Environment Engineering: Chemical Processes

Prof.Dr. Bhanu Prakash Vellanki
Indian Institute of Technology – Roorkee

Module No # 01
Lecture No # 05
Phase Equilibrium

Hello again so welcome back to the course so let us have our quick customize review of let us say couple of minute regarding what we discussed in the previous session and then we will move on to the aspects we are going to cover today right regarding the review going back to slide here.

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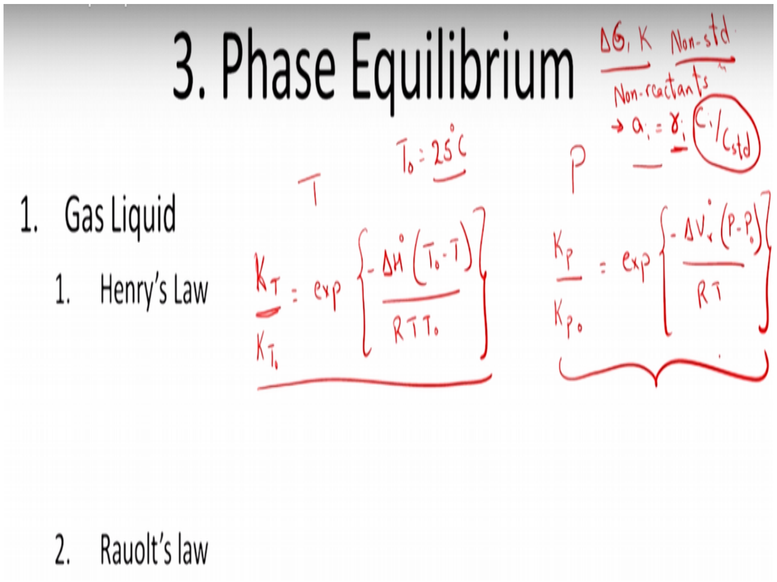

3. Phase Equilibrium

$\Delta G, K$ Non-std

Non-reactants

$\rightarrow a_i = \gamma_i \, C_i / C_{std}$

1. Gas Liquid
    1. Henry's Law

T $\quad T_0 = 25°C$

$$\frac{K_T}{K_{T_0}} = \exp\left\{\frac{-\Delta H^\circ (T_0 - T)}{R T T_0}\right\}$$

P

$$\frac{K_P}{K_{P_0}} = \exp\left\{\frac{-\Delta V_r^\circ (P - P_0)}{R T}\right\}$$

    2. Rauolt's law

So we looked at calculating delta G or I guess K or the equilibrium coefficients at non-standard conditions right and then we looked at effect of non-reactants and that context we talked about activity of the component = activity coefficient multiply the dimensionless concentration variable. So activity coefficient depends upon the ionic strength and this variable we looked at how to look at the different units different phases.

So we are run with that then we end up deriving the relevant equation that represented here for what do we say calculating equilibrium coefficient then we have different temperature rather than the standard temperature as we know is 25 degree centigrade. So how will the equilibrium change or shift whenever we have a change in temperature and so same case with pressure we again derived or I guess it is a natural corollary.

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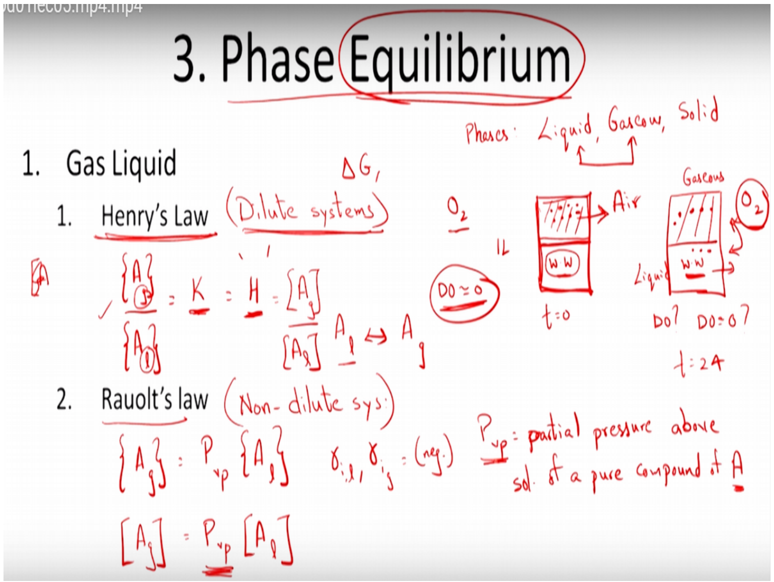

3. Phase Equilibrium

1. Gas Liquid
   1. Henry's Law
   2. Rauolt's law

So we looked at that relevant equation yes we will move on to next aspect the today we are going to start discussing about phase equilibrium now right so we are not going to go into greater detail and then we are going to look at few of the usually example that we come across in environment engineering and then we will come back to how this relates to delta G or again as we have here equilibrium right.

So Henry's law or pardon me before I go further so in general we are aware of phases right and the three phases that we usually come across our liquid, gaseous and the solid phases. So for example let us take let us say partitioning of oxygen between the gaseous and liquid or in this case water or aqueous phase this I guess. For example let us say if I get my container let us say I have 1 liter container and I fill it up half of it with waste water that has DO levels to be equal to almost 0 right.

And let us say the waste water or has DOD or demand as such and let us say this particular phase here is just the air right and this is the time 0 let us see is. So let us say is consumable time let us say 1 day let us say if I come back and measure the waste waters or water DO what you think it is going to be DO now it is still going to be 0 or it is going to change though. So in general to change depending obviously we are considering there is no DOD here let us say.

DOD of your fresh water so you will just assume that no organics or compound that can be oxidized and that the initial waste water had no dissolved oxygen and half liter of the or your know half the same that is filled with air right and now again after time = 24 hours we are trying to look at what is the condition of your particular dissolve of oxygen or what is the dissolve oxygen level in your waste water.

So obviously I guess it is going to increase not going to be 0 anymore why is that so let us say there were 5 moles I guess this is rough approximation let us say the five let us say 8 moles of oxygen in the air lay their it is not going to be the case going to look at PV = NRT and so on but for example let us say there are 8X or 8 moles of your oxygen in your air initially and there are no moles of or 0 moles of oxygen in your water because that you know that the DO is 0.

So what happens after some time depending upon kind of water or such there is going to be a partitioning of the molecule right. So in general let us say there are now 5 moles left in your air of oxygen they will be moles left in your waste water what I am trying to explain is that an equilibrium will be reached in a certain time for oxygen between the gaseous phase and the liquid phase right.

So again there is partitioning or equilibrium has been achieved with respect to oxygen in the gaseous phase. So now earlier were we had 8 moles we now have only 5 moles and another 3 moles now in the liquid phase right or here in this case water. Anyway this is very generic approximation in the right I am just trying to picture here for you so in general how do we go about it or how do we look at this aspects let us see or how can we quantify pardon me.

So in general when you are want to try to equate the activity of your particular compound in the gaseous phase to the activity of the particular compound and the liquid phase right we use so let us initially we know that we can say or call this equilibrium coefficient but for when we are trying to look at the partitioning between the gaseous and liquid phase we call that the Henry's constant H right.

So again look at this it is equilibrium of a particular compound between the gaseous phase and the liquid phase right and the ratio here let us say. So what is this mean compound A in the liquid phase is now equilibrating with compound A in the gaseous phase right. So this is what we see here and as you equilibrium coefficient is the products rise to it stoichiometric coefficient by reactants to its stoichiometric coefficient that is what we see here.

And again what do we call that here we call that the Henry's constant but keep in mind that this is applicable for dilute systems right Henry's Law is typically applicable for dilute system. So that same case we can come across or we come across Rauolt's Law and that is applicable to non-dilute systems right and what is that give us an idea about. So similarly though it gives us an idea about activity of the relevant compound in the gaseous phase = the vapor pressure of the particular compound into activity of the particular compound in the liquid phase right.

And if you want to approximate the activities by concentration you can do that assuming that the activity coefficients are small or equal right it could be coefficient in gas phase or negligible let us say right you can say that is equal to concentration of the compound in the gaseous phase times vapor pressure into the concentration of the compound in the liquid phase.

So same case here to the activity coefficients are smaller obviously this is that dilute system so that is going to be the case and say then Henry's constant is also equal to what now the concentration of the compound gaseous phase by concentration of the compound in the liquid phase pardon me right. So obvious the different between these two cases that Henry's Law is applicable when it is dilute system Rauolt's Law in non-dilute systems.

So what are that mean I guess that Q would lie in what we understand by the paper and what is that I guess the vapor pressure = the partial pressure above solution of a pure compound of A. So let us say this is a theoretical value and you take a pure compound of or pure component of A and then look at the partial pressure that particular pure component you will get vapor pressure and that is what this term is here right.

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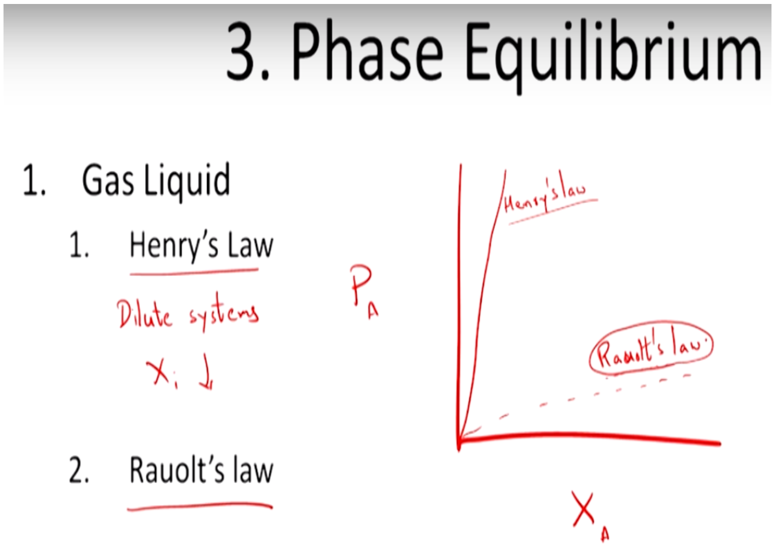

3. Phase Equilibrium

1. Gas Liquid
    1. Henry's Law

       Dilute systems

       $x_i \downarrow$
    2. Rauolt's law

So for example now to just to try to differentiate here right and if we look at a particular example here where we look at this particular graph where we have more fraction here on the X axis and the partial pressure on the Y axis of particular compound A and let us say here we have two graphs let us say and the other one let us say is this please try to take a moment and try to figure out which particular graph right would be applicable to which particular law is to there which particular graph would be applicable to Henry's law which particular one would be applicable to Rauolt's law the key obviously is that henry's law is applicable when it is dilute systems right.

So what is that mean in general the mole fraction in particular compound going to be relatively low so as you see here that the particular case here so here we see the Henry's law applicability right and in general or non-dilute systems and what do we use we use the Rauolt's law and that is what we see here right keep this in mind again in general most often not in natural system we come across Henry's law but depending upon the kind of system that we use in engineering system that we use can come across the Rauolt's Law yes.

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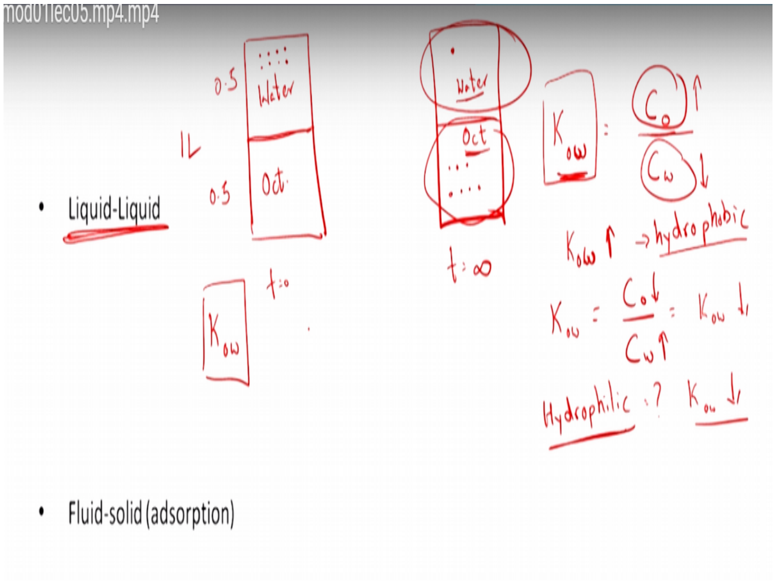

So we will move on I believe the next case would be liquid – liquid so another example that we look at is let us say we have two compounds and solvents in contact let us say one case is water so we have 1 liter of it 0.5 liter of water and again 0.5 liter methanol ethanol or such let us say okay and let us initially I have a particular compound here let us say think of it as pesticide let us say I have 8 compounds here 8 moles pardon me or hydrophobic compound here initially at time 0.

So let us say we have a considerable time I again look at what the system is around the system what would I see here let us say if it is a hydrophobic compound it does not want to stay in water and so let us say only 1 mole in water and 7 moles in methanol so here we are coming across partition of particular compound between liquid and liquid now right. So widely used metric is going to be the octonal water coefficient partition KOW right it is the concentration of compound that would stay in equilibrium with octonal partition with water.

So example what is this mean I guess instead of the methanol example right instead of the methanol example if I have this as octnal right so here if I have octnal so what is that mean am going to let us say known proportional or equal proportional of water and octonal here and I am going to put in known quantity of my particular compound and after certain amount of time am going to look at the number of moles or the concentration of the compound involved in water and also the compound concentration the compound in octonal.

Then KOW will be concentration of compound octonal right by concentration of compound in water yes so obviously if it is hydrophobic compound what is that mean it would be concentration of compound in octonal would be high and concentration of compound in the water will be less. So more or less that mean for a hydrophobic compound obviously the KOW value is going to be higher.

But it is hydrophilic compound what does that mean we know KOW value = concentration of compound in octonal by concentration of compound in so for hydrophilic and what do we know if it is would prefer to stay in the aqueous phase or in water so the denominator is going to be higher numerator is going to be lesser so what is that turn out to be that mean KOW value is going to be plus.

So that is what you see here KOW value of hydrophilic compound typically will be lower right so again this is a approximation that people look at when that trying to look at is it a hydrophobic compound or hydrophilic compound and people usually use the octonal water partitioning coefficient again KOW and these are standard values and available for most of the compounds that you are aware of let us see yes.

Again now we are moving on to the second aspect and what is that I guess here we have fluid solid absorption now.

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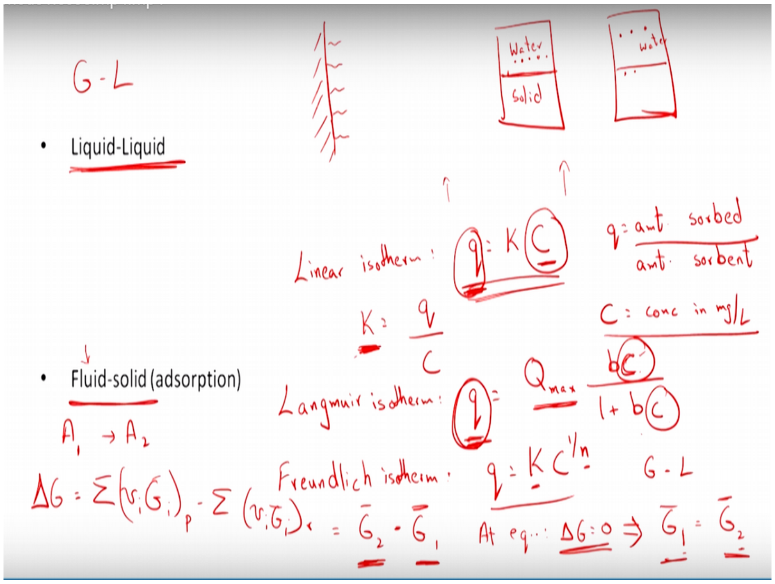

G - L

- Liquid-Liquid
- Fluid-solid (adsorption)

$A_1 \rightarrow A_2$

$\Delta G = \Sigma(v_i G_i)_p - \Sigma(v_i G_i)_r = \bar{G}_2 - \bar{G}_1$

Linear isotherm : $q = K C$

$K = \frac{q}{C}$

$q = \frac{\text{amt. sorbed}}{\text{amt. sorbent}}$

C : conc in mg/L

Langmuir isotherm : $q = \frac{Q_{max}\, bC}{1 + bC}$

Freundlich isotherm : $q = K C^{1/n}$

G - L

At eq. : $\Delta G = 0 \Rightarrow \bar{G}_1 = \bar{G}_2$

So many people might be aware of say absorption based phenomena let us say right and let us see what it is absorption or ionic let us say here I have sides for absorption to activate carbon on in a different case or in exchange let us say here I have five sides let us say right or for example may be a better example would be similar to what we had earlier so I mean this is a very rough example though keep in mind that.

So I have compound let us say in water and thus let us say solid but not .5 differentiation though I guess and so I have compound here in water so more or less I want to know how much of the compound or what fraction of the compound would be absorbed on to the solid after sometime right so I want to how much of it would be absorbed on the solid and how much of it would want to stay in water again there is going to be a equilibrium.

So let us say if it is particular compound as high affinity for the solid right then I can use my what we say absorption base process or ionic exchange base process I guess let us just call it absorption relatively principal though it is under the ambit of absorption right. So if a particular compound wants to stay in solid mode than it want to stay in water so I can go with the absorption process.

So let us look at some of the usual morals that we have we have the linear isotherm right what is that is Q = KC right again Q is the amount sorb on to the solid phase by amount of the sorbent right. Sorb on to the solid phase and Q C obviously your concentration in typical milli gram per liter and aqueous phase and whichever you are liquid phase right. So again you can think of K here as an equilibrium constant and if you want to K = Q by C is an equilibrium constant right.

So that you can get from your you can think of it but that it is not that what it is called anyway Q = KC what does an give an idea about what does an gives an idea about the partitioning between solid phase which is the concentration in Q in the solid phase how it is relates to the concentration of the compound in the aqueous phase or water or solvent and so on make sense hopefully.

So Q is the concentration of the particular compound on the solid phase C is the particular phase of the solid compound in the aqueous phase an here we have a relationship. But there are obvious drawbacks means that as you keep increasing C it can Q can go upto infinity as C can go to infinity but it is not the case. So in general we will have limited number of sides available so one model that takes into account is the Langmuir's isotherm right and Q = Q max this is defined as maximum number of sides that are available let us say.

BC / 1 + BC right C again is obviously the concentration of compound in water B is a constant and Q max is the maximum of sides available Q is the amount solved by amount of sorbent here we have relationship between concentration of compound in your phase in your concentration of your compound in your aqueous phase another isotherm widely used is the on which I believe this is applicable usually for activated carbon Q = KC 1/ N right and again these are empirical models based on which we can calculate K and values here .

So again what have you looked at here we looked at phase equilibrium right we initially looked at what is it now gas and liquid then we obviously looked at initially we looked at gas and liquid then we at liquid – liquid and then we looked at fluid and solid right so what is what we looked at for example if we want to calculate the delta G values for this phase changes what would that be now and it for example it goes from A goes from phase one to phase 2 what is that mean let us say.

You know we know that delta G = stoichiometric coefficient into GI bar of the products – stoichiometric coefficient GI bar of your reactants right. So what is that equal to now in this case so stoichiometric coefficient are more or less means G2 bar – G1 bar right. So Gibbs energy of particular compound or molar Gibbs energy of the compound in phase 2 – molar Gibbs energy of the compound in phase 1 so at equilibrium what does it mean now?

Delta G = 0 meaning G1 bar = G2 bar right the molar Gibbs energy of the particular compound in both the phases will be same when the system is at equilibrium this is how we link it at what we are we have been talking about in the previous classes.

So moving on let us see what we have (refer time: 19:47) next so we are going to look at an example but I believe it would be better if I talk about it in context of what we have here chemical equilibrium model I guess.

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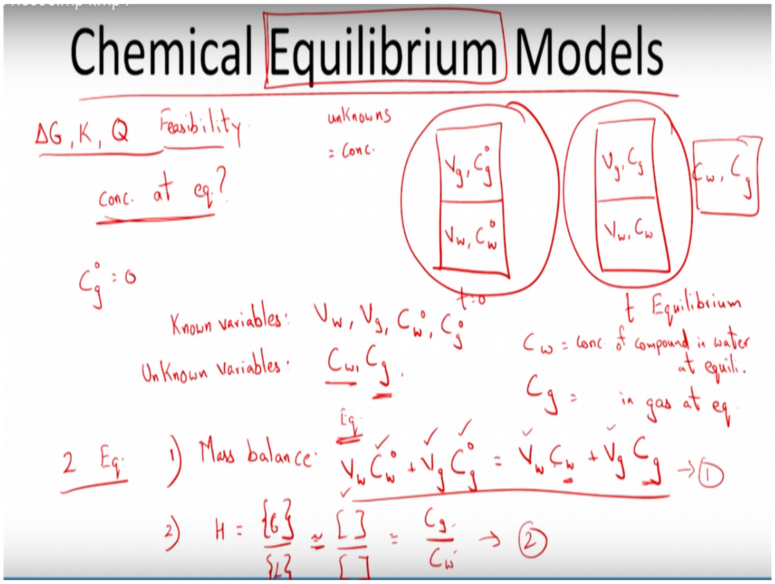

Chemical Equilibrium Models

$\Delta G, K, Q$ Feasibility

Conc. at eq.?

unknowns = Conc.

$C_g^0 = 0$

Known variables: V_w, V_g, C_w^0, C_g^0

UnKnown variables: C_w, C_g.

C_w = Conc. of compound in water at equili.

C_g = in gas at eq.

2 Eq:

1) Mass balance: $V_w C_w^0 + V_g C_g^0 = V_w C_w + V_g C_g \rightarrow ①$

2) $H = \frac{\{G\}}{\{L\}} \approx \frac{[\ ]}{[\ ]} = \frac{C_g}{C_w} \rightarrow ②$

So we have (()) (19:59) looking at delta G values or K values and activity product and so on looking at feasibility and so on right this is what we have been looking at standard condition non-standard conditions and so on yes but now let us say now I want to now step into the those aspects of talk about those aspects where I want to know the concentrations at equilibrium I want to be able to calculate that let us see right.

How to calculate the concentration at now so for this particular aspect let us say there are different models and in general obviously or particular system is that your concentrations or your unknowns are typically equal to your concentrations. So let us look at this i believe you have a small example here right.

So take a few moments to work this out so let us say initially I have a particular or volume of water right and concentration of particular compounds in water initially and then also a it is in going to be what do we say expose to a volume of gas and concentration of particular compound in a gas initially this is that time = 0 and after time T I want to be able to calculate what are my concentrations at equilibrium let us say right.

So I want to calculate concentration of compound in water pardon me concentration of the compound in the gaseous phase what are this two unknown now? To simply this particular example we are going to assume that there is no compound present in the gaseous phase initially. So please take may be a few seconds 20 to 30 seconds and see how you can work this out I guess in the mean time I am going to just list some of the variables such that we are going to calculate known values and so on but please try to calculate that right.

So okay so let us look at how to grew about this I guess so here we have two unknowns right concentration of water in the concentration of compounds pardon me in the water or a aqueous phase and concentration of compound in the gaseous phase at equilibrium obviously is to are at equilibrium obviously after this system has reached equilibrium let us say right so the key lies there the system is at equilibrium is one case.

So obviously we need to be able to develop two equations independent equations I guess what are those equations that we can think of now. So the first aspect let we always look at the mass balance so mass is always conserved the first aspect is mass balance right. So let us how we are going to look at that so what does it mean? It means that the total number of moles of compound initially = the number moles of the compound at equilibrium right.

So whatever happening is moles from water might either move to gas or vice versa and so but the total moles is constant right so what is that end up being I guess. Volume of water into concentration of water pardon me not concentration of water but the concentration of the compound in water initially + volume of gas into concentration of the particular compound in the gaseous phase initially.

So I am assuming that we can convert the unit in the relevant units I guess will be equal to the concentration of or volume of water into concentration of water concentration of the compound at equilibrium in water right + volume of gas into concentration of compound at equilibrium at gaseous phase. So let us write that down because I have miss spelling that right this is what we have so this is a mass balance right.

So more or less we are equating the total mass before equilibrium to the mass after equilibrium right initially and after equilibrium so that that mass balance it is a simple mass balance they are going to be a variations of obviously we are going to cover that later on right. So here what here what are the known values.

So we know K again concentration of the compound in water initially that is something we know we know the volume of water volume of gas we know that this particular variable or compound in the gaseous phase initially so we are still with two unknowns right and one equations right to thus water is missing here we need one other equation here right to be able to solve that obviously key is that it is a equilibrium model right.

The equilibrium between gaseous and the aqueous phase that something we need to consider at and what is that I guess here and we know that the Henry's law or the Henry's constant is going to give us the what we say ratio of activity of the compound in the gaseous phase right and the gaseous phase let us say to the liquid phase right.

So if I am going to use what do we say the concentration or approximation that by concentration so that is going to be equal to concentration of gaseous phase by the concentration in the aqueous phase at equilibrium. So now I have two equations right and two unknowns and with that I can I will be able to solve the relevant you know system here. So what are you looking for here always I guess right you are trying to identify the known or the variables and obviously develop equations to be able to solve them.

In general widely used equations in the particular system or the environment engineering what are they going to be they are going to be mass balance right typically mass balance or almost always and what else can we look at? We can look at charge balance right again something people mess so may be will have that in homework one example problem on charge balance the charge needs to be balance no particular solutions will be charged right.

So what else now and then the equilibrium models or equilibrium balance models so these are some aspects and we are going to look at so obviously here we have looked at a generic example now right but this is not going to work every time though so how can I go about it let us say here I have an example but before I further I need to talk about some other aspects here right so let us look at that.

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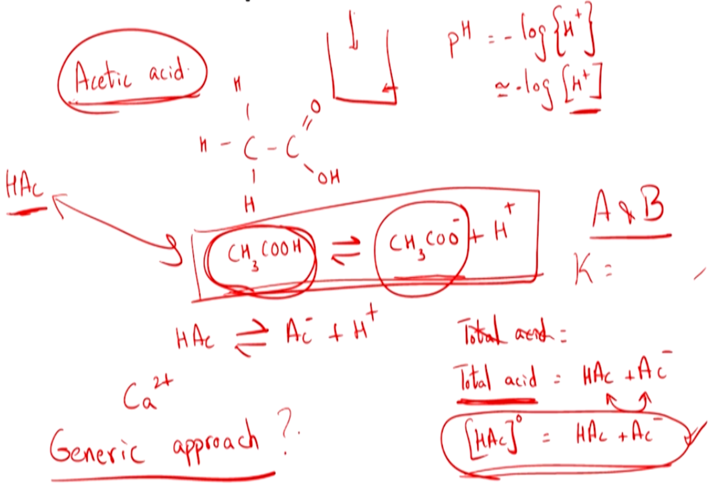
Chemical Equilibrium Models



So now let us say we have acetic acid and solution let us say or let us say I have beaker of water and let us say I am putting that in acetic acid in this particular solutions and I know the concentration of this particular acetic acid initially and I am putting that up in here we are talking about very simple model here and I want to able to calculate the PH of this particular solutions.

Once the acetic acid has been what do we say added to the solutions and PH is – log activity again activity of H + give us an idea about the concentration or activity of H+ in solution which people approximate by – log concentration of H + right H is the negative logarithm of activity of H +. Now how do I go about this now? So there are different way so let us look at one way that people can consider let us say yes CH3 CO and OH right.

So this is acetic acid 3CO OH right so it can behave as an acid and dissociate or try to donate the proton H + so this can existence or will exist in equilibrium with the de protonated form the CH 3CO – this is the protonated form because it has the proton and this is the deprotonated form so this is what you see here yes and this is some background information obviously we are going to look at this in greater detail over section related to the as it send basis.

Anyway this is one particular example let us I am still trying to calculate the PH of my solution and I only know the initial concentration of acetic acid that I put into my solution right. So I am going to approximate or use the nomenclature H AAAC2 what do we say approximate C3 COOH so right HAC is nothing but CH3 COOH in my what we say nomenclature here. So as we know HAC can been in equilibrium with AC - down at H + how do I calculate this now what I am messing and how do I calculate this and go about it.

So there are different ways right so one aspect certainly that you can consider is something it would stake constant now right so people would general look at total acid right and total acid is something will decide as not total acid pardon me yes let us go with total acid or total state or total acid will be HAC + AC. So the total acid that I had initially is going to be an either of this form right yes.

The HAC naught that i had initially it is going to be in the form of either HAC or AC – and so this is like a an equation and addition equation and I can use that with the other equilibrium morals that I have for example for this equation I will have K value equilibrium constant value right or acid dissociation constant and I will be able to solve the system right. So this is one way to go about this chemical equilibrium model yes.

But the issue here is that if I have any other compound let us say that form a complex with ST let us say CA2 + let us see right that will then interfere with this equation no more with the total acid equation be valid. So how do we go about this right so you want to develop a generic equation at generic equation pardon me generic approach that will suit all the needs right all your needs.

So that is what we are going to discuss in our next class so with that I will end today session and thank you.