CO3 and that is what you see here. **(Refer Slide Time: 11:57)**

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Let us say species distribution right so at pH of 3.2 what would CO3 2- usually be present as because the pKa 1 is 6.3 everything would be present as its protonated form, so that is why you see that 99.9% of CO3 is present as H2CO3 and very little is present as HCO3-. So just for sake of understanding where we are let us try to see what it would be at around pH 4.5 which is our endpoint right okay.

It looks like I need to go further down okay that is close enough now for me or let me go further down 20 and then 18 pardon me 19 right. So let us look at view species distribution now. So yeah this is the relevant species distribution and why did I choose pH 4.5 because I wanted to look at the relevant distribution for CO3 2- at the equivalence point we discussed earlier right.

So we see that almost all the HCO3- is consumed but you still have some HCO3- or 1.5% and 98.5% is present as H2CO3. This is at that pH 4 and similarly for the pKa values we know that for phosphoric acid at 2.3, 6.8 or 6.3 and 10.3. So you can calculate them accordingly I guess right. So because we looked at pH of 4.5, we see that most of it should be present as H2PO4- because the pKa 1 is 2.3 right.

So that is what you see here 99% is present as H2PO4- yes again so we are going to go back to the output menu and I am going to say selected sweep results.

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This will give me a better idea obviously. So with pH how is CO3 2- concentration going to change? It is obviously going to increase and that is what you are going to see here right and that is what you see here in the total was 0.01 so which is 10 power -2 and that is what you see here right. The maximum can be 0.01 here and same case which has 3PO4 what would you expect here?

Initial was 0.01 at pH 0, as we keep increasing the pH what you see here? We see that it is decreasing right. So that is what you see here, anyway so I am going to say print to excel and then to save time I end up drawing the graph. So let us go back to our particular system here. **(Refer Slide Time: 14:28)**



Let me see where I have the graph, so here is the graph so how did we end up with that? We end up with this graph. I just plotted the relevant values from those sweep results. So let us

try to understand the system here and try to look at the carbonate system first H2CO3 and that is here and you see that decreasing so obviously the pKa value is around 6.3 right and then HCO3- and where is that?

That is around here and you see that that is increasing while H2CO3 is decreasing right and obviously the point at which both the concentration are equal that is going to be the pKa 1 which for your H2CO3 system. What are the pKa values? pKa values for the first one is 6.3, the second one is around 10.3 and what is it for your phosphoric acid system H3PO4? It should be around 2.3, 6.3 or 6.7.

I am not sure and then I think around 11, you know these are approximate values okay. So let us look at this system again and now we are going to look at CO3 2- and that is out here. So around pKa of 10.3 right, 10.3 is the pKa 2 you see that it is equal in concentration to HCO3yes anyhow we understood that carbonate system and then moving on to the phosphate system what do we have here? H3PO4.

Where is that here? That is the orange so that is here and as you see that the pKa is 2.3, so it has you know there is particular pKa here and then you see HPO4- so as we looked it earlier at 4.5 all of it would be present as your H2PO4- right and that is what we looked at here. So again now I think you get the trend. So I think what are we trying to look at now? We are trying to look at pH 4.5 because that is our titration end point and let us say initially we said our titration was starting at pH 3 or 13 pardon me.

I said that we are resuming that the solution starts at pH 13. So we let us try to recap what we are up to so that we do not lose track of what we are, what we are trying to do here. So we are trying to look at those cases when the theoretical definition of alkalinity would not be the same as what you would measure in the lab right. In the lab what do you do? You add acid or titrate with acid to decrease the pH till 4.5 and calculate the amount of acid.

And when will that work fine or when will both of the relevant numbers be similar when you know carbonate system is the only acid-base system present in considerable quantities anyway but let us say if we have you know solution where we have other what we say acid-base species in this case for example we looked at the phosphoric acid. So we are trying to analyze how would the system change or you know how would behave.

So again what we are trying to look at was earlier only HCO3 2- right where is CO3 2-, yes CO3 2- and HCO3- can take up the protons as you are going from pH 13 to pH 4.5 right but now what are the other species that can also you know consume your proton. You have PO4 3- here right, this is at your pH 13 so you have PO4 3- that can consume your proton right and what else would you have.

You would also have HPO4 2- where is that here? So HPO4 2- 2 can consume your proton right and you can also obviously have your H2PO4- where is that? That is blue, this particular species to consuming your proton as you try to bring down the pH from 13 to 4. Earlier only the pardon me what was it? CO3 2- and HCO3- were what we had to look at right but now we also need to consider the other conjugate base species of the phosphoric acid.

So these need to be taken into your account right, so earlier the only species that could you know neutralize your particular acid or the proton were CO3 2- and HCO3- but now what do you have? You have the other conjugate base species, they are PO4 3- and what is the HPO4 2- and H2PO4- right. So let us look at let us say how the equations would change, let us say in this particular or kind of a system.



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Let me try to write that down right here so that hopefully we can get some particular case, so the alkalinity equation if you are trying to calculate it again this is not the theoretical definition but let us just try to calculate that or estimate it let us see. What is it going to be? So we are going to write down our usual formula first which would have the carbonate species and OH- and such right HCO3- +2 times CO3 2- right.

So this is something that we know from our theoretical definition itself but we now additionally have the phosphoric system let us try to plug that in I guess. So here we know that we need to consider H3PO4 and what else + or – we will decide later, H2PO4-, HPO4 2-right and PO4 3-. So obviously you know which would be the positive and which would be the negative, obviously the bases would be the positive right.

Those which can neutralize your acid, so positive would be the bases right and the negative would be the acids right. So that is one case and then we need to look at what is the coefficient going to be. So in general we can assume that let us say you know it is PO4 3- can take in 3 protons and you know go to its protonated state of H3PO4. So I can say that the coefficient is going to be 3 right.

But that is not the case here. Why is that? Because we are stopping the titration at 4.5 itself right. Let us say I am starting from 13, I am going from here to here but I am stopping the titration at this particular point and at this particular point or the pH 4.5 what is this present as, it is only present as H2PO4 right. So it is not going all the way down or to its not down pardon me all the way protonating to H3PO4 that is what I am trying to point out here.

So here it is only going to be able to take 2 protons here right and here it is only going to be equal to 1 and this is my reference here right. Then, this is going to be 0 here, hopefully that makes sense and again why is that? Our alkalinity titration end point is 4.5 right, so we are only concerned with those particular bases which would be present which would coming to play when we are going or bringing down the pH to 4.5 right?

So if I had let us say my titration end point to be pH 1 then I could have written 3PO4 3-2HPO4 2- 1 and bla bla and so on but here I am still concerned with the H2CO3 equivalence point. So PO4 3- what can you transform into it? You can first transform into HPO4 2- right and then H2PO4-, it can only take 2 protons, it cannot go all the way down to H3PO4 because the pKa is 2.3 here right.

So that is the difference that we see here make sense hopefully right. Again so here again now if you measure the relevant theoretical not measure the theoretical pardon me measure the practical value of alkalinity. So it should hopefully be equal to what we just came up with here right. Hopefully that make sense, yes again it is nothing but you just want to consider those bases that would come into play in your pH range of interest and here our pH range of interest is not 14 to 0.

But let us say 14 to pH of 4.5 right. So if it was 14 to 0 then I would have taken all the other you know coefficients as in 3 times of PO4 3- or 2 times of HPO4 2- and so on but here I am stopping my titration at only 4.5. At that particular pH 4.5, we see that the relevant speciation for the phosphoric system it just ends with HPO4 2- which is my H2PO4- pardon me which is my reference yes.

So that is why PO4 3- can only take 2 protons to change state not state pardon me to move to its conjugate acid what we say species which is H2PO4- because why is that again we are only stopping our titration at the endpoint which is 4.5 here right. So that is the case here. So let us move on I guess right and we already looked at theoretical definitions now.





We looked at the practical definitions and we looked at when is it that both are not equal and how to will be able to calculate that yes we looked at that particular aspect. So now let us say we are going to move on and see how the system would change when I add a strong acid to my particular system, the second case is when I add a strong base to the system and the third case is when I bubble carbon dioxide gas through my particular system right. So let us write down the theoretical definition here again. We are again just if we are considering theoretical definition that means we are assuming that carbonate system is the only relevant species you know system present here right and I have this particular definition here +CO3 2-*2 times because it can take up 2 protons, so here if I add an acid let us see. What does that mean?

It means I am adding H+ right, so in effect you know it is going to decrease my alkalinity by so when I increase the acid right it means I am increasing my H+ concentration right or not increasing let us say I am adding H+ right, I am adding H+ so how would alkalinity increase now? Obviously alkalinity is going to decrease because it is –H+ right, I am adding H+ keep that in mind.

I know there is a minor interplay of words that I need to be careful about I am adding H+ by adding H+ obviously all the other species concentrations would change and bla bla yes but in effect if you are looking at it holistically how would it change compared to initially, it will only change by the amount of H+ you are adding to the system right. So that is what you see and how is that going to decrease. So for 1 equivalence per liter of acid added, it is going to decrease by 1 equivalent per liter of your alkalinity.

Yes, so whenever you increase or add acid by 1 equivalent per liter your alkalinity is obviously going to decrease by 1 equivalent per liter. So that is what we see here but now let us say if I am looking at the condition of the base where I add OH- let us say to my particular system as in I am adding OH- here so as you see here you know what would that lead to? It will lead to an increase in my alkalinity right.

Again keep in mind that the alkalinity is going to change and all the other variables are going to change to but if I am just comparing case 1 alkalinity 1 and alkalinity 2 and the only difference between 2 and 1 is that here I added some base right some known concentration of base let us see how is that obviously going to change. So the alkalinity of 2 is going to be equal to alkalinity of 1+ this OH- not that I added to this particular solution.

Yes, so that is what it means here, so again if I add 1 equivalent per liter of OH- so how will my alkalinity equation change? It is going to increase by 1 equivalent per liter right and that

is what we see from this particular equation. So that is relatively easy you know alkalinity is nothing but acid neutralizing capacity more or less, so obviously if you are adding acid, as it is more or less not more or less it is near to alkalinity.

So you are going to decrease that and if you are going to add a base you are now increasing the ending up, increasing the pH and the relevant conjugate bases. So it is going to have a positive effect on your particular alkalinity. So again by 1 equivalent per liter we just looked at the relevant equations but trickier aspect would be to consider when CO2 is bubbled through your particular solution or when CO2 is in equilibrium with your particular solution right.

So what is happening there? Let us try to understand system first. I believe we did talk about this earlier. So CO2 in the gaseous phase, so in equilibrium with the aqueous phase can transform to H2CO3 right and what will that transform to now, that can dissociate into either H+ okay let me come back to this later when I try to point out what it is people are up to. So usually people just you know look at this particular aspect that CO2 you know when the equilibrium will form H2CO3.

And since H2CO3 is an acid right and people go back to this particular case here and they you know look at you know acid right I am adding an acid to the system so people assume that their alkalinity is going to decrease. So keep in mind that you know yes H2CO3 is being added to the system so the pH level decrease yes because we are adding an acid but would alkalinity decrease to that is something that we need to look at.

And let us see where the key lies here so H2CO3 can dissociate into H+ and HCO3- and which can again further dissociate into H+ and CO3 2- right. So this is the key here, so let us say if I am just looking at this particular dissociation. So by adding H2CO3 or 1 equivalent per liter of H2CO3, I am increasing the concentration of H+ by 1 equivalent per liter and also HCO3- by 1 equivalent per liter right.

And so what does that mean? So here -1 and +1 so both of them just cancel each other out right or if let us say there is you know a more complete dissociation so for each equivalent of H2CO3 right and if I am looking at this particular dissociation let us say what is happening

here for each equivalent of H2CO3 that is going to be you know and put it into your solution, you are going to have 2 equivalence of H+ right and 1 equivalent of CO3 2-.

So if I look at this particular case right what is that transform into 2H+ but keep in mind here that it is equivalent. So if I look at the molar concentration, it is going to be 2 times so -2 and +2 of CO3 2- they again cancel each other out. So in effect when you bubble carbon dioxide through your particular system though the pH will decrease right, you are adding the other species like HCO3- or CO3 2- let us say, your alkalinity is constant right and so this is the key take-home message.

So when you bubble carbon dioxide which is an acid through your particular system you know obviously you are adding an acid so the pH is going to decrease right but the other variables too are going to be affected and what are those variables obviously here they are going to be HCO3- and CO3 2- right. So H+ and HCO3- they cancel each other out and 2H+ and CO3 2- they cancel each other out right or 2H+ and 2 times CO3 2- they cancel each other out.

And thus we end up with no change in alkalinity yes so this is the key aspect that we need to look at because we are going to end up widely looking at the applications with respect to this particular take-home message right. So now let us move on to one aspect you know let us try to briefly summarize what it is up to and then we will be done for today's session right.

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So obviously until now we have looked at alkalinity yes and we looked at why it is important to right it is the acid neutralizing capacity. So obviously conversely we are also going to talk about acidity right but acidity people look at you know different aspects so people call that as base neutralizing capacity right. So that is easy to understand but unlike alkalinity people do not look at just one endpoint, they look at different end points depending upon what it is that you are trying to understand about your system.

For example, in your alkalinity or acid neutralizing capacity you end up at equivalence point of 4.5 and that is it you are done with it but for what do we say base neutralizing capacity or acidity right what do people look at, they look at 3 particular equivalence point, one would be when you are trying to only measure the strong acids present in the solution and the other extreme would be when you are trying to measure all the acids present in the system and the other one phenolphthalein acidity in between both these particular equivalence points.

So we are going to discuss this particular aspect in the next class and for today's session I am done and thank you.