

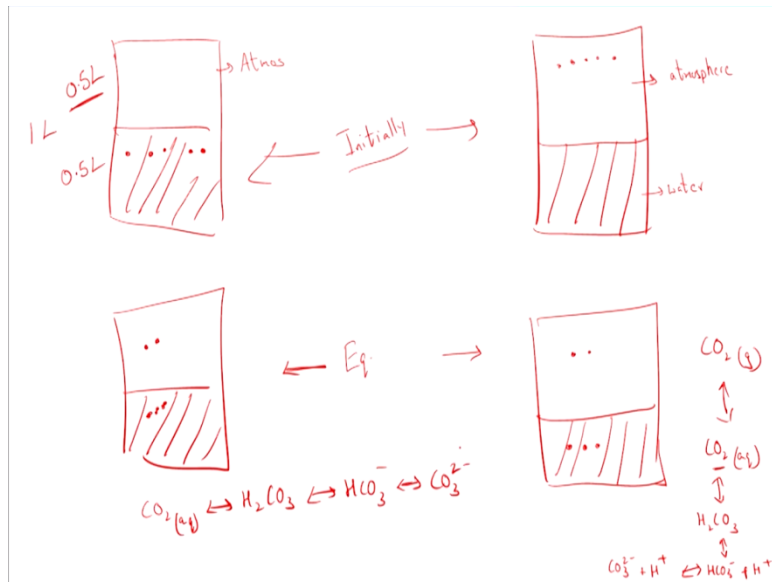
**Environment Engineering: Chemical Processes**  
**Prof.Dr. Bhanu Prakash Vellanki**  
**Department of Civil Engineering**  
**Indian Institute of Technology – Roorkee**

**Module No # 05**  
**Lecture No # 23**  
**Carbonate System: Open System**

Hello everyone welcome back so we have discussed the issue with respect to the closed system for the carbonate equilibrium right so we have carbonate as an  $H_2CO_3$   $HCO_3^-$  – and  $CO_3^{2-}$  and we looked at what were the relevant equilibrium concentration is going to be if you added the relevant compounds right initially and also we looked at how to use VMINTEQ in particular scenario and today we are going to move on to the much more complex system we it is going to be a open system.

And what is the difference here so earlier it was not open to atmosphere but now let us say the three particular species right  $H_2CO_3$   $HCO_3^-$  and  $CO_3^{2-}$  are open to the atmosphere. So while  $HCO_3^-$  – and  $CO_3^{2-}$  by themselves you know do not change phase  $H_2CO_3$  as you know right is going to stay in equilibrium with carbon dioxide in the aqueous phase and this carbon dioxide will equilibrate with the open system now right.

**(Refer Slide Time: 01:31)**



So let us see what that is let us try to present that in a better manner so here we have let us say this is water and this is atmosphere here. So let us say initially I have no carbon dioxide in the water or no carbonate system in the water I have nothing there initially and then let me say that I am 5 moles of CO<sub>2</sub> here initially in the atmosphere right and after equilibrium this is initially and after equilibrium has been achieved let us say what is it going to be I mean I guess we need to look at the relevant Henry's constant or such.

But now let us say you know there might only be 2 moles in the atmosphere and 3 moles now in the water so what is happening here when the carbon dioxide is changing phase from the gaseous phase to the aqueous phase and this particular CO<sub>2</sub> in aqueous phase can further be or will further be in equilibrium with H<sub>2</sub>CO<sub>3</sub> and will which will further be in equilibrium with HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> which will again further be in equilibrium with CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup> right.

So what happens to your system now if you have no moles of carbon dioxide in your aqueous phase or in the water and if you had some moles of carbon dioxide in the gaseous phase so you are going to have carbon dioxide between the system and then you will carbonate system you know H<sub>2</sub>CO<sub>3</sub> HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> being formed and also consequently simultaneously bringing down the pH.

So let us look at the inverse case what can happen here so let us say I have water here initially right and I have five moles let us say of carbon dioxide and if there is not carbon dioxide in my atmosphere here right. So for example assume that this is 1 liter container and it is 0.5 liter of water 1.5 liter of air as atmosphere or air I guess that has no carbon dioxide in it. So after equilibrium as been reached what is going to happen now?

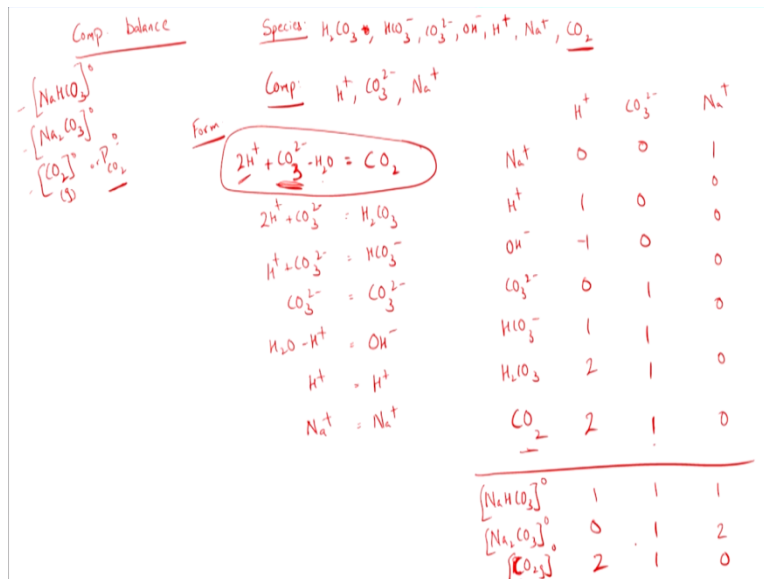
So this is the case similar to what we looked at just earlier when the carbon dioxide move from the gaseous phase to the aqueous phase but now we have inverse where that we have some moles of carbon dioxide in the aqueous phase and none in the gaseous phase. So now you are going to have transfer of carbon dioxide from the H<sub>2</sub>O to CO<sub>2</sub> aqueous to CO<sub>2</sub> gaseous right.

So what is going to happen or what can happen is that after some particular time the equilibrium will be achieved and now let us say that the only going to be three moles of carbon dioxide here and moles of your carbon dioxide in the gaseous phase and these three moles and what forms

will that be. They will be either CO2 dissolve or aqueous form which will be in equilibrium in H2CO3 which will be unique equilibrium with HCO3- which will be equilibrium with CO3 2- right.

So it is a fine balance now right you choose or you know let us say try to vary any of this variables it is going to effect all the other variable here right so it is a balance now right somebody walking a tight rope now right you pushing it someway it is also going to effect all the other aspect of the variables. So for this particular system now we are going to analyze how to go about it so it is a complex case so let go through that step by step I guess right.

**(Refer Slide Time: 05:10)**



So again component balance again component balance right and we need now look the species so we are going to first list all the species that are going to be present in the aqueous phase H2CO3 so when we write H2CO3 more or less means it we are also referring to carbon dioxide in the aqueous phase and HCO3- and CO32- and then OH- and H+ right and let us say in this particular example 2 are adding NAHCO3 NA2CO3 right and also that there is some initial concentration of carbon dioxide in the gaseous phase.

So we have three particular variables here not variables inputs here I guess so PCO2 is partial fraction of carbon dioxide initially right so these are the three aspects we have and obviously now what else are missing we also missing sodium right and these more or less as you see the list

of species we have just listed right how many do we have we have 6 species than more or less similar not more or less it is similar to what we have listed in our closed system.

But obviously now the it is an open system and which of these species or you know now you are going to have species carbon dioxide in the gaseous phase that is going to be in equilibrium with your  $\text{H}_2\text{CO}_3$ . So now we are going to list the carbon dioxide and this is the one in the gaseous phase right this is the new species here.

And so obviously again components so we are going to again choose  $\text{H}^+$  and  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}$  and let us see if we can get 2 or you know from all over species with these three components. So I guess the only new species that we need to look at it is carbon dioxide so let us do a check with respect to that first and then move on to or write in the other equation so here what am I trying to form here.

I am trying to form  $\text{CO}_2$  and it is more or less  $2\text{H}^+ + \text{CO}_3^{2-} - \text{H}_2\text{O}$  should be equal to  $\text{CO}_2$  and these are my formation equations right. So more or less 2 H here and I am going to subtract here is  $\text{CO}_2$  or  $\text{H}_2\text{O}$   $\text{CO}_3^{2-}$  now that is fine so we have  $2\text{H}^+ + \text{CO}_3^{2-} - 2\text{H}_2\text{O}$  we now are able to use or you know use the building blocks of H and CO3 total and be able to form  $\text{CO}_2$ .

So we do not need any other or addition component to be able to form our new species which is carbon dioxide so now we can move on and we just missed all the other species  $\text{H}_2\text{CO}_3$  and  $\text{CO}_3^{2-}$   $\text{CO}_3^{2-}$   $\text{OH}^-$   $\text{H}^+$   $\text{Na}^+$ . So we are going to put down what we looked at in the last example I guess and it is going to be again  $2\text{H}^+ + \text{CO}_3^{2-}$  right same case here and again  $\text{H}_2\text{O}$  and 1  $\text{CO}_3^{2-}$  and here it is going to be only  $\text{CO}_3^{2-}$  and here it is going to be  $\text{H}_2\text{O}$   $\text{H}^+$  and here it is going to be  $\text{H}^+$  and  $\text{Na}^+$ .

So we can move on to in writing a tableau  $\text{H}^+$   $\text{CO}_3^{2-}$  and  $\text{Na}^+$  let us go from easier to more complex species  $\text{Na}^+$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$   $\text{HCO}_3^-$   $\text{H}_2\text{CO}_3$  and what else we are missing here 1, 2, 3, 4, 5, 6 and obviously carbon dioxide and then the recipe species what are they  $\text{NaHCO}_3$   $\text{Na}_2\text{CO}_3$   $\text{CO}_2$  and partial pressure or carbon dioxide in the gaseous phase initially right so this so this is what we have and so let us plug them in and here it is going to be 1 and 1, 2, 3, 4, 5, 6 and the contribution here should be 1 2 and 0.

And similar we are going to write down H first H total and no contribution here 1, -1, 0, 1, 2 and for carbon dioxide we see that we need 2 again right and that is from these particular equation so CO3 total again 0 here, 0 here 1, 1, 1 and again 1 and where do we get this 1 from this particular equation here right and so moving on at the recipe species again it is going to be 1, 1 and 1 right and here it is going to be 1, 0 and here it is going to be 2 right.

And so now we done with our tableau right and the key here that we need to look at is with respect to jacking down your H total with respect to your carbon dioxide and here you have a new species and the carbon dioxide in the gaseous phase and that is something you need to take care of right.

**(Refer Slide Time: 10:39)**

$H_t = \text{constant}$   
 Initial:  $H_t = H_{t,l} + H_{t,g}$   
 After equilibrium:  $H_t = H_{t,l} + H_{t,g}$   
 $H_t = H_{t,l} + H_{t,g}$   
 $\frac{V_g}{V_l} (H_{t,g}^* - H_{t,g}) = \Delta H_{t,g,l}$   
 $V_l \cdot H_{t,l} + V_g \cdot H_{t,g}^* = V_l \cdot H_{t,l} + V_g \cdot H_{t,g}$   
 $V_l \cdot H_{t,l} = V_l \cdot H_{t,l} + V_g (H_{t,g}^* - H_{t,g})$   
 $H_{t,l} = H_{t,l} + \left\{ \frac{V_g}{V_l} (H_{t,g}^* - H_{t,g}) \right\} = H_{t,l} + (\Delta H_{t,g,l})$

So we will move on to the next crucial aspect right in general we just write down H total and we are going to write that down something and so on and we say that is going to be equal to constant right so I whole setup or approach is based on component balance are that the total component does never or ever change.

But here the issue is that let us say depending upon initial concentration of carbon dioxide in aqueous and gaseous phases right it has an carbon dioxide and move from either gaseous to aqueous or aqueous to gaseous thus if you just look at the balance on liquid or aqueous form or the just the gaseous form you are not going to be able to look at a conservative quantity right again I am going to repeat myself.

So here we are trying to look at component balance right and what is that now I want to look at balancing a conservative quantity something that changes or does not change with respect to your system right and if you are looking at this particular open system and trying to balance the H total in just the liquid phase let us say right or the aqueous phase how is that going to be effect?

Anyway let us say if any carbon dioxide in the gaseous phase dissolves in your aqueous phase you are going to relevant increase in your H total right but that is not going to work right why is that again H total needs to be conservative. So let us look at how to go about it the only key is that if we look at holistically now so the total initial H right or in H total both in liquid and gaseous phase is going to be equal to H total in both the liquid and gaseous phase after equilibrium.

Let us see what we are talking about here so let us say you know this is my liquid or aqueous or water phase here and this is water and this is my gaseous phase here and this is the initial so for example if there is H total 1 here and H total 2 here an what is the H total is going to be equal to  $HT1 + HT2$  this is initially now but after equilibrium let us say after equilibrium has been achieved let us say right.

Co carbon dioxide can move to gaseous to aqueous or aqueous to gaseous so now it is going to change so now we are going to have  $HT3$  and  $HT4$  now right.  $HT3$  is the H total in the aqueous phase  $HT4$  in the H total in the gaseous phase so this is after equilibrium now H total here is going to be equal to  $HT3 + HT4$  now right. So again the total number of moles are going to be constant.

So obviously we need to look at the volume two so the H total you know before and after your particular equilibrium is going to be the same and so thus here I am going to assume equal volume so we also need to take into account the relevant volumes of our gas and liquid right and that is the approach here right and what is the approach the total H or total component in both the gaseous and liquid phases in before equilibrium is going to be the same as the total H or the total component H in the gaseous and aqueous phase after equilibrium so thus is something we are going to write down.

So let us develop the generic case first right so we are going to look at different variables volume of liquid volume of gas right  $H$  total in the liquid phase initial and  $H$  total in the liquid after equilibrium and also  $H$  total in the gaseous phase initial and also  $H$  total in the gaseous phase in equilibrium right so these are the different variable we are going to consider here.

And now let us look at the balance here and the moles are  $H$  total initially and I am going to try to represent that particular case or this particular case now and volume of the liquid into  $H$  total liquid initially + volume of gas into  $H$  total in gaseous phase initially.

So this is the initial condition that we just describe now right so this is the total  $H$  in both the gaseous and aqueous form what is that going to be equal to be at equilibrium more or less the relevant variables that we are going to list here right volume of the liquid into  $H$  total of the liquid after equilibrium right so this is what we have.

So again we have the component balance but we are taking into account that the system is an open system as in there can be transfer of your particular  $H$  total between the gaseous and aqueous phase either from the gas to aqueous or aqueous to gaseous. Again think of this now  $H$  can either move from  $H_2CO_3$   $HCO_3^-$  similarly think of it as it can move from gaseous to aqueous phase so that the same case here we are taking that particular transformation into account here.

So we need to obviously simply this further let us go ahead so I am more or less interested in  $H$  total here in this case so I am going to have that here  $V_L$  into  $H$  total of  $H$  total in the aqueous phase at equilibrium is going to be equal to  $V_L$  into  $H$  total in the aqueous phase initially + volume of the gas into  $H$  total in the gaseous phase initially –  $H$  total in the gaseous phase at equilibrium right.

So what is that mean now so the  $H$  at equilibrium in the aqueous phase is going to be that present initially and the change between the  $H$  total in the gaseous phase so again let us try to understand what we just looked at here we are trying to look at  $H$  total in liquid phase in the equilibrium will obviously be equal to the  $H$  total in the liquid phase initially + the change from gas to liquid that we are going to from observe let us say can be positive or negative.

So let us try to simplify this too so H total in the liquid phase is going to be equal to H total in the liquid phase at or initially + volume of the gas by volume of the liquid into change in H total in the gaseous phase initially and finally so easy for use and understanding I am going to write it in a particular variable and I am going to express this particular set of variable as let us going to be equal to delta + delta H total right change from gas to liquid phase i guess right.

I am just approximating not approximating I guess using a different nomenclature so that whenever I mention H total is going to be H total gas to liquid right so this is term that I am going to be use for my particular ease of understanding I guess what is that giving an idea about? It is giving an idea about the change in H from gaseous to liquid phase per unit volume of the liquid right. So that is what we have here so keep this in mind let us again try to understand this.

**(Refer Slide Time: 18:12)**

$$\Delta H_{t,g-l} = \frac{V_g}{V_l} (H_{t,g}^o - H_{t,g})$$

$$2H^+ + CO_3^{2-} - H_2O = CO_2$$

$$\Delta H_{t,g-l} = 2 \Delta CO_{2,t,g-l}$$

$$\Delta CO_{2,t,g-l} = \Delta CO_{2,t,g-l}$$

$$H_{t,g} = [H^+] - [OH^-] + 2[H_2CO_3] + [HCO_3^-]$$

$$H_{t,g} = H_{t,g}^o + \Delta H_{t,g-l} = [H^+] - \frac{K_w}{[H^+]} + 2[H_2CO_3] + [HCO_3^-]$$

$$CO_{2,t,g} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

$$\Delta CO_{2,t,g-l} = \frac{V_g}{V_l} (CO_{2,t,g}^o - CO_{2,t,g})$$

$$= \frac{V_g}{V_l} \left( \frac{P_{CO_2}^o}{R_i} - \frac{P_{CO_2}}{R_i} \right)$$

$$= \frac{V_g}{V_l R_i T} (P_{CO_2}^o - P_{CO_2})$$

$$P_i V_i = n R_i T$$

$$\frac{n}{V} = \frac{P}{R_i T}$$

So we have just try to understand this so we just looked at that I guess delta H T from gaseous to liquid is going to be equal to VG / VL into H total initially in the gaseous phase right is the initial yes -H total in the gaseous phase at equilibrium right. Again this gives us an idea about HT change in the gaseous phase to the liquid phase right so that is what we have here so let us understand here I guess in terms of what we looked at.

So in general we are looking at carbon dioxide equilibrium between the gaseous and aqueous phase let us look at that relevant formation equation right so in general we have 2H+ + CO32- -



$H_2O =$  your  $CO_2$  right and this is your formation equation that we have listed previously right so let us try to understand the change in term of variable right so the  $\Delta H$  total from gas to liquid is going to be equal to two times the change in carbon dioxide total from gas to liquid so whenever there is a change in one mole let us say carbon dioxide there is going to be a effect of two moles on  $H^+$ .

So that is what we are talking here and same case here  $\Delta CO_3$  total gas to liquid is going to be equal to 1 times  $\Delta CO_2$  total gas to liquid so more or less both these equations ore from these particular equation here yes and we are now going to take this further again similar to what we discussed in the previous.

And let us see what we had there and I believe we know can always express  $\Delta CO_2$  total from gas to liquid in terms of partial pressure of  $CO_2$  but we are going to look at that later on right anyway where do we have here let us get this done here that is going to be equal to  $CO_2$  total initially in the gaseous phase –  $CO_2$  total initially or not initially pardon me equilibrium in the gaseous phase into  $V_G$  by  $V_L$  right.

And so I can express this as  $V / V_L$  into looking  $P_V$  into  $NRT$  what is this going to be equal to this is going to be partial pressure of  $CO_2$  initially by  $RT$  – partial pressure of  $CO_2$  at equilibrium by  $RT$  and where is this from here we have  $PV = NRT$  or ideal gas law right and so you are  $N/V$  which is your concentration here is going to be equal to  $P/RT$  and that is what we have here and that is going to be  $V_G / V_L$  into  $RT$  into initial partial pressure – the equilibrium partial pressure right.

Anyway this is something we are going to use later on down the line right so let us move further so we have our  $H$  total let us say and what is that equal to now this is  $H$  total in the liquid phase is going to be equal to concentration of  $H^+$  - concentration of  $OH^-$  + two times the concentration of  $H_2CO_3$  right + 1 times concentration of  $HCO_3^-$  let us look at the tableau once and that is what we see here 1, 2, 3, 4 and obviously carbon dioxide that here we are only looking at liquid phase we are going omit carbon dioxide here for now right.

But obviously what is this going to be equal to now this as you know going to be equal to  $HT$  now it is going to be the one initially + any change from the gas to liquid right and that is what

we have here yes and that is what we looked at here and that is going to be equal to the concentration of  $H^+$  -  $K_w$  by concentration  $OH^-$  + two times the concentration of  $H_2CO_3$  + 1 times the concentration of  $CO_3^{2-}$  right.

So let us try to simplify the particular equation here we have we still have multiples in the unknown equation so we need to be able to simplify to such an extent that we only have couple of variables here right and let us look that. So first we are going to simplify  $H_2CO_3$  and  $HCO_3^-$  and how do we do that we know that  $CO_3$  total in the liquid phase anyway again keep in mind that we are going to do the balance only on the liquid phase here is going to be equal to  $H_2CO_3 + HCO_3^- + CO_3^{2-}$  this is from your particular balance components right.

**(Refer Slide Time: 23:30)**

Handwritten equations and derivations:

$$H_2CO_3 = \alpha_0 \cdot CO_{3t,l} \leftarrow \alpha_0 = \frac{H_2CO_3}{CO_{3t}}$$

$$HCO_3^- = \alpha_1 \cdot CO_{3t,l}$$

$$H_{t,l} = \frac{[H^+] - K_w}{[H^+]} + (2\alpha_0 + \alpha_1) \cdot CO_{3t,l} \leftarrow$$

$$CO_{3t,l} = \frac{K_H \cdot P_{CO_2}}{\alpha_0}$$

$$H_{t,l} = \frac{[H^+] - K_w}{[H^+]} + (2\alpha_0 + \alpha_1) \cdot \frac{K_H \cdot P_{CO_2}}{\alpha_0}$$

$$H_{t,l} = H_{t,l}^0 + \Delta H_{t,l} = H_{t,l}^0 + 2 \Delta CO_{2,g-l}$$

$$= H_{t,l}^0 + 2 \Delta CO_{3t,g-l}$$

On the right side of the slide, there are definitions for  $H$  and  $K_H$ :

$$H = \left\{ \begin{array}{l} H_2CO_3 \\ HCO_3^- \end{array} \right\}$$

$$K_H = \left\{ \begin{array}{l} CO_2(aq) \\ H_2CO_3 \end{array} \right\}$$

$$K_H = \frac{CO_2(aq)}{P_{CO_2}} = \frac{[H_2CO_3]}{P_{CO_2}}$$

$$K_H = \frac{\alpha_0 \cdot CO_{3t,l}}{P_{CO_2}}$$

And let us move on to the next slide and so thus  $H_2CO_3$  and also comes in your equilibrium particular values what will they be equal to now it will be equal to alpha naught or what is alpha naught now  $H_2CO_3 / CO_3$  total so thus we are going to have  $CO_3$   $H_2CO_3$  into alpha naught into  $CO_3$  total right so let us have this here though  $H_2CO_3 = \alpha_0$  into  $CO_3$  total.

So the key here is that you know this is something similar to what we looked at earlier so let us simplify that also come back to what I am trying to drive towards it is going to be alpha 1 into  $CO_3$  total and I am going to plug this in previous equation and what is that going to be equal to so that  $H$  total quick phase is going to be equal to  $H^+ + K_w /$  concentration of  $H^+$  right + two times alpha naught + alpha 1 into  $CO_3$  total right is that 2 here.

And where do we have that please  $2 \times \alpha_{\text{naught}} + \alpha_1$  into  $\text{CO}_3$  total right but here the key is that we can never depend upon  $\text{CO}_3$  total in the liquid phase right that can change whenever there is transformation of carbon dioxide from the gaseous to the aqueous phase right so here we are going to look at variables or how to connect or you know connect the dots between  $\text{CO}_3$  total and partial pressure of carbon dioxide let us look at that now.

So you may have your Henry's constant right and you know it will give an idea about concentration in the gaseous phase to the concentration in the aqueous phase right and again we talked about this that the units can be you know the different kinds of constant depending upon the units so you can even define  $H$  let us say I call  $H$  now though has the aqueous concentration by the gaseous concentration as in again keep in mind that still Henry constant but depends on the units either we have the numerator and denominator above you know or the vice versa right.

So again this is what we are going to use now for purposes of simplicity right the Henry constant is going to be equal to concentration in aqueous phase right  $\text{CO}_2$  in the aqueous phase / concentration in gaseous phase is going to be equal to  $P_{\text{CO}_2}$  and we know that this is going to be equal to  $\text{H}_2\text{CO}_3$  concentration /  $P_{\text{CO}_2}$  and what is that mean Henry's constant or  $K_H$  written in the form of aqueous and gaseous keep in mind that we are defining  $K_H$  as aqueous / gaseous concentration is going to be equal to  $\alpha_{\text{naught}}$  and this is from here again this equation  $\alpha_{\text{naught}}$  into  $\text{CO}_3$  total in the liquid by partial pressure of  $\text{CO}_2$ .

So what is the take home message here that is  $\text{CO}_3$  total in a liquid phase is going to be equal to  $K_H$  into  $P_{\text{CO}_2} / \alpha_{\text{naught}}$  and I am going to be plus this in this particular equation and thus I am going to end up with  $H$  total in the liquid phase is going to be equal to  $H^+ - K_w / H^+ + 2 \times \alpha_{\text{naught}} + \alpha_1$  into  $\text{CO}_3$  total in the liquid phase am I done with it now? I mean pardon me I am still I guess we need to plug that in right the relevant equation that we have just derived  $K_H$  into  $P_{\text{CO}_2}$  by  $\alpha_{\text{naught}}$  right.

So again what are we trying to do here we are trying to express these variables in terms of relevant what do we say the variables you would come across in open system so instead of using  $\text{CO}_3$  total.  $\text{CO}_3$  total would be relevant if it is only a closed system but if it is open to the

atmosphere right you are concerned with the partial pressure of carbon dioxide or which more or less mean the carbon dioxide in the gaseous phase.

So thus we have been trying or we tried to successful in  $\text{CO}_3$  in terms of partial pressure of carbon dioxide that is going to be at equilibrium keep in mind that these are the values at equilibrium right. So are we done here though not yet why is that we still have  $H$  total liquid is  $H$  total liquid initial which is what you know right this is what you know. You know this is initial concentration +  $\Delta H$  total liquid to gas or gas to liquid this is the change that you are aware of.

So we still we need to be able to figure out how to express this particular variable or change in your particular  $H$  total from gas to liquid in there and that is what we are going to do here and what is that going to be equal to and where is this equation from this is from more or less this particular mass balance right we have that particular mass balance here.

So let us try to come back to here let us try to see that so that is going to be equal to  $H$  total initially in the liquid phase + 2 times  $\Delta \text{CO}_2$  gas to liquid right and this is something again we try to look at earlier. We saw that for every mole of  $\text{CO}_2$  or one component of  $\text{CO}_2$  let us say or 1 species of  $\text{CO}_2$  that is going to change from gas to liquid we have component of  $H^+$  to change here so that is what we have here and then we are going to express in terms that we know that is again going to be  $H$  total in liquid + two times  $\Delta \text{CO}_3$  total that is the liquid right.

**(Refer Slide Time: 29:41)**

$$\begin{aligned}
 H_{t,l} &= H_{t,l}^0 + 2 \Delta CO_{3t,g-l} \\
 &= H_{t,l}^0 + 2 (CO_{3t,l} - CO_{3t,l}^0) \\
 &= \frac{H_{t,l}^0}{\checkmark} + 2 \left( \frac{K_H P_{CO_2}}{\alpha_0} - \frac{CO_{3t,l}^0}{\checkmark} \right) \\
 &= \left[ H \right]^+ - \frac{K_w}{\left[ H^+ \right]} + (2\alpha_0 + \alpha_1) \frac{K_H P_{CO_2}}{\alpha_0}
 \end{aligned}$$

$p^H, H_t, P_{CO_2}$   $p^H, H_t, CO_{3t}$   
 Open Closed sys.

So continuing from our previous slide right H total L at equilibrium is going to be equal to H total in the aqueous phase initially + 2 times the change in CO3 total from gas to liquid right and let us try to simplify this further we know that CO3 total and liquid phase at equilibrium is going to be equal to CO3 total and the liquid phase initially again this is initial we know what this particular value is + the change in CO3 total from gas to liquid.

Again this is similar to what we derived earlier with respect to H total liquid is going to be equal to H total initially in the liquid + delta H total change from gas to liquid more or less the same now we have this particular variable and so continuing from here delta CO3 total gas to liquid is going to be equal to CO3 total in the aqueous phase at equilibrium - CO3 total initially in the aqueous phase so I am going to plug this in here that is going to be equal to H total initially in liquid phase is something that you know right.

You know what it is you are putting in initially in your water and that is going to be equal to 2 times CO3 total liquid or at equilibrium - CO3 total initially and the aqueous phase and that is going to be equal to H total initial at aqueous phase + two times and how did we express this as PH as PCO2 by alpha naught - CO3 total initially at equilibrium not equilibrium pardon me initially in your aqueous phase.

But we check this variable when we have that CO3 total is going to be equal to KH into PCO2 / alpha naught and that is something we have and so this as we know is now equal to concentration

of  $H^+$  -  $K_w$  / concentration of  $H^+$  + two times  $\alpha_0$  +  $\alpha_1$  into  $K_H K_{CO_2}$  at equilibrium right  $\alpha_0$  right and this = this and this is variable that you know this is equal to the  $H$  total initially.

So that is something that you know and this particular variable  $HCO_3$  total initially or in the aqueous phase is something that you know how much putting in into your system and  $H^+$  is the  $H^+$  concentration of equilibrium  $PCO_2$  is the concentration of carbon dioxide in the gaseous phase at equilibrium and thus let us say we can identify the relevant variables what are they here they are going to be  $PH$   $H$  total and partial pressure of  $CO_2$  this is the one in open system.

But what was it in close system it was  $PH$   $H$  total and  $CO_3$  total and this was you know closed system right so again earlier in the closed system the relevant variable were  $PH$   $H$  total and  $CO_3$  total that were present that are going to be present at equilibrium but in this case though we have slight variation why is that it is no more close system it is an open system so thus the  $CO_3$  or  $H_2CO_3$  is going to be in equilibrium with  $CO_2$  in the gaseous phase right.

So now the relevant variables are  $PH$   $H$  total and partial pressure of carbon dioxide in the gaseous phase right so in the next class so in next lecture session anyway we are going to look at the application of VMINTEQ in the open system and then we are going to move to titration and so on and I guess with that I will done for today's lecture session and thank you