Physico-Chemical Processes for Wastewater Treatment

Professor V. C. Srivastava
Department of Chemical Engineering
Indian Institute of Technology Roorkee

Lecture - 12

Aeration - 1

Good day everyone and welcome to this lecture. In the previous lectures actually we started studying regarding the treatment process and there are basically three stages of any water or wastewater treatment and those three stages are physical, then followed by physical it may include chemical as well. So, it is physico-chemical followed by biological treatment, which is also called a secondary treatment and then tertiary treatment which is generally also physico chemical in nature.

And there are various unit operations which are followed in all these treatment methods and these unit operations may be placed in the treatment unit at different places. So, within effluent treatment plant these treatment units or unit operations may be differently placed depending upon the characteristics of the water, amount of water being generated and also the what is the requirement or designated use of that water later on.

So, depending upon these units are placed. So, among the primary treatment units there are a number of units which are there. And in the last lecture, we studied regarding the flow equalisation basin. So, flow equalisation basin what it does is that, it equalises the flow rate and also it homogenises the characteristic of the water.

So, further treatment is easy and also the secondary units and tertiary units which are there they can always operate at maximum condition or optimised condition and their efficiency is maximised. So, flow equalisation basin is one of the first units it may be there along with some other pre-units which may be like removal of grit et cetera and after that flow equalisation basin and after flow equalisation basin there is a high possibility of an aeration unit also.

This aeration unit may also be mixed with the flow equalisation basin itself that means the aeration may be performed within the flow equalisation basin also. So, there is a high possibility so today we are going to start section on aeration. We will be studying aeration in great detail. And in one of the lectures like today, we will be trying to understand the basic formulas by which the solubility of gases at any temperature in water may be calculated.

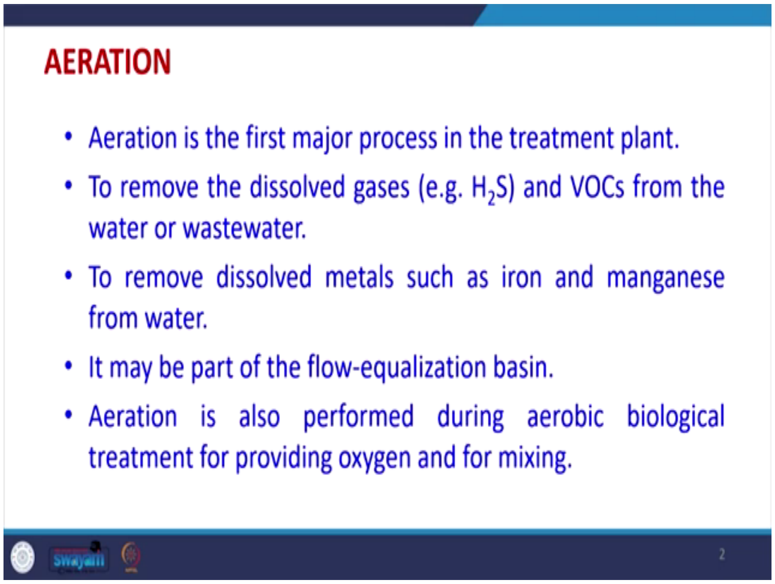
So, this is very, very important and it depends upon Henry's law or Henry’s equation and using the Henry’s constant, we can determine lot of all the solubility of gases in the water or wastewater. So, certainly some alteration is required for determining the values in actual wastewater, but we will be continuing this basic information further and we will be trying to study the, what are the aeration things, how the aeration can be found out, what is the rate of oxygen transfer or air transfer and how it is dependent upon various mass transfer resistances and other things.

So, this will be the second step within the aeration after the first basic step with respect to solubility. Thereafter, we will try to understand that what are the various aerators which are commonly used in the industries as well as various treatment plants which are there and thereafter, we will try to solve some of the problems and understand that how we can do the preliminary design of a aeration unit with respect to finding out the volume of the unit et cetera under certain conditions. So, this is the plan for whole plan for understanding the aeration and other things.

Now, aeration is very common in day to day life also, we see aeration that they we see aeration while going to any hill station like Nainital if you go, you will be finding that if you are on the top of the hill looking at the Naini lake, there is some bubbles, big bubbles or big things happening inside the lake.

And actually, what is being done is that the air is being diffused inside the nanny lakes so that the aeration of the water happens. So, this is common. Similarly, if we go to swimming pool, so, we will be finding that the swimming pool water is always aerated and that may be aerated in the form of some fountain may be there any other place are nearby and aeration is happening in different ways. And similarly, other places fountains are very common and fountains are good method to aerate any water which contains some dissolved gases or otherwise.

(Refer Slide Time: 06:02)



AERATION

- Aeration is the first major process in the treatment plant.
- To remove the dissolved gases (e.g. H_2S) and VOCs from the water or wastewater.
- To remove dissolved metals such as iron and manganese from water.
- It may be part of the flow-equalization basin.
- Aeration is also performed during aerobic biological treatment for providing oxygen and for mixing.

So, we will start with so why why we require aeration first thing and where it is use. So, in the treatment plant aeration is one of the first major process. So, it may be used individually also and it may be there in the flow equalisation basin also. If it is certainly part of inline flow equalisation. So, this is there. Now, to remove aeration is used to remove dissolved gases. So, many types of gases like H_2S, ammonia, chlorine, et cetera may be present in higher amount, if suppose water is being taken from ground.

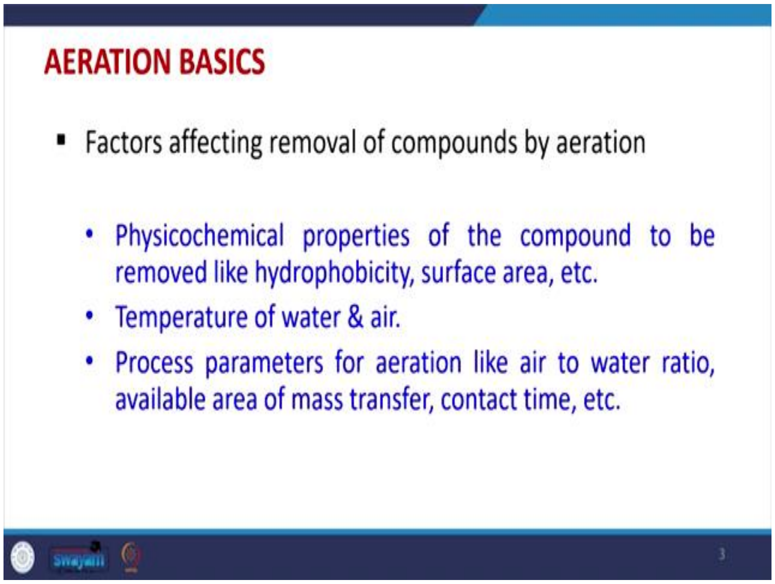
So, and we have to use it further for drinking. Similarly, lot of wastewater is discharged from various industries they may contain high amount of dissolved gases. So, we want to remove these dissolved gases, so we have to use aeration. So, lots of VOC's volatile organic compounds can be removed via using aeration.

Similarly, some of the dissolved metals like iron magnetic et cetera can be removed using the aeration method. So, it is there already told it this aeration unit may or may not be the part of the flow equalisation basin itself. Aeration is also within the treatment plant, aeration is very it is a must for any aerobic biological treatment process.

So, aeration is always done in ASP Activated Sludge Process and some other processes as well. And aeration is done for not only for providing oxygen, because oxygen is essential for microorganisms to respirate and during that process they use the various pollutants which are present in the water as nutrient and you convert them into CO_2 and H_2O.

And along with that, aeration is very necessary for mixing also. So, mixing helps in avoiding the settling of the various microorganisms which are commonly called as mixed liquor suspended solid in the case of activated sludge process. So, it is avoids that mixing it provides the mixing and avoids the settling of those microorganisms which are there. So, aeration is very essential and it may take place at various places and it may happen individually or along with the flow equalisation basin.

(Refer Slide Time: 08:54)



AERATION BASICS

- Factors affecting removal of compounds by aeration
  - Physicochemical properties of the compound to be removed like hydrophobicity, surface area, etc.
  - Temperature of water & air.
  - Process parameters for aeration like air to water ratio, available area of mass transfer, contact time, etc.

Now, there are many factors which affect the removal of compounds by aeration. And first and foremost are the physico chemical properties of the compound or gases which are likely to be removed. So, these may be their hydrophobicity, the molecular size, surface area et cetera. Similarly, temperature of the water and air both are very important in aeration. We will understand these things in detail later on.

Similarly, a lot of process parameters which are there inside the which have to be designed properly in the aerator like air to water ratio, what is the amount of air that we are using with respect to water. So, that becomes very important, available area of mass transfer. So, this aspect we are going to study in detail as well as the contact time because it may require certain amount of contact time before the actually the gases come out of the interface and go into the atmosphere.

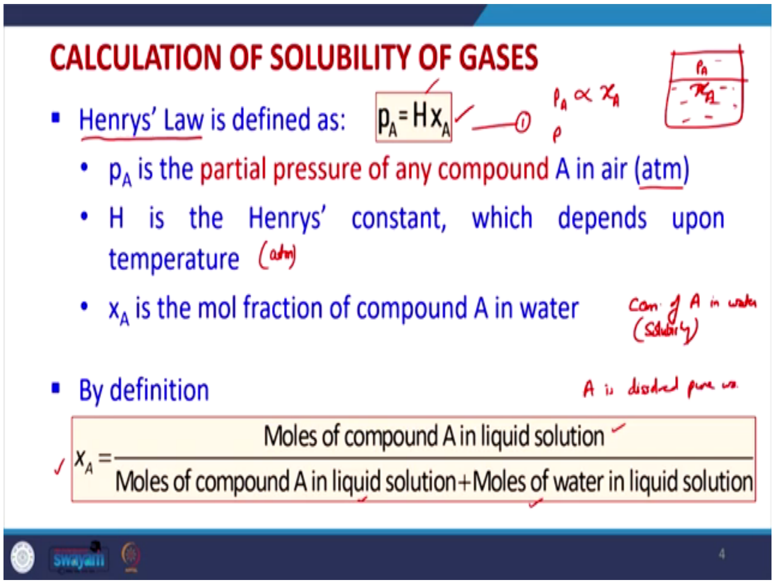
So, for this to happen depending upon the amount of gases and components present in the water, it may require certain contact time and that contact time is dependent upon whether the compound is hydrophobic hydrophilic. So, all those aspects become very, very important in aeration.

Now, what we will do is that, we will start with some of the basics of the aeration before going further. And what are those basics? Now, in the if you remember that previously we had told that there is a certain solubility limit of any gas in water and that gas like for oxygen it was in one of the question like the saturated oxygen concentration in the water is around 9.9 milligram per litre at 20 degrees centigrade. So, this was stated in one of the lectures previously.

Now, how do we know that okay, this is 9 milligram per litre at 20 degrees centigrade? What will be the solubility limit at 14 degrees centigrade or at 10 degrees centigrade? And this is true for oxygen, what about CO_2. Because CO_2 is different gas as compared to O_2. What about ammonia, nitrogen, helium et cetera.

So, for finding out what are the solubility limits, because these solubility limits are very very important in designing the aeration unit and we know the what is the saturation value if the there is high amount of gas is present in the water. So, it will can be removed only up to a up to the saturation limit it cannot go beyond. Similarly, if the gases are below the saturation value, they will always try to reach the saturation value. So, these are this saturation value is very important parameter and it helps in the design of the equipment’s which are there in the aeration units.

(Refer Slide Time: 11:47)



CALCULATION OF SOLUBILITY OF GASES

- Henrys' Law is defined as: $\boxed{p_A = Hx_A}$ —①
  - p_A is the partial pressure of any compound A in air (atm)
  - H is the Henrys' constant, which depends upon temperature (atm)
  - x_A is the mol fraction of compound A in water
- By definition

$$x_A = \frac{\text{Moles of compound A in liquid solution}}{\text{Moles of compound A in liquid solution} + \text{Moles of water in liquid solution}}$$

$p_A \propto x_A$

p

Con. of A in water (Solubility)

A is dissolved pure wa.

Now, going further. So, one of the important laws or equations which are used for finding or calculating the solubility of gases is Henry's law. So, we use the Henry's law all of us studied these Henry's law the basic definition in class 10th, 12th et cetera. So, this is very well known. So, one of the basic forms of Henry's law is that the partial pressure of any gas in the vapour space above any liquid water liquid air interface is directly proportional to mole fraction of that gas in the liquid phase.

Henrys' Law is defined as:

$$p_A = H\,x_A$$

Where, p_A is the partial pressure of any compound A in air (atm); H is the Henrys' constant, which depends upon temperature; x_A is the mol fraction of compound A in water.

$$x_A = \frac{\text{Moles of compound A in liquid solution}}{\text{Moles of compound A in liquid solution} + \text{Moles of water in liquid solution}}$$

So, suppose we have a we have a beaker here and there is some water which is kept here. So, amount of any gas which actually be present in the vapour space if it is suppose it is closed. So, amount of this partial pressure of gas will be proportional to the mole fraction of the that compound in the liquid phase. So, this is called as Henry's law.

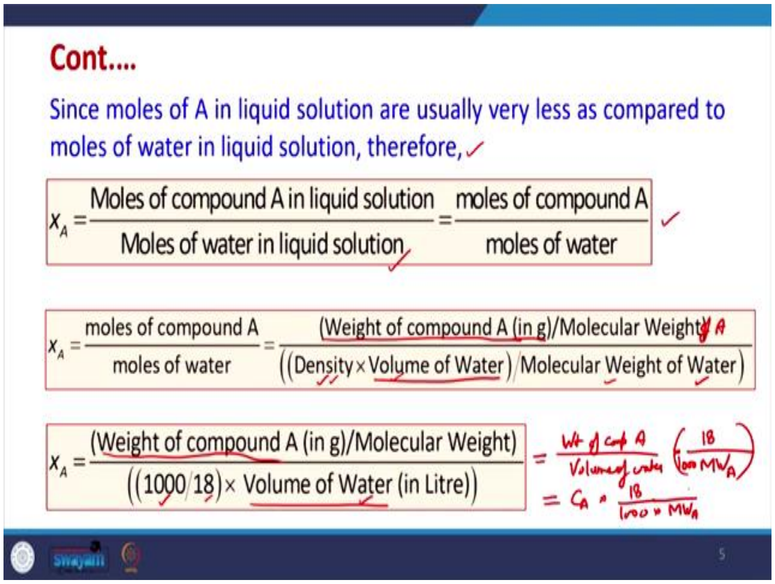
Now, and the proportionality constant is called as the Henry's constant which is given here. So, this is that this is the basic definition and now, within that PA is the partial pressure of any compound in the air and the unit. So, this unit partial pressure may be in the atmosphere or any other pressure unit. Similarly, H is the Henry's constant which depends upon the temperature.

So, for this particular equation which is given here if we consider it 1, so, for this case it is unit will be atmosphere, this is so, because we have kept the partial pressure in atmosphere. So, whatever is the unit of partial pressure that will be the unit of Henry's constant. Now, X_A is the mole fraction of compound A in the water. So, this is there, now, our aim from this equation is to find out the concentration.

So, this is why we want that we know X_A mole fraction, so, we have to convert the mole fraction into something like this, which is like concentration of A in water. So, concentration of A in water is basically what is this this is solubility. So, this will give the value of solubility in the water. So, this is what we are going to find out derive the equation and this is very very necessary for understanding many things.

Now, by definition if we go by definition, the mole fraction is defined like this moles of compound A in the liquid solution divided by moles of compound A in the liquid solution plus moles of water in the liquid solution. So, what we are assuming that only A is dissolved in water and that to pure water. So, we may proceed like this.

(Refer Slide Time: 14:45)



Cont....

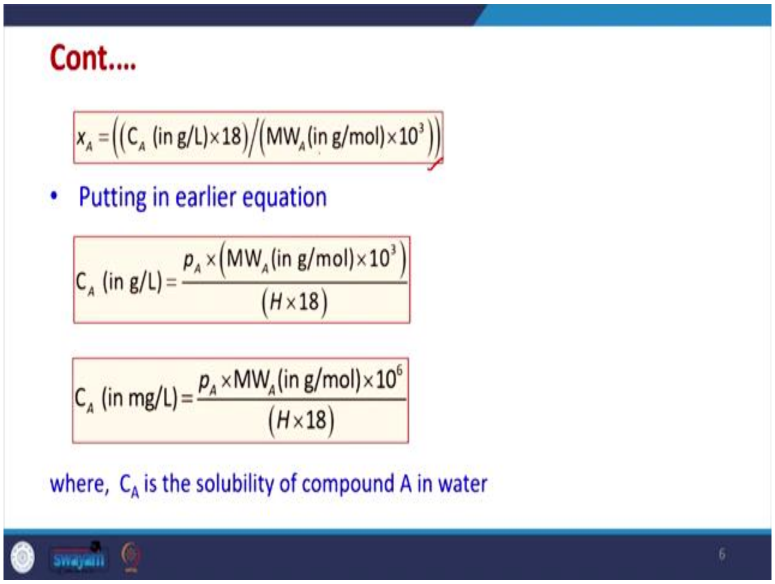
Since moles of A in liquid solution are usually very less as compared to moles of water in liquid solution, therefore, ✓

$$X_A = \frac{\text{Moles of compound A in liquid solution}}{\text{Moles of water in liquid solution}} = \frac{\text{moles of compound A}}{\text{moles of water}}$$ ✓

$$X_A = \frac{\text{moles of compound A}}{\text{moles of water}} = \frac{(\text{Weight of compound A (in g)/Molecular Weight of A})}{((\text{Density} \times \text{Volume of Water})/\text{Molecular Weight of Water})}$$

$$X_A = \frac{(\text{Weight of compound A (in g)/Molecular Weight})}{((1000/18) \times \text{Volume of Water (in Litre)})} = \frac{\text{Wt of cmp A}}{\text{Volume of water}}\left(\frac{18}{1000\ MW_A}\right)$$

$$= C_A \cdot \frac{18}{1000 \times MW_A}$$



Cont....

$$\boxed{x_A = \left(\left(C_A \text{ (in g/L)} \times 18\right) / \left(MW_A \text{(in g/mol)} \times 10^3\right)\right)}$$

- Putting in earlier equation

$$\boxed{C_A \text{ (in g/L)} = \frac{p_A \times \left(MW_A \text{(in g/mol)} \times 10^3\right)}{(H \times 18)}}$$

$$\boxed{C_A \text{ (in mg/L)} = \frac{p_A \times MW_A \text{(in g/mol)} \times 10^6}{(H \times 18)}}$$

where, C_A is the solubility of compound A in water

So, in the second step this now, if we assume that moles of A in the liquid solution will always be very, very less because the it is only up to a certain limit and that limit is very less so, it always is negligible as compared to the moles of water in the liquid solution itself. So, under that condition where we are assuming that moles of A in the liquid solution are much much less as compared to moles of water in the liquid solution.

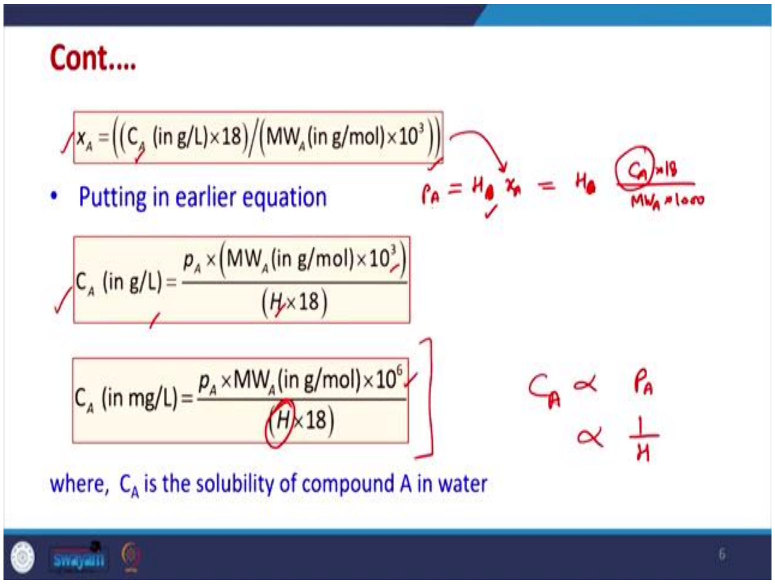
So, in this case, we can neglect the moles of compound A in the liquid solution and the equation becomes like this. So, moles of compounds A in the liquid solution divided by moles of water in the liquid solution so, we can represent like this. Now, moles of compound A can further be represented as weight of compound A in gram divided by molecular weight of A. So, this is like molecular weight of A.

Now, for moles of water. So, what we are doing is that, we are dividing this again weight by the molecular weight of water and weight of water can be represented like density of water into volume of water. So, this is very easy to manipulate and we can easily do this. Now, once we do this, what we do is that we try to take out this molecular weight of the compound A divided by volume of water.

So, this is our basic interest is there in this particular two things. So, we can manipulate little bit. So, this is a same equation is written or what we can do is that for density we know it is around 1000 gram per this is 1000 kg per litre for water. So, we can take that idea, so, sorry 1 kg per litre, so, in place of 1 kg we are writing 1000 gram. So, this is 1000 gram per litre of the water and 18 is the molecular weight of the water. So, that also we have kept here. Now, we can further manipulate this equation into such a manner that weight of compound A and volume of water, these are of our primary interest.

So, we convert that into, so, this becomes C_A in gram per litre. So, this is this become, if we can write like this, so it will become weight of compound A divided by volume of water. So, this is there and this is what is we are interested in more and in addition, there will be molecular weight of compound A. So, this is at the bottom and similarly 18 will go up. So, 18 will be here and divided by 1000. So, these are additional terms which are there and this actually is concentration of A in the water and this is equal to 18 divided by the 1000 into molecular weight of A. So, this is what is represented here.

(Refer Slide Time: 17:56)



Cont....

$$x_A = \left(\left(C_A \text{ (in g/L)} \times 18\right) / \left(MW_A \text{(in g/mol)} \times 10^3\right)\right)$$

- Putting in earlier equation

$$p_A = H_A x_A = H_A \frac{C_A \times 18}{MW_A \times 1000}$$

$$C_A \text{ (in g/L)} = \frac{p_A \times \left(MW_A \text{(in g/mol)} \times 10^3\right)}{(H \times 18)}$$

$$C_A \text{ (in mg/L)} = \frac{p_A \times MW_A \text{(in g/mol)} \times 10^6}{(H \times 18)}$$

$$C_A \propto p_A$$
$$\propto \frac{1}{H}$$

where, C_A is the solubility of compound A in water

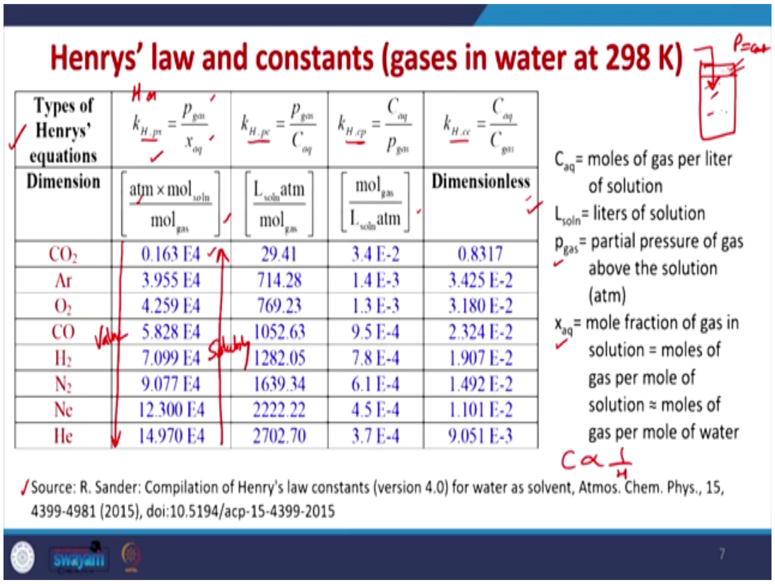
And now going further we can write the same equation you can see here, so, this is same written here and so, this way, we can write X_A as like this. Now, if X_A is known, then what we can do is that we can use this X_A in the equation, which was written earlier P_A equal to H_A X_A. Now, we can substitute this X_A in this equation and then try to find out the concentration because we want to write in terms of concentration.

So, it becomes H_A C_A into 18 divided by molecular weight of A into 1000. So, this is this will be there and from that we take out the C_A so C_A in gram per litre will be equal to P_A into molecular weight into 1000 divided by the Henry's constant sorry this will be H and this will be a 18. So, H with respect to A we can write like this also. So, this is in gram per litre, and in milligram per litre, it will be 10 raise to 6 here. So, this way we can find out that concentration or solubility of any compound in water.

So, this is the basic derivation or equation by which. So, for finding out this we require the Henry's constant so, this is there. So, this also tells two things the C_A is directly proportional to the partial pressure and also it is inversely proportional to Henry's constant. But this Henry's constant which is there, what is its unit that is very very important.

Because Henry's law or equation can be represented two different forms. This is only one of the form, there are different forms and in the literature or in the front problems will be finding that Henry’s constant the unit is always not atmosphere or any pressure unit. It may be entirely different units for HR represented. So, we will we are going to discuss that also.

(Refer Slide Time: 20:22)



Henrys’ law and constants (gases in water at 298 K)

$P = atm$

Types of Henrys’ equations	$k_{H,px} = \frac{p_{gas}}{x_{aq}}$	$k_{H,pc} = \frac{p_{gas}}{C_{aq}}$	$k_{H,cp} = \frac{C_{aq}}{p_{gas}}$	$k_{H,cc} = \frac{C_{aq}}{C_{gas}}$
Dimension	$\left[\frac{atm \times mol_{soln}}{mol_{gas}}\right]$	$\left[\frac{L_{soln} atm}{mol_{gas}}\right]$	$\left[\frac{mol_{gas}}{L_{soln} atm}\right]$	Dimensionless
CO_2	0.163 E4	29.41	3.4 E-2	0.8317
Ar	3.955 E4	714.28	1.4 E-3	3.425 E-2
O_2	4.259 E4	769.23	1.3 E-3	3.180 E-2
CO	5.828 E4	1052.63	9.5 E-4	2.324 E-2
H_2	7.099 E4	1282.05	7.8 E-4	1.907 E-2
N_2	9.077 E4	1639.34	6.1 E-4	1.492 E-2
Ne	12.300 E4	2222.22	4.5 E-4	1.101 E-2
He	14.970 E4	2702.70	3.7 E-4	9.051 E-3

Value

Solubility

C_{aq} = moles of gas per liter of solution

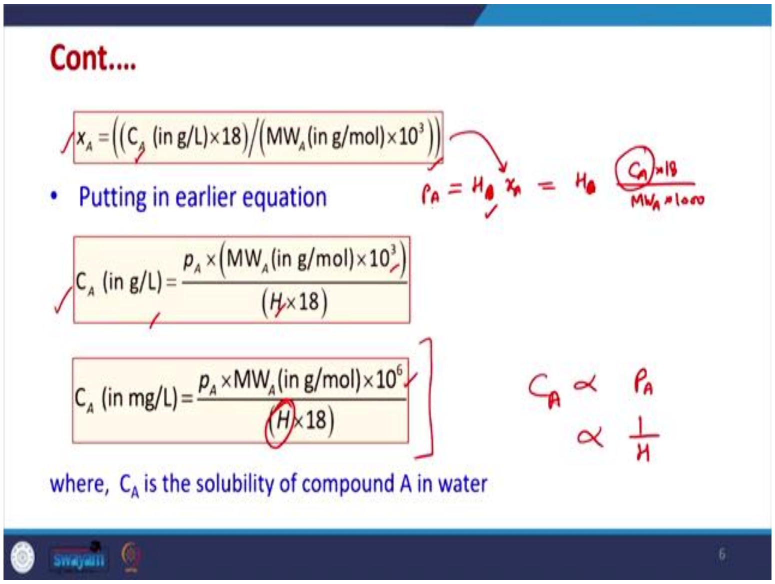
L_{soln} = liters of solution

p_{gas} = partial pressure of gas above the solution (atm)

x_{aq} = mole fraction of gas in solution = moles of gas per mole of solution ≈ moles of gas per mole of water

$C \propto \frac{1}{H}$

Source: R. Sander: Compilation of Henry's law constants (version 4.0) for water as solvent, Atmos. Chem. Phys., 15, 4399-4981 (2015), doi:10.5194/acp-15-4399-2015



Cont....

$$x_A = \left(\left(C_A \text{ (in g/L)} \times 18\right) / \left(MW_A \text{(in g/mol)} \times 10^3\right)\right)$$

$$p_A = H_A x_A = H_A \frac{C_A \times 18}{MW_A \times 1000}$$

- Putting in earlier equation

$$C_A \text{ (in g/L)} = \frac{p_A \times \left(MW_A \text{(in g/mol)} \times 10^3\right)}{(H \times 18)}$$

$$C_A \text{ (in mg/L)} = \frac{p_A \times MW_A \text{(in g/mol)} \times 10^6}{(H \times 18)}$$

$$C_A \propto p_A$$

$$\propto \frac{1}{H}$$

where, C_A is the solubility of compound A in water

Now, going further, so, I already told there are different types of Henry's equation possible. So, this is the one that we have discussed. So, in that case what we did is that Henry's constant was represented like K_H so here it is represented by K_H we can write like H also. So, H or K_H, here there is one thing more to remember, we have given some subscripts. So, and these subscripts are given because, how the equation is used depending upon that subscript has been notified here.

So, the first equation that we studied here partial pressure of gas divided by mole fraction of that compound in the aqueous phase was there. So, this is there partial pressure of gas in the solution and X aqueous is the mole fraction of gas in the solution. So, if this form is there we write P_X. So, this is P and this is X so, that is why P_X for other cases these is like P_C then C_P because and then C_C.

So, there are different notations their units are different remember their units are different and in the literature you will be finding all these forms. So, never get worried, that Henry's constant value has been given in different units it is possible and we have different equations of same Henry's law which are represented in differently.

Now, the second equation is that, that the Henry's constant is equal to the partial pressure of gas divided by the concentration of the compound in the aqueous phase. So, this is there so, we can directly use to find out concentration, but this is the more common value. So, we use this. Similarly, the opposite also may be given. So, depending upon the unit what we should do is that, we should try to see the unit which is given for Henry's constant what is the dimensions which are given. So, generally it may be atmosphere only or any pressure unit so, it is possible you can find it here atmosphere is there because mole mole will go off so mole it will be only written atmosphere for the Henry's content in this case this is there.

Now, for the second equation it will be given like litre or metre cube anything into pressure unit divided by moles of gas. So, this this is concentration mole per litre and partial pressure maybe any pressure unit. Similarly, the opposite is possible and there is a dimensionless form also which is there.

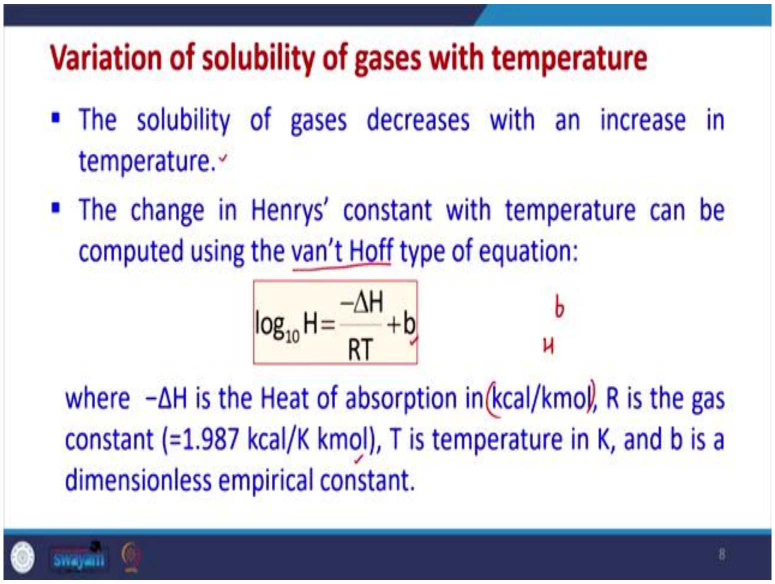
Now, going further there are the values of Henry's constant at for various gases in for the condition of water at 298 kelvin is given here and the values are represented here and these have been compiled from this source and now, all these values are for different gases like carbon dioxide, argon, oxygen, carbon monoxide, hydrogen and nitrogen, neon, helium et cetera.

Now, these values are represented and these values are kept in this manner the values are always increasing. So, this is a one thing which is given here the values are always increasing. Now, in the previous slide we had discussed that the C_A is directly proportional or inversely proportional to H. So, that means, if the partial pressure of gas is constant or otherwise we can put like this. So, we have a closed enclosure and it is having certain what is there that water is suppose filled in this case and now gas is being pumped in.

So, depending upon the vapour space which is there, so, if this vapour space is constant or the partial pressure of the gas is constant, then the solubility of gas will be always inversely proportional to the Henry's constant, under same pressure partial pressure condition the solubility of CO_2 will be highest that means, and solubility of a helium will be lowest because it has higher value.

And since the C is inversely proportional, so we will always the values are increasing in this manner, but the solubility will increase in this manner. So, that means, but this is only true for the condition where the partial pressure is constant, but partial pressure has lot of effect, because in the natural environmental conditions, the partial pressures are different. Now, and we will understand this by solving some problems.

(Refer Slide Time: 25:20)



Variation of solubility of gases with temperature

- The solubility of gases decreases with an increase in temperature.
- The change in Henrys' constant with temperature can be computed using the van't Hoff type of equation:

$$\boxed{\log_{10} H = \frac{-\Delta H}{RT} + b}$$

b

H

where −ΔH is the Heat of absorption in (kcal/kmol), R is the gas constant (=1.987 kcal/K kmol), T is temperature in K, and b is a dimensionless empirical constant.

The change in Henrys' constant with temperature can be computed using the van't Hoff type of equation:

$$\log_{10} H = \frac{-\Delta H}{RT} + b$$

where −ΔH is the Heat of absorption in kcal/kmol, R is the gas constant (=1.987 kcal/K kmol), T is temperature in K, and b is a dimensionless empirical constant.

Going further. Now, there is always a variation of solubility of gases with temperature. So, the solubility of gases, already we have learned in the temperature is one of the important parameter during physico chemical characterization, and then physical characterization temperature important because with increase in temperature, the solubility of gases decreases and solubility our interest is more in the oxygen. So, oxygen solubility also decreases.

So, any thermal power plant et cetera, they cannot increase the temperature of the water beyond a certain value, so, generally only 10-degree rise is permitted. So, this is there and that is why the solubility of gases decreases with an increase in temperature. Now, if this is so, so certainly the Henry's constant will also vary with change in temperature, and that effect can be accounted for by finding out certain parameters.

So, the change in Henry's constant with temperature can be computed using one type of equation. So, this type of equation is there and were like here it is represented log 10 H is equal to minus of delta H divided by RT plus b, where R is the universal gas constant and its unit may be any other unit also only one unit is given here.

And delta H is the heat of absorption in kilo calorie per mole, it may be any other unit also it is possible to change the unit or any other unit, then T is the temperature in kelvin and b is a dimensionless less empirical constant, which can be used to find out the values of Henry's constant at other temperatures, et cetera.

Now, if we knew the value of b, and if we know the, then we can find out the value of H at any other temperature, and if we can find out any other temperature, we can understand that what is the solubility. So, this is very, very important thing and this idea not only this the partial pressure is also very important.

So, that is why in the, if you go to buy purchase a canned cold drink. So, any canned cold drink always contains CO_2 and depending upon the pressure at which that cane has been filled. So, what is the pressure of that cane? Whether it is 2 bar, 3 bar, 5 bar et cetera depending upon that the amount of CO_2 dissolved in that cold drink will be different and if that is different, the taste will be different and also the cost will also be different.

So, this is very, very important and it depends upon H value. And once the solubility of CO_2 is different, the pH condition may also change inside the cold drink. So, both temperature, partial pressure they are very important factor in solubility of any gas inside the temperature. Today, we will end this lecture and we will continue with solving some of the problems in the next lecture and then further continuing with other theories.

Further with respect to how the oxygen transfer takes place inside any aviation unit and what are the various resistances et cetera and what are the factors along with the temperature that affect the oxygen transfer rate or the air transfer rate inside any aeration chamber or in bio reactors also because most of the bio reactors also require oxygen and there also there are a lot of resistance which are there. So, we can understand both aeration unit and biological reactors how the oxygen transfer take place together. So, this way we are ending today's lecture and we will continue on aeration topic. Thank you.