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

## Lecture - 33 Mixing of Two Solutions and Conservative Quantities – II

So hello everyone welcome back to our lecture session. So you are looking at mixing problem right when we mix solution A and solution B with different pH and different alkalinities and we end up calculating the pH of the mixture and I believe we looked at cases, two cases, one how to work it out by hand and one obviously how to work it out by VMINTEQ which usually ends up being faster and more efficient too right.

Again but you need to have a grasp of the fundamentals otherwise you are going to go a miss that is the reason we try to work it out by hand use. So here we have 2 other parts of same question, but some of them or at least the third one is a bit more complex. So let us try to see how we can go forward right.

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	Water A	Water
		В
pH	7.2	8.4
alkalinity (mg/L as	200	400
CaCO <sub>3</sub> )		

A volume of 2 liter of a water A is mixed with 3 liter of water B.

a) what is the pH of the mixture?

b) what would be the pH of the mixture if it were to equilibrate with carbon dioxide in the atmosphere ( $P_{co2} = 3.8 \text{ E-4 atm}$ )? c) what would be the pH of the solution if 1 E-3 M HCl were added after it

equilibrated with the atmosphere?



So let us just look at this next part of the question, we have what would be the pH of the mixture if it were allowed to equilibrate with carbon dioxide in the atmosphere. So earlier let us say this was a closed system right and now what are we considering it here that it is an open system right. So let us go back to VMINTEQ here.

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And we already plugged in the relevant values and I think we ran the VMINTEQ where is the output.

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-1	1.29996-08	1.37546-08	-2.881		
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So we had a pH of 7.8, but this as we just looked at it is for a case of the closed system and now we want to look at how do we go about it if the partial pressure of the carbon dioxide. So now your solution let us say is now in equilibrium with this partial pressure of carbon dioxide and that is given us 3.8 \* 10 to the power -4 atmospheres and this is your solution that you looked at initially in case A right.

So now what is the new values or such so we need to look at some of the relevant aspects. So again what are these aspects that we need to look at. So if you remember what we discussed with the respect to alkalinity, and if you can recollect what we discussed right. So if you

bubble carbon dioxide through a solution obviously H2CO3 is going to be increasing or not increasing let us say depending on the concentration, H2CO3 concentration is going to be affected and let us say now it can increase in this particular scenario let us say.

Thus the pH will come down that is fine, but we did look at the relevant equation for alkalinity and we saw that bubbling carbon dioxide through the particular solution or equilibrium with carbon dioxide will not affect alkalinity in any manner right. So alkalinity is going to be constant. So that is the key aspect that you need to consider here. So again like earlier or similar to the previous case we are just going to understand how to get this done by hand right.

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So what are the fundamental aspects here, so here we have alkalinity = alpha 1 + 2 times alpha 2 \* Co3 total + Kw/H+ - H+ right. This is something that we have used in the previous session too. So I do not need to elaborate. So again first we are going to look at how to calculate this by hand. So the key is we have let us say alkalinity, yes, but we do not have Co3 total right and wise that now your partial pressure of Co2 right that is going to equilibrate with your solution now, right.

So there is going to be an exchange of Co3 total or Co2 here in this case between and here H2Co3 right. So the Co3 total will change here yes. More or less Co2 it is nothing but a component you know, you can express it in terms of Co3 2- or it is going to thus effect Co3 total. So the Co3 total in the liquid phase + Co3 total in the gaseous phase = Co3 total total I

guess right, I should have expressed that in a better manner, but here we are going to cancel this particular case yes.

While the total Co3 of the entire system is going to stay the same because there might be an exchange of Co2 between the gaseous and the liquid phase you know the Co3 total in the liquid will change, but one key aspect that we discussed was that alkalinity which we define as, how did we define that, on the basis water the OH- and HCo3– and 2 times Co3 2- right, -H+.

This is not going to be affected when you increase the carbon dioxide concentration, so why is that. So Co2 equilibrate in solution with H2Co3 right. So H2Co3 can either dissociate to H+ and HCo3- or if I look at complete dissociation H2Co3 can dissociate to 2H+ and Co3 2-. So if I plugin let us say this particular case here and this equation what do I see, 1 HCo3-increases, but then H+ also increases so both of them cancel each other out so there is no effect on alkalinity.

So same case here, again, if I look at the case where H2Co3 completely dissociates. So increase of 2H+ and increase of 1 of Co3 2-, but because of the equivalence the effect is going to be twice. So 2 times that -2 times of H so again that is going to cancel each other out and again there is going to be no effect on alkalinity.

So again we are just trying to refresh what we discussed in the previous classes that if you bubble carbon dioxide though the solution. So you might or you will probably see a change in the pH right, but you will not see any change in the alkalinity of your particular solution right. This is the key that we are going to look at. So again looking at some of the few aspects what we discussed earlier.

So we need to come up with the way to understand the Co3 total of the system right. In this case obviously we were trying to look at Henry's constant, right. Henry's constant which is usually expressed as H, what is that equal to concentration in the or activity in the gaseous phase by activity in the aqueous phase right. So gaseous phase activity we look at partial pressure and in this particular case activity of H2Co3 right, which I am going to approximate obviously by the concentration, PCo2/H2Co3 concentration right.

So this is the particular case for Henry's constant which the units are atmospheres per molar units right, but let us say I am going to consider another particular case of what to say molar per atmosphere units. So then it is going to be = H2Co3 concentration/partial pressure of Co2, right. Again Henry's constant has different units when the units are atmospheres per molar units.

So this is the particular definition obviously, when obviously you know I am going to look at the inverse unit's same case I am going to just look at the inverse of the variables here right. Anyway you know people use them depending on the situations. So here I am going to look at this particular case of Henry's constant, right. So how can I further simplify this, we talked about this earlier.

So I am going to write this down here KH = what now alpha 0 times Co3 total/partial pressure of Co2 right. That implies that Co3 total which is what I am going to calculate is going to be equal to what now, KH times PCo2/alpha 0. Again keep in mind that in this particular case KH the units of the Henry's constant R molar units per atmosphere, not atmosphere per mole right.

So that is the one case that we are going to look at, again this something we derived earlier. So now I can plug this in here right.

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$$A_{1K} + = (x_{1} + 2x_{2}) C_{0} + \frac{K_{u}}{[n^{2}]} - [n^{2}] C_{0} + \frac{K_{u}^{2} c_{0}}{\alpha_{1}}$$

$$A_{1K} = (\alpha_{1} + 2x_{2}) \frac{K_{u}}{\alpha_{1}} \frac{P_{co}}{\alpha_{1}} + \frac{K_{u}}{[n^{2}]} - [n^{2}]$$

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Let me just write this down in the next particular slide so I have alkalinity + or = alpha 1 + 2 alpha 2 \* Co3 total + kw/concentration of H+ - concentration of H+. So now we had a new

relationship what was that, we had Co3 total, Co3 total was or = KH \* partial pressure of Co2/alpha 0 is that right. KH yes that is right, so I can plug this in this equation so now I will have alpha 1 + 2 alpha 2 \* Henry's constant obviously it is a constant partial pressure of Co2/alpha 0 + kw/concentration of H+ - concentration of H+ right.

So what do I have here I know that by bubbling carbon dioxide through the solution the alkalinity does not change. So I still have the alkalinity right. In this particular case alkalinity is the known value yes, and what else do I have. I have the partial pressure of Co2 yes and from this I can solve for what now, I can solve for H+ concentration, right. The only unknown in this particular equation what is that now.

It is H+ right again as you know alpha 1, alpha 2 and alpha 0 are just functions of H+. So from this particular case I can solve for H+ and obviously I can now analyze the system right. So this is by hand obviously again it is going to be tedious now to be able to solve these particular what do we say this particular equation obviously you can use XL and solver function within that maybe depending on time we can look at that later.

But now we are going to skip through and look at how to calculate this particular or go though by VMINTEQ, analyze this system by VMINTEQ right. So let us switch back to VMINTEQ and where do we have that here and view edit list, this is something we already have plugged in from the previous lecture session.

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These were the values of H total and Co3 total we calculated from the component balance right and now though I need to have a new case or new variable. What is that obviously okay and the case is that now I have a new partial pressure of Co2 that is in equilibrium and what is that, it is 3.8 \* 10 to the power -4 atmospheres right. So I need to go back to VMINTEQ here. So I am going to gases and specify.

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So here I can specify different gases as choose a gas among the database, but because it is carbon dioxide you know that is something usually built in okay. So here atmospheric partial pressure is 3.8 \* 10 to the power -4 atmosphere which is given and you can specify a multiple of that if you want to, but in our question I guess for the sake of ease we already have the PCo2 given as 3.8 \* 10 to the power -4. So I do not need to change this particular multiple.

For example, it was 7.6 \* 10 to the power -4 then I can change this to 2 right, but here it is just 3.8 \* 10 to the power -4 which is similar to our question so I am just going to leave that as 1. I am going to add that, right, so if I look at list of fixed species now there is going to be an additional species which is carbon dioxide right.

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And back to main menu and now I am going to run VMINTEQ I guess yes and there was some minor issue here. Let me go back to looking at this particular case, where is this view edit list and working. So that is fine and so obviously now the pH is now higher and what is it now.

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It is going to be 8.98 right. So what does that tell you though. Whereas this particular case so now the pH we end up with was 8.98 and earlier the pH we calculated was 7.88 right. So earlier case one when we had just the solution, the pH was 7.88 and now when we have it in equilibrium with partial pressure of Co2, the pH came out to be 8.98 and why is that let us say, maybe because the partial pressure that would be in equilibrium with 7.88 that is going to be higher let us see.

So what happened was carbon dioxide or H2Co3 entered into the system or left the system, right and that is why you had an increase in pH and that is what you see here, pH is 8.98. So in this particular case what happened now. The carbon dioxide or H2Co3 left the system and that is why you see an increase in the pH. So just for the sake of analysis try to understand system, let us try to increase this particular value and see what you would come up with.

So I am going to go back to input menu, going to go back to gases so here let us say instead of 1, right, I am going to have let us say let me go with 5 for now, random value adds and back to back menu and again run MINTEQ right and so again now you see that the pH has fallen, but not to a great extent. It has now fallen to 8.3. Let us go back and change it again or increase the concentration and let us say I am just for the sake of this is the theoretical aspect right 100 let us say right.

I am going to add that, add that and back to main menu and run MINTEQ and now you see that the pH is starting to fall further right.



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So let us go back to our particular case. So what do we see here when there was no partial pressure of Co2 or Co2 with equilibrium, we end up with I think something around pH of 7.88 closed system, when it was an open system right. There was no partial pressure of Co2 here or no Co2 in equilibrium with this particular solution. Open system, so this was the close system. We end up with pH of 7.88.

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And when we took an open system when let us say you know your particular solution could be in equilibrium with the solution at partial pressure of Co2, not solution pardon me, the gas of partial pressure of Co2 at 3.8 \* 10 to the power of -4 atmospheres, right and what happened now we saw that the pH increased to the particular value of 8.98, pardon me, right and why is that because you can obviously understand that.

So the pH increased what does that mean now, if the pH decrease, you would have understood that let us say Co2 entered the system right and form H2Co3, but here in this case compared to case A of case B you see that the pH increase, it is now 8.98 right. So what does that mean. So H2Co3 left the system right. So thus you know the pH decreased, not decreased pardon me, the H+ concentration decreased so thus the pH increased that is what we see here.

So just to illustrate that I ended up what do we say increase in the concentration of partial pressure of Co2 to 100 times this value of 3.8 \* 10 to the power -4 right or 3.8 \* 10 to the power -2. So in that case when I increase that partial pressure of Co2 the case 3 let us say PCo2 I increased to something around what is it now 3.8 \* 10 to the power -2 atmospheres right and then I think we came up with the particular value what was that.

We came up with pH of 7.0 right, we came up with the value of pH of 7.02. So I increased it by 100 times compared to this case 1 and case 2 right. So compared to this particular case what is happening here. So case 1 again we looked at 3.8 in 10 to the power -4, we see that

Co2 left the system that is why the pH increased, but case 2 when I increased the partial pressure of Co2 to a very high value which was 100 times given in this case 1.

I see that the pH fell, so what does that mean, it means that Co2 entered the system, Co2 entered the system, right H2Co3 was formed and that is why the pH fell. In this case what do I understand that the Co2 left the system, right. So that is what you see here and that is the difference between this case of 8.98 pH and pH of 7.02 right. So again let us go back to the VMINTEQ here right.

And we will try to solve for the last question here and so this is slightly complex case obviously and what do we have here, what would be the pH of the solution if 10 to the power -3 molar HCl were added after it equilibrated with the atmosphere. So the key is now we are adding 10 to the power -3 molar units of HCl right. So let us see how to analyze the system. So first we need to obviously have the relevant values from the previous run or iteration.

So let us go back to VMINTEQ. So I am going to go back to gases again. So the case was that it is 3.8 \* 10 to the power -4, so I need to get that back there, so I am going to add that here.

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Back to main menu and run MINTEQ right. So obviously again we are going to have that pH 8.98 right because I decrease the concentration of partial pressure of Co2 or decrease the concentration of Co2 gas. So I need to again calculate Co3 total right and H total so I am going to do that here yes. Let us go to print to excel.

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Let us try to calculate Co3 total first so that is going to be = H2Co3 + HCo3 + Co3 2- and enter.

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So we have something like 6.1 \* 10 to the power -3. So now we are going to try to calculate H total. So H total = H+ - OH- + 2 times H2Co3 + HCo3 – and enter. So now I have 2 values here what are they 6.1 \* 10 to the power -3 and let me write this down right. So that we do not skip through that again, my excel slide here is somewhere here okay, it is 6.1 \* 6.148 \* 10 to the power -3.

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CO_{34} &= & 6.148 \times 10^{3} \\
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And what is my H total? H total = 5.836 \* 10 to the power -3 right. So that is what we have here. So again let us go back to the question and understand that, understand where we are at right. So here again the key is that we need to analyse the system from part B why is that because it says the question number C says or part C says we are adding HCl, but after the solution equilibrated with the atmosphere right.

So that is why I am going to go with that right and how much HCl am I adding, 10 to the power -3 molar HCl. So let us go back to this particular case, VMINTEQ back to input menu so now there is no more gas so it is already after equilibration. So let us see I am going to list a fixed species, delete this species and why is that because now we do not have that particular equilibrium anymore.

But now I am going to change my particular scenario here with respect to H total and why is that because I add HCl right at so that HCl 0 at 10 to the power -3 molar concentration, right that is what we have here. So obviously what is going to change here. Once we are going to look at it by hand yes. So what is going to change is Co3 total is going to change, think of that now. So what are the aspects that are going to change now. Co3 total it is just H2Co3, HCo3- and Co3 2-.

But you are just adding HCl. So there is no effect on Co3 total so that is going to be a constrict, yes, so that is one particular aspect. Obviously the pH will fall because you are adding H+ or HCl, the strong acid so that is something you need to calculate so what else can you calculate though. So you know the alkalinity from the previous session right. You know

the session before that you know the alkalinity and you can calculate by subtracting this particular acid concentration from alkalinity you can calculate the new alkalinity.

What am I trying to say here (()) (20:25) so alkalinity you know after addition of HCl I will have this it is going to be equal to alkalinity initially from part B right – concentration of acid or strong acid added right and why is that again, just think of this now alkalinity is the equation was HCo3- + Co3 2- \* 2 + OH- - H+. So when I am adding HCl what does that mean, that means I am increasing the concentration of H+ or you know adding acid here, right.

So that means alkalinity is going to decrease so that is why I say that in part C I guess right we are in C. So alkalinity after addition of HCl is going to be alkalinity initially that we calculated from or we can calculate from part B - HCl 0 right. So what is that equal to now. Let us try to see that here. That is equal to  $6.4 \times 10$  to the power -3 right – and what is this particular case it is  $1 \times 10$  to the power -3.

So that is = 5.4 \* 10 to the power -3, right that is the alkalinity for this particular case that is going to decrease by the amount of acid you plugged in and what else do we have we also have Co3 total that is given right and what is that equal to Co3 total = 6.148 \* 10 to the power -3 or let us say 6.2 \* 10 to the power -3, right. So by hand how can I solve this. I still know that the alkalinity equation.

So I have this particular here, so alkalinity = alkalinity with HCl after addition of HCl which is this value = alpha 1 + 2 alpha 2 \* Co3 total + Kw/H+ - concentration of H+ right. So what do I have here, I have alkalinity after addition of HCl which we just calculated here right. I also have Co3 total, so this is from part B more or less right. So I calculated this or I have this let us say and I just need to now be able to solve for H+ right.

So that is the only unknown so I can solve for H+ here again and I will be done with my particular scenario right. So now let us look at how to solve this by VMINTEQ now right. (Refer Slide Time: 23:04)

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So what can I do here let us say or alternatively I can also be look at total H by hand so that is something we are going to just discuss. So how can I do that so total H how much did we calculate that to be total H was 5.836 \* 10 to the power -3 from part B right. So in part C right what am I doing, I am adding HCl right at 10 to the power -3 concentration. So what does that mean the total H or H total after addition of this HCl is going to be H total initially + addition of the concentration of this HCl right.

And what is that equal to 5.836 \* 10 to the power -3 that is H total initially from part B + how much acid am I putting in here that is going to be = 10 to the power -3, right. So that is going to be = 6.836 \* 10 to the power -3. So again earlier we looked at it with respect to Co3 total and alkalinity right after addition of HCl another way to calculate by hand is to look at the effect on total H and how is that, so how are you increasing or how are you affecting H total here.

So H total right you are only adding acid which is going to be affected by increase in H+ so that is why you know H total after addition of HCl is going to be equal to H total initially plus the concentration of strong acid that you are plugging in. So strong acid meaning I am assuming that everything or all the acid is going to dissociate so all the H + is going to be donated here, right or is going to stay in the solution.

So that is why I have HCl here and with that I now have H total given here. So from this what can I calculate I know that H total is going to be = H+ - OH- + 2 times H2Co3 right + HCo3-, right this is our usual case. So H total after HCl though right, so this H total after HCl

addition is going to be = H+ -Kw/H+ right + 2 times alpha 0 + alpha 1 \* Co3 total right. So what do I have in this particular equation this we have known value.

Alpha 0 and alpha 1 are functions of H+ and Co3 total is the known value which we calculated here in the previous slide. So here this is just a function of H+ and now I can calculate after by hand or manipulation or using excel. Let us say if you want to I can calculate H+. So we looked at 2 cases when we looked at the effect on alkalinity which is going to decrease because you added HCl or on H total which is going to increase because you are adding strong acid right.

So here there are 2 cases so the next case is how to solve this by VMINTEQ. (Refer Slide Time: 26:10)



So VMINTEQ, so how do I solve this now. So again I am going to plug in H total after addition of HCl and also what else please Co3 total after addition of HCl which is still going to be Co3 total initially right and why is that because HCl is not going to effect Co3 total, yes and here H total HCl what was that equal to, let us look at that H total after HCl addition was = 6.836 \* 10 to the power -3 right and what was the Co3 total value, did we calculate that somewhere.

Co3 total was 6.148 \*10 to the power -3 right by VMINTEQ let us see how we can cut down on the time and make it more efficient. So again in VMINTEQ we just need to plug in the values of the total components and which is what we are going to do. So I am going to switch

to VMINTEQ here so obviously first case is I need to check that there are no gases right, list of fixed species so nothing here.

So then I need to edit my list what is the concentration of H+ here I need to look for that here please one second okay. H total is 6.836 \* 10 to the power -3, right. So let me plug this in 6.836 right and next I need to edit the Co3 total and I need to first have that particular component here Co3 total. So now I need to check it is 6.148 \* 10 to the power -3.

So 6.148 \* 10 to the power -3. I am going to add that to the list so view edit list 6.836 \* 10 to the power -3 and 6.148 \* 10 to the power -3 and back to the main menu and now I am going to run MINTEQ.

Stand Milling, Colord				
File Options				
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M2C03 (aq)	6.3310E-04	6 9362E-04	-2.159	
0.005	1 27896-02	147966-07	4.775	
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View species distribution	Display saturation indices	Equilibrated mass distribution	•	
View species distribution	Display saturation indices	Equilibrated mean distribution	Back to I	zhrg annus
View species distribution	Display saturation indices	Equilibrated mean distribution	Back to i	yut menu

### (Refer Slide Time: 28:18)

Now obviously I see that the pH is now less, it is 7.2 right so let us understand the system here. So I now ended up with the pH of 7.2 right. So let us go back that particular case where we looked at comparison of different pH here this case. So initially for closed system it was 7.8 from part A right for part B after we let it equilibrate with the atmosphere 3.8 in 10 to the power -4 we saw that the pH increased to 8.98 and why is that because you were to left the system.

And in part C considering this solution which is now let us say assuming it is a closed system again not open to the atmosphere anymore. So the initial pH was 8.98 we can calculate the Co3 total, we can calculate H total right and from this particular case we plugged it in VMINTEQ and we ended up with the value of what is that please 7.2, right. So obviously

why is that because I am adding a strong acid HCl 0 of concentration of 10 to the power -3 molar right.

So again let us just try to understand system, close system different cases given right and we ended up with the pH of 7.8 open system Co2 escaped into the atmosphere and thus our pH increased yes. So Co2 left the system yes in fact H2Co3 left the system right. So that is why the pH increased and that is why it went to 8.98 and then after that we added again HCl right and then obviously you are going to see a decrease in the pH and that is what you see here.

So we are now, at this stage you should now be comfortable to understand the basics of fundamentals behind the acid base systems and also be able to use VMINTEQ to be able to solve you particular scenario right. So with that we will end today's session and in the next session I believe we are going to look at the last aspect with respect to acids and bases that is going to be the case when your theoretical definition of alkalinity is not consistent with the practical measurement that you come across, okay and with that I will end today's session and thank you.