Environment Engineering: Chemical Processes
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Module No # 06
Lecture No # 26
VMINTEQ: Buffer System
Buffer Intensity: Introduction

Hello everyone so welcome back to our latest lecture session say again as the (()) (00:30) we are going to look at or have the brief summary of what we discussed in the last class I believe we are talking about or discuss in greater detail with respect to applications of VMINTEQ or visual MINTEQ to be able to predict your titrations yes so that is something that going to help you n cutting down you time yes and then starting talking about briefly about buffers so let us look at where we are?

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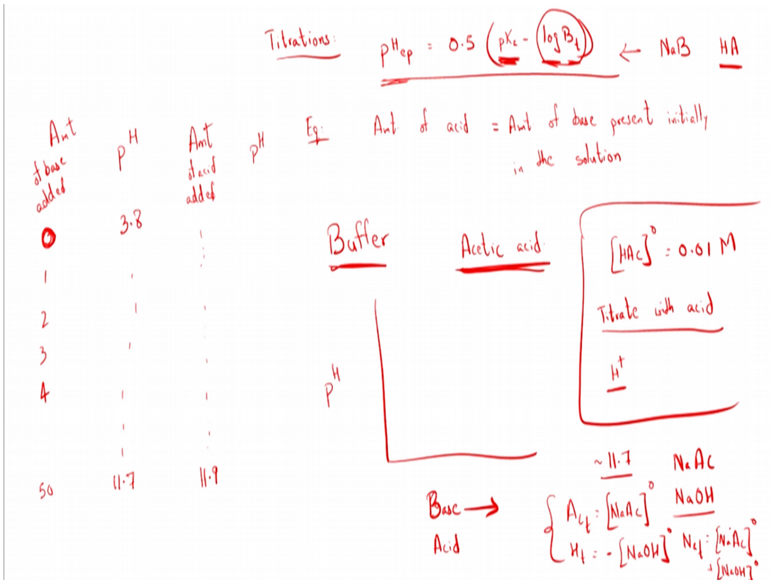

So we have been talking about titrations right and we came up with calculating relevant equivalents point and that was I believe it was 0.5 PKA – log total days or weak acids present or this is something that we derived right and I think this I derived when we had weak acid or conjugate base titrate again in known concentration of strong acid so for this particular case we derived this.

So from here we can clearly see that the PH of the equivalent point is going to be near the PKA right or more or less half of the PKA – log BT but because it is logarithm of total base right so the effect of the concentration of total base might be relatively less but the PKA is going to be the major factor so that is what you see here right. And again what is this equivalent point that is when the amount of acid added is equivalent to the amount of base present initially present initially in the solution.

So in effect what is this mean so we have some base here in our solution we know what is the base so that is why we have PKA of value or that particular base or the weak acid pardon me weak acid or base you know so we have the we know the base but we did not know the concentration so what are we trying to do we are trying to titrated with a known concentration of a strong acid.

So what is it you are trying to achieve here you are trying to see to it that we are going to consume all your base right by titrating with your acid yes so once you reach that particular equivalent point what is that mean so the amount o acid that you are titrate that with or titrated that I guess right or consume is going to be equal to amount of base that is initially present so then stoichiometric we can obviously calculate what is the concentration of the base that is present in your solution.

So that is with present to titration and then we move down to looking at VMINTEQ right and looked at titration and also the sweet menu right where you can change one parameter which in that case was PH but again the titration menu would be much more helpful when is it now when you are going to look at let us say complex titrant say when you have more than 1 constituent in your burette right in the previous example we looked at we just add an acid but let us instead of acid we had other constituents let us say other cations or anions which you are titrating again particular solutions.

Then you particular titration menu is going to do much more helpful right so we are done with that and then we moved on to buffers right and then buffers what is the role and why are trying to look at buffers because when we have a buffer in system they can resist the change in PH by either direction either decrease in PH or increase in PH they are going to resist the PH but obviously at not all the PH values at a particular set of PH values depending upon the kind of buffer you use.

Anyway we are going to discuss hat in greater detail but in general buffer again what are we trying to look at or what do we need to understand we need to understand that buffer can resist the change in PH in when you add either in acid or a base right the key is either you add an acid or base and in that particular contest we went ahead and looked in particular graph right when we looked at addition of acid and addition of base and try to identify the those of regions where you know the buffer capacity is high or the solution acts are good buffer and also those ranges of PH where the solution would not act as a good buffer.

So I believe we looked at in generic example but of the purpose of understanding the system better let us try to again go back to VMINTEQ and use titration and then let us see with respect to acid acetic acid is something that we have as an example used widely in the previous lecture session right of frequently pardon me. So we are going to look at that particular example anyway let us look at the example here.

So we are going to talk look at buffer and I am going to identify those regions where the solution which as acetic acid right where it is going to behave as good buffer let us say or going to give a good buffer I guess is (()) (05:41) I should not use the good buffer I should have said buffer intensity where the buffer intensity is relatively high right so we are going to look at that particular aspect.

So let us go back to our VMINTEQ here right and let me see that I am going to have addition of particular let me see okay I do not have anything here back to main menu so I am going to start with acetic acid so what do I need to have H right and let me go with acetic and 0.01 molal add to the list and again hesitate and I need to add the ionic compound which I believe I did same concentration right let me view and edit the list 0.01 and 0.01 so I am going to go back to main menu.

So what is it I am trying to achieve here I am trying to see to it that so what am I trying to achieve here that I am trying to see to it that I get a graph where I have PH here and then when I add an acid or base here in the first case obviously my system going to change and then when I add an acid again how is my system going to change and the example I am going to look at is acetic acid and we know that the PKA of acetic is what now I think 4.76 or 4.75.

Anyway VMINTEQ should take care of that and so now we are going to develop this graph for this example I am going to assume that initial concentration of acetic acid is know HAC or you know CH3COH is going to be 10 to the power of 1- 2 molar or 0.01 molar right so again what is the example we are going to look at that initially we are going to have HAC naught = 0.01 molar right.

And then I am going to set up the system such that I am going to titrate right and in this context I am going to obviously set that the H+ concentration changes so again back to ZMINTEQ here. So we already added the relevant components but now we need to look at the titration mechanism here so here is the number of titration steps let us say I am going to have 50 to be able to capture the side range of PH and then PH is the only output I am looking or I am now looking at concentration of the other aspects or the other variables like estate or the protonated form of the estate and so on.

So then going on to the titration manager I am going to choose a huge volume of the solution to be titrated what is that because I want to see to it that the concentration of these particular consequence in these particular solution do not change again I believe this is something we discuss one of the classes recently so think this where we are having or you know setting up the system in such a way that we have 10,000 of these units now the solution why is that.

So let us say if I just took 100 and I added 20 ML or 20 units of titrant you know the total volume is going to be 120 or the concentration are going to change so to get around that what we are trying to do we are going to create a hypothetical situation or look at hypothetical situation pardon me when you know we have a huge volume right you know in this case 10,000 units and I am going to tighten it with let us say 20 or in this 50 times with one unit each so 10,000 and 50 does not make much different in the concentration of the relevant components.

But obviously for this to be achieve or you know for my objective to be achieved which is changing PH I need to increase the concentration of acid or base that I am putting in right. So again let us come back to the system. So here I am having the huge volume and then I have let us say volume of titrant to be 1 so in 1 unit and it is only going to start at second step because I want to know what the initial concentration is going to be right and then I am going to add a base because I know that initially the PH is going to be less because I put in acetic acid so where is the base here okay.

So and here the base because I need add the negative value here right so it is going to be – 3 let us say you know that is something I believe I looked for trial and error earlier so let us save that so what is this mean I am adding three most per liter of the base – indicates it is a base but obviously the components in the VMINTEQ only have H+ right not OH- . So again save and save and back to multiuse menu and here 50 steps so 50 steps of one unit each of the titrant and PH is going to be my output.

So save and back and I am going to run the VMINTEQ right and obviously the first case we can look at is because I am just adding HAC obviously PH is going to be in the decreasing 3.38and the number of titration here are 50 as you can see or iteration pardon me and then I need to look at the selected sweep results and I see that with my increase in base concentration problem 1 means 0 base added and -3 molal at 1 unit concentration is added at problem 2 and so on hence so forth until we reach 50 unit I guess.

So as you see the PH is initially less or acetic and then as you keep adding the base you see that concentration keeps increasing and then we end up with the concentration of basic region. So here keep in mind that the final PH is 11.6 why because we look at the titration with respect to the acid we are going to try to start from this particular PH anyway what can I do I print this to excel and I guess it is somewhere out here and here we have the relevant data right.

So I am going to close this because I have saved what it is that read earlier we are going to come to that later right and so again let us look at what we just have let us come back to our slide. So for now we have particular you know data where we have PH and amount of base added right so initial base PH was pardon me around 3.8 and this base was 0. So 1, 2, 3, 4 and 5 until 50 and I believe we ended up with PH of 11.6 or 7 right.

So now I am going to choose second case where I am going add acid amount of acid added right but now I am going to start from 7.7 or 11.9 I believe and then I am going to look at the decrease in PH so that I can have the relevant graph so let us go back to VMINTEQ and look at how to go about it right I am going to come back here hit my list obviously right and estate I am going keep that as same but to be able to come up with the higher PH value right.

So now initial PH should be around 11 point what 7 so I am going to say that I added NAOH and also NAAC right NAAC is a base conjugate base so the PH would be would be relatively basic but it probably not be or certainly not be as high as what is it now 11.7 so I am also going to add in NAOH to be able to take the PH to around 11.7 right so let us go with 1 trial.

So let us see what we have here so H needs to negative obviously so we are going to go back to the key here and – so this means I am adding the base NAOH and this is the NAAC so I am adding NAOH and NAOC right back to main menu and obviously I need to add the sodium and let us look at where that is KLM and A right and here I am add as 0.02 so add to that list so again what is that mean initially adding NAAC and NAOH right so that is the case how we are running up with these particular case right.

Anyway in case people are confused you know let us go back to the slide and come back to so what are we adding here and here we adding HAAC naught initially but to be able to start with a PH near 11.7 we are now adding NAAC base and also NAOH right. So what is why you know the estate total is going to be equal to the NAAC added initially and H total is going to be equal to negative concentration of NAOH added initial and you know from background that we have added in the previous classes and obviously NA total is going to equal to sum off NAAC add initially and NAOH add initially so his is the trail I am going with.

So let us go back to where we are list of component so this is the relevant component here or these are the relevant component here back to main menu and maltase problem and sweep so I am going to still stick with 50 ah you know titration steps and I am still going to look at PH but at the titration manager where earlier we you know added a base right that is what -3 indicates we need to add a acid now.

So to be able to able to have a comparable graph I am going to keep the concentration of acid same and all the other units is same right. So I am going to read this component again go back to finding H right and then I am going to say that it is going to be equal to the same concentration of base that was added earlier. So save and next save and back to maltase sweep menu and save and back and now I am going to run the VMINTEQ right.

So obviously the first case that we end the PH of the 11.9 so 11.9 is bit higher than 11.7 which is what we are aiming for but to save time we are going to go ahead and look at this particular step for trial and error right. And so then we are trying to look at circuit sweep results so initial PH was high because we add NAAH NAOH in our system and then we end up what do we say adding the acid and obviously as you see the PH decrease and decreased will around 4 or so right.

So that is what we have here again I am going to print this to excel and so on but to save time we already have relevant data in an excel sheet.

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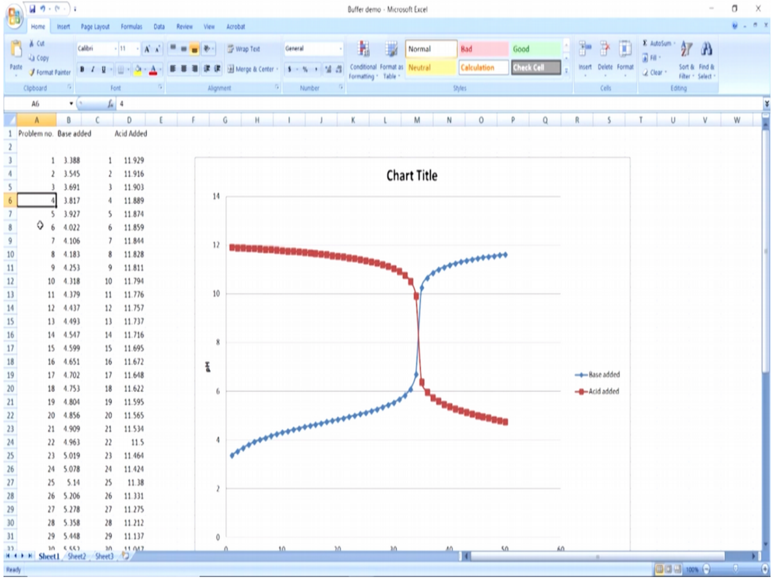

Problem no.	Base added		Acid Added
1	3.388	1	11.929
2	3.545	2	11.916
3	3.691	3	11.903
4	3.817	4	11.889
5	3.927	5	11.874
6	4.022	6	11.859
7	4.106	7	11.844
8	4.183	8	11.828
9	4.253	9	11.811
10	4.318	10	11.794
11	4.379	11	11.776
12	4.437	12	11.757
13	4.493	13	11.737
14	4.547	14	11.716
15	4.599	15	11.695
16	4.651	16	11.672
17	4.702	17	11.648
18	4.753	18	11.622
19	4.804	19	11.595
20	4.856	20	11.565
21	4.909	21	11.534
22	4.963	22	11.5
23	5.019	23	11.464
24	5.078	24	11.424
25	5.14	25	11.38
26	5.206	26	11.331
27	5.278	27	11.275
28	5.358	28	11.212
29	5.448	29	11.137

So let us look at what I have so here I have the titration step here 1, 2 and so on in the first case we have the case where we have added the base these are the results so we that the PH increased and the second case I have acid added right that is why we see that the PH is decreasing and then I plotted this here and this particular graph and we see PH on the Y axis and acid and base are on the X axis.

So let us see the blue color legend is for the base added so we started around PH3 that is what we see here 3.3 and we started adding the base and we see that the PH increased right that is what we see here and with respect to the acid we started at around PH 11.9 right and then started adding the acid at equivalent quantities and we see that obviously decrease around I believe 4 I guess 4.2.

So now we are going to try and understand this graph right this is similar to what we looked at earlier but keep in mind that we are looking at specific example here when we had acetic acid or estate in the solution the relatively similar concentration which what is it now 10 power -1 molar right. So in one case we looked at adding the base from a lower P from take the lower PH to higher PH the other case we looked at bringing down the PH from around 11.9 to 11.4 or you know 4 I guess.

So that is what we are looking at and what is the point of success we are trying to identify those zones and the particular system where if you have acetic acid present will you have buffer capacity right or buffer intense. So we are going to look at that let us say so obviously we are going to look at those zones where the PH changes relatively changes right the change in PH relatively less with the change in acid or base added.

So obviously as you can see what is that mean that whenever the slope is less or when it is less steep that means that change in PH you know for example if I look at it region let us say it means that in this particular region you know you need to add a lot of base or lot of acid right so if you look at this region we need to see that you know to go from PH around 12 to let us say 11 let us go with 11 so let us say 11 here I need to add 20 units of that three moles per liter of acid and same case here to go from OH of around 4 to PH to PH of around 5 let us say I need to add around 20 units of base right.

So what is that now for small change in PH or large what we say amount of acid or base is required so the acts as a good buffer in this particular region right so coming back to this region what do you see. You see that this slope is very steep here right so what is that mean for a small change in PH as in or a even with a addition of small base so let us look at this particular region right what do you see even with few quantities units of acid or base added but PH is changing from 10 to 6 or again going from 6 to 10.

So in this particular region we see that the system acts as very poor buffer right again obviously at the higher PH when because the logarithmic scale you know as you go to the extremes the to change in you need of add lot of base lot of acids again you will see that the system acts as a buffer or good buffer at the extreme PH values.

So again what do we see around PH 4.76 we see considerable what do we say buffer capacity so we are going to come back to this keep in mind that we are looking for small changes in PH even considerable quantity of base or acid is needed so that is when you say your system that your buffer is worthwhile for you to be able to use at that particular range of PH. So for example here the take home message is are that you know let us say you have the buffer that does not mean it going to resist the change in PH at all the PH right.

So you see that their only the particular ranges you know within which you know the particular buffer is in this acetic acid and the state are going to act as good buffers that is the key here so their only specific ranges we are going to try to identify what these ranges are and so on and hence so forth yes so let us move back to our system here.

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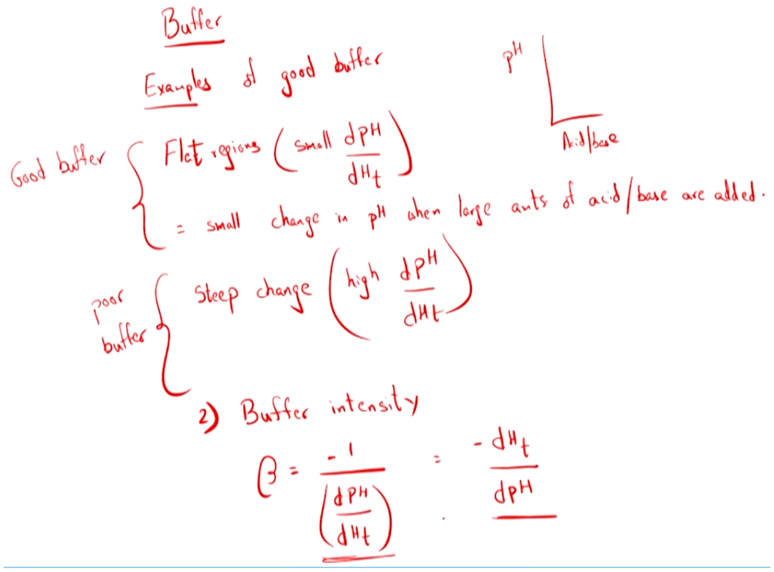

Buffer

Examples of good buffer

Good buffer { Flat regions (small $\frac{dpH}{dH_t}$)
= small change in pH when large amts of acid/base are added.

poor buffer { Steep change (high $\frac{dpH}{dH_t}$)

2) Buffer intensity

$$\beta = \frac{-1}{\left(\frac{dpH}{dH_t}\right)} = \frac{-dH_t}{dpH}$$

So we looked at these particular graphs and we done with looking at buffer right example of good buffer what are they I guess example of good buffer how can you identify them you can identify by looking at the PH versus the PH versus acid or base added with graph right and you see that flat region right what is that mean when there is a small change in PH with change in either acid or base edition DPH / DT that DHT pardon me.

So again what is that mean that means small change in PH when large amounts of acid or base of added this is what we see. So in this particular flats regions we see that the system is a good buffer so obviously conversely what is that mean when we have steep portions or you know steep change in PH or steep change in slope pardon me or you know high slope DPH / DHT right.

So in this cases the system acts as an poor buffer right so again H total not H because this is some mistake that people make thinking that this is a change in PH which change in H + why is that because H total takes into account both the acid and the base added but H+ takes in account only the acid added right so when we are looking at change in the PH when resisting the change in PH when either the acid or base is added so thus we need to look at that particular aspect which is H total here right DP / DHT.

So now we are try to quantify what is that we are up to right again you do not need to mug up the this derivations are such same case with equivalent point derivation or any other derivation we looked at the objective is able to understand the basics or fundamental behind what we have observe or the equation that you typically end up using because in general they are bound by some assumptions.

And obviously you know when those assumptions are not valid your equations are invalid to so in general though when we looked at or you know we try to use equation or such blindly or especially the derived equation you know without having an understanding about underline you know not fruitful in long term to end up just mugging up the equation so again we do not need to mug up derivation you need to have the understanding of we are looking at right so let us to back to where we are.

So now we are going to look at a new particular term that is called the buffer intensity right so beta is what we are going to use it so what is this how can you define that let us say obviously how can you quantify that so we are looking at we are trying to bring a relationship with the change in PH whenever H total is added right and you know that when the region is flat or when the slope is less the buffer intensity is high and when the slope is high or the steep is slope the buffer intensity is less.

So obviously it is inversely proportional thus so – 1 / the slope which is the PH / DH total right so this is what we have so this is the total intensity and that is going to be equal to – DH total / DTH right people might look at it keep mind this is the source of your particular buffer intensity. So in the next set o slides or you know few minutes we are going to try to calculate this particular buffer intensity again why is this buffer intensity useful thought right.

Let us say you know you are trying to you know and this is your engineering system and you want to add a particular acid or a base or conjugate acid system to be able to resist the change in PH so how do you know how much amount of acid or base is going to add for that you know you are going to need buffer intensity right you will first need to be able to estimate what is the allowable range of PH but you are fine with as in are you okay with the PH let us say you are trying to maintain your system at PH7 are you okay with system swinging from 6 to 8 or do you want to have very highly buffer solution where you are only fine with 6.9 to 7.1.

So obviously if it is if you are okay with if you can live with PH change from 6 to 8 right you need to have remarkably high buffer intensity and if you pardon me low buffer intensity right again if you are again high PH change so that means your buffer intensity can be less but you are fine with it if you are want to be able to maintain a system within a narrow range in this specific example let us say 6.9 to 7.1 you obviously need high buffer intensity right.

So in the next session we are going to look at this particular derivation with respect to buffer intensity and we are going to try to link that to relevant aspect that we know what are they now. Obviously we know that going to PKA right certainly PKA and also the amount of base or you know this total base that is present in your solution. So we are going to first apply that to a monoprotic and then to diprotic acid and look at the relevant aspects their and I guess we are running out of time so with that I will end today’s session we will continue that the other aspects in the next session thank you.