Electrochemical Technology in Pollution Control

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Lecture – 04
Properties of solution 1

Welcome to the class again. In the last class we have discussed about the atomic structure and also some fundamental terms of aqueous chemistry and we have to view in this session we are going to discuss about the properties of the solutions. And I have defined some numbers some technical terms which we commonly use in all our day to day life and in chemistry also.

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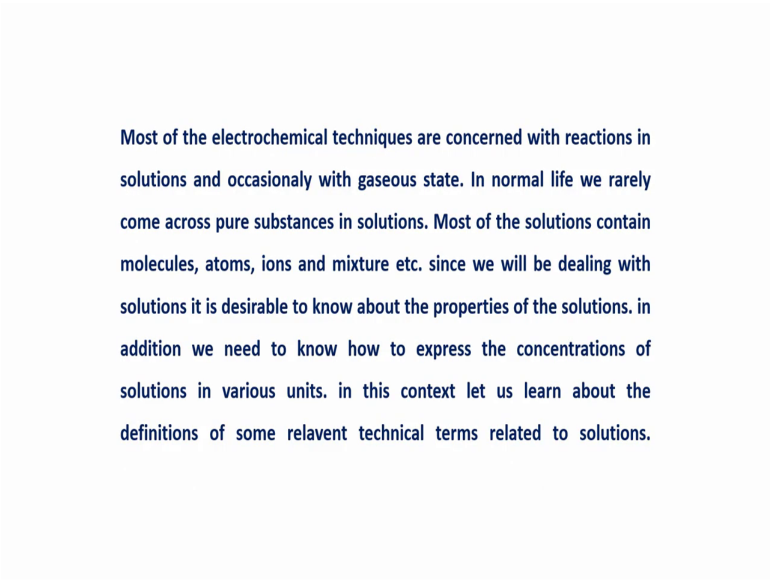

Most of the electrochemical techniques are concerned with reactions in solutions and occasionaly with gaseous state. In normal life we rarely come across pure substances in solutions. Most of the solutions contain molecules, atoms, ions and mixture etc. since we will be dealing with solutions it is desirable to know about the properties of the solutions. in addition we need to know how to express the concentrations of solutions in various units. in this context let us learn about the definitions of some relavent technical terms related to solutions.

So, most of the electrochemical techniques are concerned with the reactions of solutions and occasionally in the gaseous state and most of the solutions contain molecules, atoms, ions, mixtures etcetera, since we will be dealing with solutions it is better to know about how to express the concentrations of the solutions in various units. A lot of IIT students are asked questions in this area express the concentration of one by a particular unit into another concentration units, 99 percent of the time I see that most of the students fail in converting from one unit into another unit.

So, anyway that is a data part since we also have lot of engineers in our in my course it is better to recapitulate basically this is all high school stuff only that is second PU stuff and let us learn about the definitions this I have already covered in the last class, but for your benefit I want to quickly do it once again.

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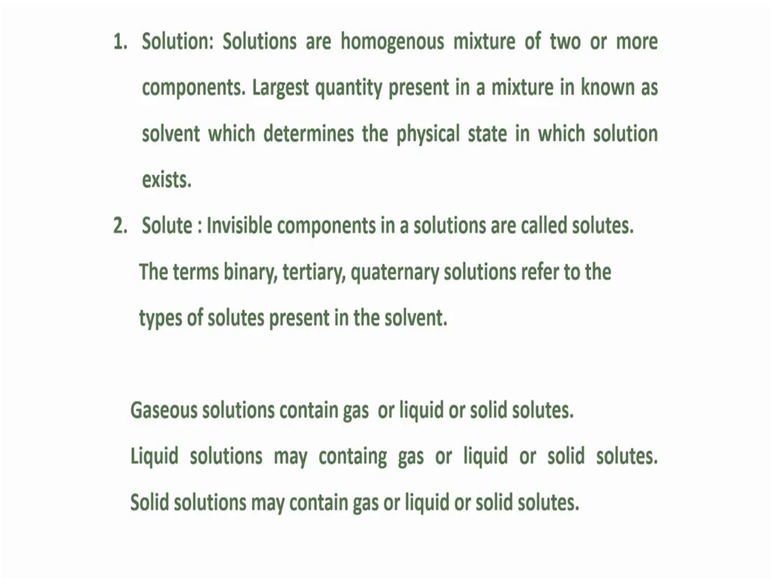

1. Solution: Solutions are homogenous mixture of two or more components. Largest quantity present in a mixture in known as solvent which determines the physical state in which solution exists.
2. Solute : Invisible components in a solutions are called solutes. The terms binary, tertiary, quaternary solutions refer to the types of solutes present in the solvent.

Gaseous solutions contain gas or liquid or solid solutes.
Liquid solutions may containg gas or liquid or solid solutes.
Solid solutions may contain gas or liquid or solid solutes.

So, solution is substance which contains a solvent and a another component that is dissolved in that that is solute. So, we have defined solute and solution. So, solution is in large larger quantity solute is in smaller quantity. So, solution or solvent is a major component in a solution and solute would be a minor component, solute can be any number 1, 2, 3, 10, 100s maybe 1000s depends ok.

So, we have solutions of different substances that is gaseous solutions containing gas liquid or solids, we can have liquid solutions containing gas or liquid or solid solutes and we can have solid solutions that is solid solutions only. They may contain gas for example, there are a lot of gas sponge a metal iron you can you would have seen with lot of blisters you know those things contain contained gas at one time. So, they are all solid solutions containing gases.

They may contain liquids if you break a lot of stones you will see that there are some stones in which some water would have been held lot of our folklores contains stones containing water and water in the stones. So, when the stones break water comes out and that is right like we can also have solid solutions, solids that is something like alloys and mixture alloys and mix mixtures mixture solutions.

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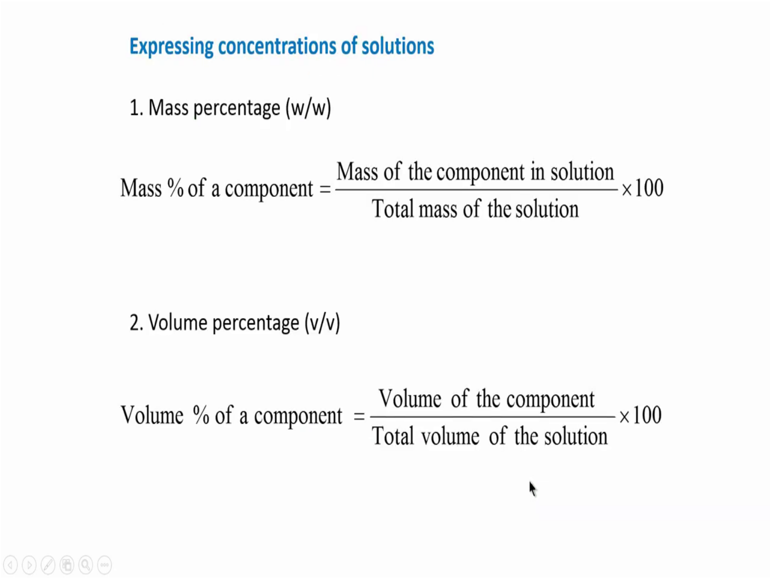

Expressing concentrations of solutions

1. Mass percentage (w/w)

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in solution}}{\text{Total mass of the solution}} \times 100$$

2. Volume percentage (v/v)

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of the solution}} \times 100$$

So, we have expressed concentration these are the standard terms one is mass percent of a component that is the mass of the component divided by total mass of the solvent or solution multiplied by 100 and we have volume percent that is 100 to 100 percent again it can be told volume of the component divided by the total volume of the substance, so many ml of a solute in so many ml of the solution like that. This is a very standard solution whenever we say give me coffee I will say put 5 grams in 100 ml that is how coffee is made put 2 grams in 100 ml I do not want coffee I want only a small 0.5 gram like that we can express volume component.

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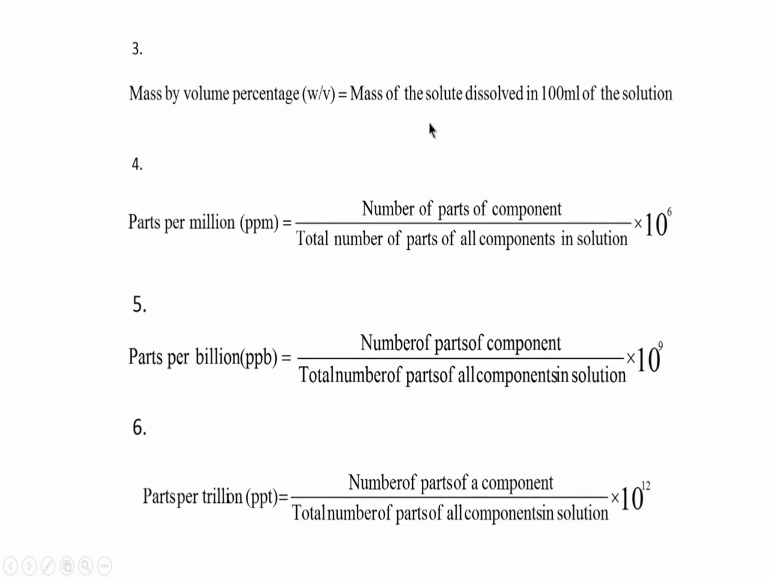

3.

Mass by volume percentage (w/v) = Mass of the solute dissolved in 100ml of the solution

4.

$$\text{Parts per million (ppm)} = \frac{\text{Number of parts of component}}{\text{Total number of parts of all components in solution}} \times 10^{6}$$

5.

$$\text{Parts per billion(ppb)} = \frac{\text{Numberof partsof component}}{\text{Totalnumberof partsof allcomponentsin solution}} \times 10^{9}$$

6.

$$\text{Partsper trillion (ppt)} = \frac{\text{Numberof partsof a component}}{\text{Totalnumberof partsof allcomponentsin solution}} \times 10^{12}$$

And then we have mass by volume component that is mass of the solute dissolved in 100 ml of the solution not necessarily 100 ml, but it is denoted by v whatever is the volume then we have parts per million that is number of parts of component contained in 10 raise to 6 parts of the solvent, that is on number of parts of a component total divided by total number of parts of all components including the solvent. So, that is 10 raise to 6 that is ppm and ppm is also known as micro gram per milliliter or milligram per k n grams per k g ok.

So, 1000 times smaller than that concentration is parts per billion that is 10 raise to minus 9 to express substances in parts per billion level what you should do is take number of parts of component divided by total number of other solvents etcetera and multiply it by 10 raised to 9. Then we also have parts per trillion level that is one in 10 raised to 12 this thing that is known as pico grams pico grams per ml that is 10 raised to minus 12 that is ppt parts per trillion. We also have femto grams that is 10 raised to minus 15 etcetera, but they are not very relevant to our studies in this.

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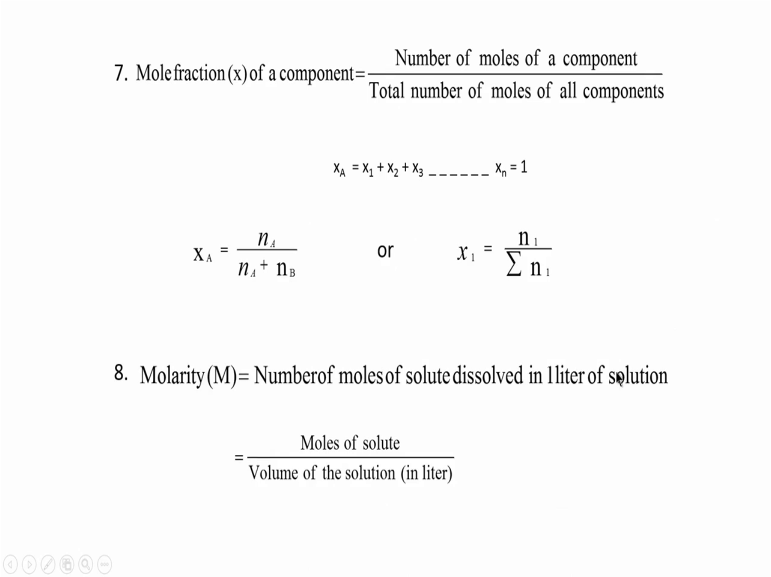

7. Mole fraction (x) of a component $= \frac{\text{Number of moles of a component}}{\text{Total number of moles of all components}}$

$x_A = x_1 + x_2 + x_3$ ______ $x_n = 1$

$x_A = \frac{n_A}{n_A + n_B}$ or $x_1 = \frac{n_1}{\sum n_1}$

8. Molarity (M) = Number of moles of solute dissolved in 1 liter of solution

$= \frac{\text{Moles of solute}}{\text{Volume of the solution (in liter)}}$

Then I have defined a mole fraction that is total number of moles of a component divided by total number of all components. So, if I have x 1, x 2, x 3 etcetera substances dissolved in a solvent I would say that the mole fraction of A is given by n a divided by n a plus n b plus n c plus there whatever it is all other components or I can simply write sigma n 1, n 1 divided by sigma n 1 plus n 2 plus n 3 like that we can write.

Then I have defined what is known as molarity, molarity is number of moles of solute dissolved in 1 liter of the solution. So, molarity is nothing, but atomic weights of these substances in grams and then dissolved in 1 liter suppose you only want you want 1 liter 1 gram 1 molar sodium chloride all you have to do is take 23 gram of sodium and 30 grams of chloride chlorine and then mix them that is sodium chloride that makes it 58. So, if you dissolve 58 grams of sodium chloride you have one mole of solution we should dissolve it in 1 liter. So, the definition goes like this moles of solute divided by volume of the solution in liters.

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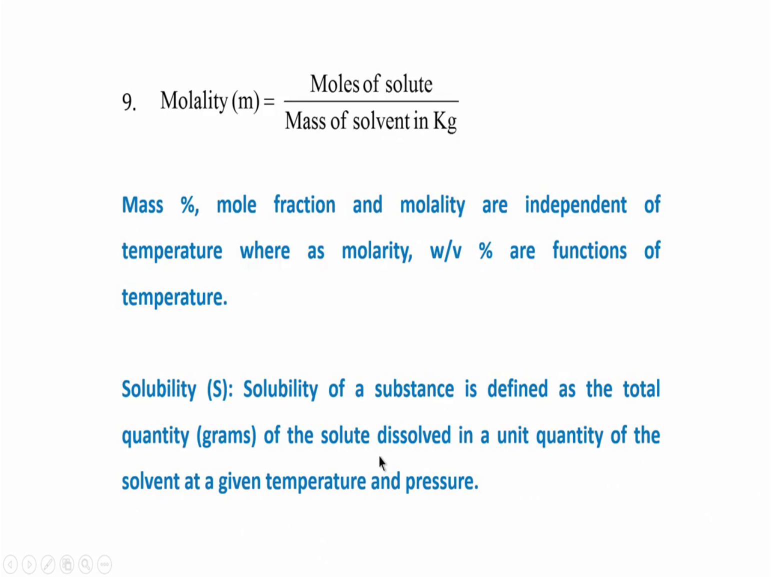

9. $\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in Kg}}$

Mass %, mole fraction and molality are independent of temperature where as molarity, w/v % are functions of temperature.

Solubility (S): Solubility of a substance is defined as the total quantity (grams) of the solute dissolved in a unit quantity of the solvent at a given temperature and pressure.

There is one more parameter that is molality that is a one is molarity, another is molality. So, lity so, molality is defined as moles of the solute that is same as atomic weights of the substances divided by mass of the solvent in kg, in the molarity we have volume of the solvent in liters. So, mass percentage mole fraction and molarlity are all independent of the temperature whereas, molarity and weight by volume are functions of temperature. So, because the solubility keeps on increasing with temperature sometimes it may decrease also so, but it is a function of temperature and pressure also.

So, what is solubility? Solubility of a substance is defined as the total quantity of the solute dissolved in a unit quantity of the solvent at a given temperature and pressure and you have to specify the time, you have to specify the temperature, you have to specify the pressure, take the solvent and take the solute say that so much has been dissolved in so many ml of the solvent at this temperature and pressure. So, that is solubility.

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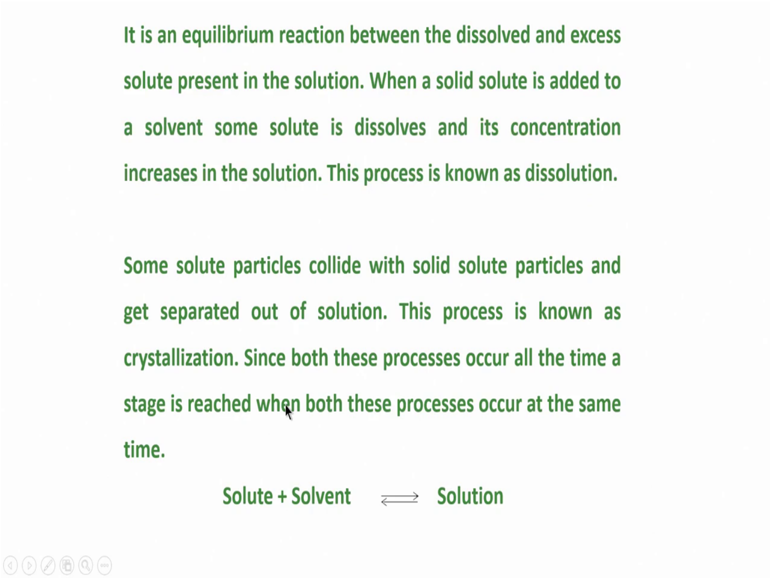

It is an equilibrium reaction between the dissolved and excess solute present in the solution. When a solid solute is added to a solvent some solute is dissolves and its concentration increases in the solution. This process is known as dissolution.

Some solute particles collide with solid solute particles and get separated out of solution. This process is known as crystallization. Since both these processes occur all the time a stage is reached when both these processes occur at the same time.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

Now, we have some a sort of equilibrium solution a reaction between dissolved and excess solute present sometimes what happens is you keep on you take solvent, I want you to imagine that you have 1 gram 100 ml of water you keep on adding sugar into that it will dissolve add more sugar it will dissolve add more sugar it will dissolve until a stage comes when it can dissolve no more sugar. So, that is an equilibrium reaction between the dissolved sugar and undissolved sugar and the solvent given amount of solvent that is at a particular pressure and temperature ok. So, this process is known as dissolution.

So, some solute particles collide with solute with solvent particles and some solute particles also and they get separated out of solution, that is what is happening whenever we add extra salts into the solution that is how it can no more dissolve. So, this process is known as crystallization. So, you prepare a totally saturated solution just leave it there, imagine honey in your house honey if you just keep it like that there will be sugar crystals at the bottom.

So, how do they form? Because the water evaporates and solute particles that is sugar particles will collide with other sugar particles will collide with other solvent solutions and then precipitate and crystallize the process is known as crystallization. Since both these processes occur at all the time a stage is reached when both these processes occur at the same speed otherwise at some stage it must keep on dissolving at some stage it must keep on precipitating out. So, I have an equilibrium solution a reaction that is solvent plus solute is a solution.

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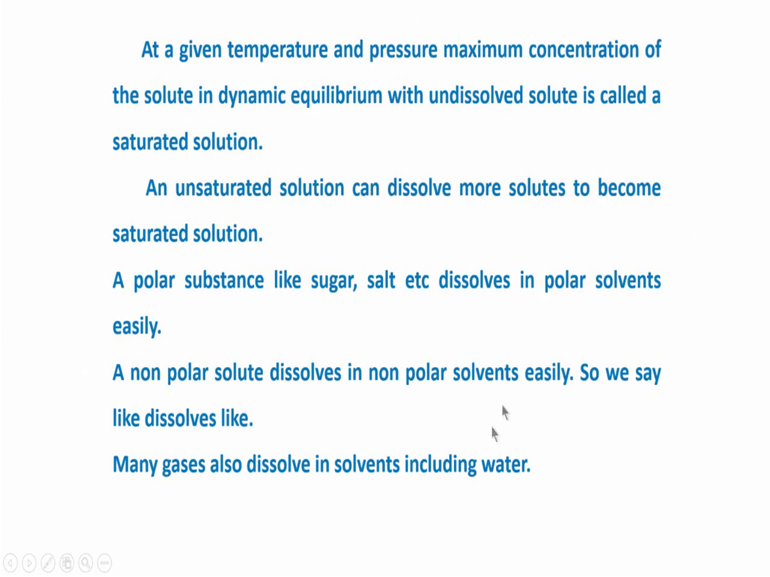

At a given temperature and pressure maximum concentration of the solute in dynamic equilibrium with undissolved solute is called a saturated solution.

An unsaturated solution can dissolve more solutes to become saturated solution.

A polar substance like sugar, salt etc dissolves in polar solvents easily.

A non polar solute dissolves in non polar solvents easily. So we say like dissolves like.

Many gases also dissolve in solvents including water.

And at a given temperature and pressure maximum concentration of the solute would be in dynamic equilibrium with the un dissolved solute such a system is called a saturated solution. So, for all practical purposes what you should do is keep on adding until it dissolves no more, so that is a saturated solution. So, data is available in the databases and other places Google if you hit, what is the solubility, what is the of say sugar, what is the solubility of salt in water, what is the solubility of particular chemical in a solvent like that lot of database is available.

So, an unsaturated solution can dissolve more solute whereas, a saturated solution cannot dissolve any more. So, a polar substance like sugar, salt etcetera they dissolve in polar solvents, that is water we the most polar solvent what we know in the world is water.

So, whatever is a solvent for many things in the environment that is why we have water pollution in our hand, whatever we throw reaches the rivers reaches the water reaches the sea reaches the well so, water gets polluted. So, water is being a polar substance it will dissolve many things. A non polar solute dissolves in non polar solvent. So, fundamental rule polar substances will dissolve in polar solvents, non polar substances will dissolve in non polar solvents very fairly simple to understand. So, we say like dissolves like ok.

So, many gases also dissolve in solvents that is also a situation which is very common in our day to day life, whenever we have acid rain in the environment we have sulfur dioxide dissolving in rainwater. So, we get acid rain. So, if you get caught in a situation first time rains in the season they will bring down all the sulfur dioxide, nitrogen oxides and other things in the form of rain and if they fall on your skin you may get irritation, it depends upon the concentration of sulfur dioxide, nitrogen oxides, etcetera in the atmosphere. So, many gases also dissolve in the solvents including water. So, the solubility of a solid in liquid is influenced by Le’ Chateliers principle.

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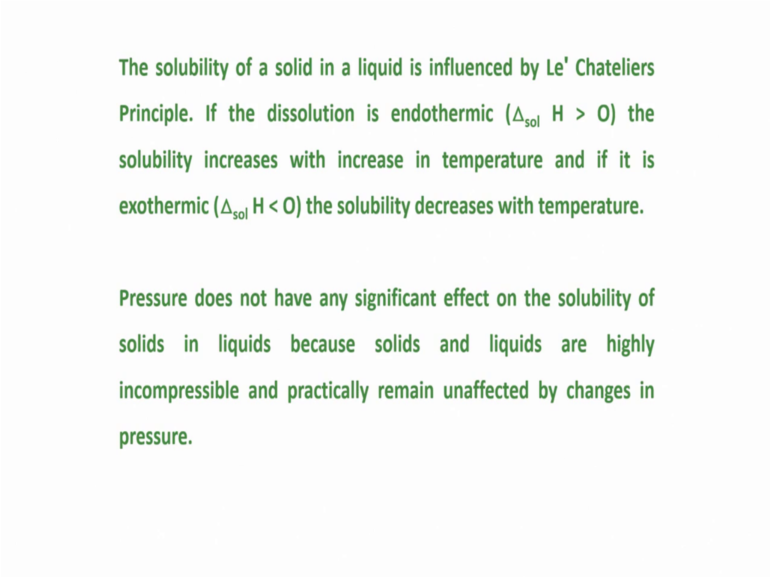

The solubility of a solid in a liquid is influenced by Le' Chateliers Principle. If the dissolution is endothermic ($\Delta_{sol} H > O$) the solubility increases with increase in temperature and if it is exothermic ($\Delta_{sol} H < O$) the solubility decreases with temperature.

Pressure does not have any significant effect on the solubility of solids in liquids because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

So, what is Le' Chateliers principle? If a solution in general Le' Chateliers principle says that if I have a system I put any I try to change any conditions in a system the system will react in the opposite way to reduce the impact of the of the change that we want to induce in the given system.

So, you take a ball press it on one side other side it will expand you press this side it will expand on the other side that is a very simple way of physically putting, but lot of chemical reactions also chemical reaction systems. They do react to the same way if I try to bring in a change in the reaction conditions, if I increase the temperature solubility will increase if I increase the decrease the temperature solubility will decrease so, in such a way that the system is unaffected by other things.

So, the solubility is influenced by this Le' Chateliers principle, if this dissolution is endothermic that is delta H is less than greater than 0 delta solubility and change in the solubility heat you know a change in the heat of the solution is greater than 0; that means, it absorbs heat from outside to dissolve that is known as endothermic.

So, if it absorbs heat from outside the system will cool down. So, you try to take water and sugar or salt it becomes cool cooler then the you know room temperature. So, such reactions are known as endothermic and that also follows the Le' Chateliers principle. So, the solubility will increase with increase in temperature if I increase the temperature the system should dissolve more.

So, if it is exothermic there are some substances when you dissolve in water it heats up, you take water add a few flakes of sodium hydroxide it gets hot you can not hold it, take sulfuric acid add a little bit of water it becomes hot. So, they are all exothermic reactions they give out the heat so, to the surroundings. So, the glass that is holding the sulfuric acid and water system it becomes hot. So, such reactions are known as exothermic. Here we say delta H of the solution change in the enthalpy of the solution is greater than 0. So, the solubility decreases with temperature.

So, pressure does not have any significant effect on the solubility of solids and in liquids also to some extent. So, the liquids are highly incompressible and practically remain unaffected by changes in the pressure. So, if there are gases they do get affected by change in the pressure, but the if it is solid or liquid they do not get affected much.

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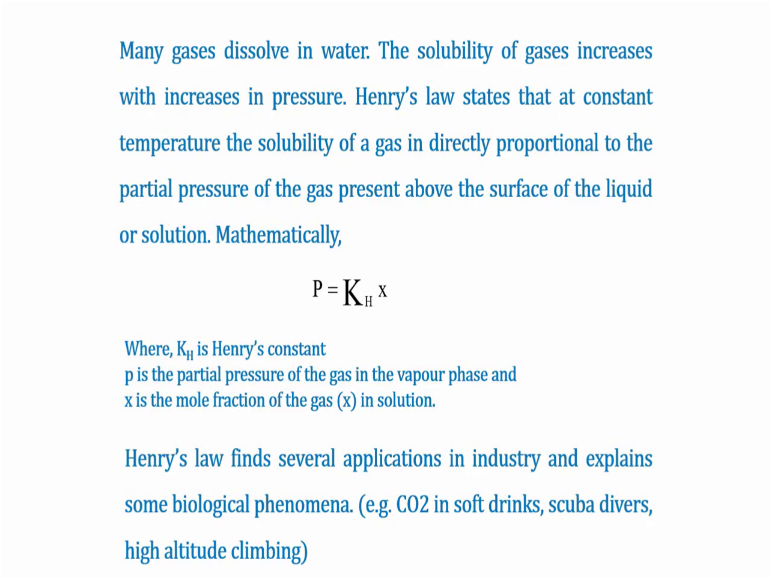

Many gases dissolve in water. The solubility of gases increases with increases in pressure. Henry's law states that at constant temperature the solubility of a gas in directly proportional to the partial pressure of the gas present above the surface of the liquid or solution. Mathematically,

$$P = K_H x$$

Where, K_H is Henry's constant
p is the partial pressure of the gas in the vapour phase and
x is the mole fraction of the gas (x) in solution.

Henry's law finds several applications in industry and explains some biological phenomena. (e.g. CO2 in soft drinks, scuba divers, high altitude climbing)

So, many gases dissolve in water, the solubility of the gases increases with increase in the pressure this we have already seen. So, there is a law that states that and that law is known as Henry's law way that states that at constant temperature the solubility of a gas is directly proportional to the partial pressure of the gas present above the surface of the solution.

This is a very simple law what you should remember is imagine a substance a beaker containing water and a gas above that. So, the gas will dissolve in water the solubility of the gas that is dissolves will be proportional to the pressure of the gas that is maintained above that is that is what it is Henrys law is about.

Mathematically we can express it like this that is P is equal to K H into X, here K H is a proportionality constant known as Henry’s constant, P is the partial pressure of the gas in the vapor phase. So, what is partial pressure? So, this is a concept lot of people do not know actually I want to tell you that partial pressure is you know you have number of gases in the atmosphere; the total amount of pressure that you see is the sum of all different gases present. So, the partial pressure of one gas is a is only the pressure exerted by one particular component of a gaseous mixture.

So, in Henry’s law coming back to this p is the partial pressure of that gas in the vapor phase that is above the liquid layer surface and X is the mole fraction of the gas. So, this law finds several applications in the industry and explain some biological phenomena for example, we put carbon dioxide in soft drinks soda you know scuba divers dissolve lot of nitrogen in their blood because their partial pressure of nitrogen increases underwater and in high altitude climbing also we have this partial pressure of the gases atmosphere becomes less. So, they carry their own breathing cylinders air cylinders is not it. So, that is about Henry’s law.

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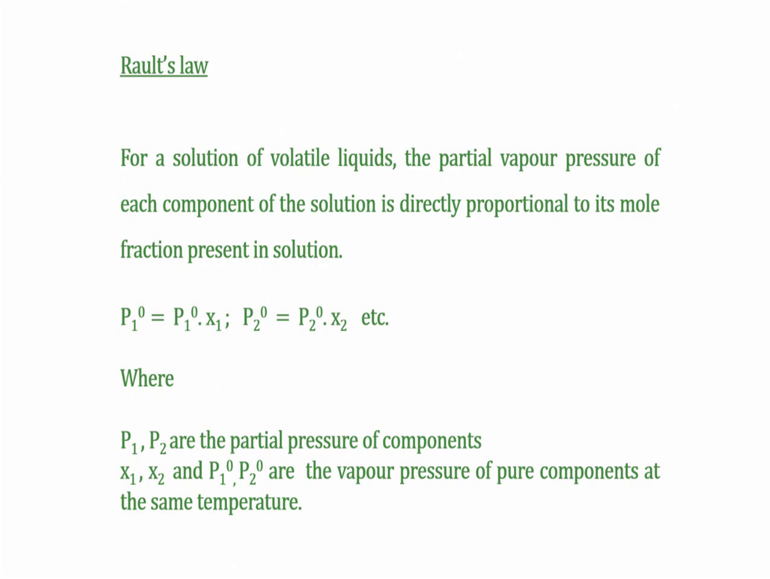

Rault's law

For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

$P_1^0 = P_1^0 . x_1$; $P_2^0 = P_2^0 . x_2$ etc.

Where

P_1, P_2 are the partial pressure of components
x_1, x_2 and P_1^0, P_2^0 are the vapour pressure of pure components at the same temperature.

Now, we have what is known as Rault's law. So, will become more technical now Rault's law is a it reads like this for a solution of volatile liquids the partial vapor pressure of each component solution is directly proportional to it is mole fraction present in the solution.

So, this is something like the other way. So, what is happening here? I have a solution I have lot of gases in that in the solution dissolved in that. So, that will also exert pressure it will be in equilibrium with the pressure with the vapor phase above the liquid surface. So, the partial pressure of each gas in the vapor phase is proportional to how much is there in the liquid phase that is how Rault's law is present. Mathematically we can say that first one component P 1 is P 1 and P 2 are the partial pressures of the components in a particular system.

So, X 1 and X 2 and P 1 and P 1 naught and P 2 naught are the vapor pressure of pure components at the same pressure. So, P 1 naught is proportional to P 1 naught into X 1 and P

2 naught would be P 2 naught 0 into X 2. So, here it is a there is an error here it should not be P 2 0 P 2 naught here it should be please make a correction if you are doing here it should not be P 2 naught it should be P 2 only and here also it should be P 1 on the left side ok.

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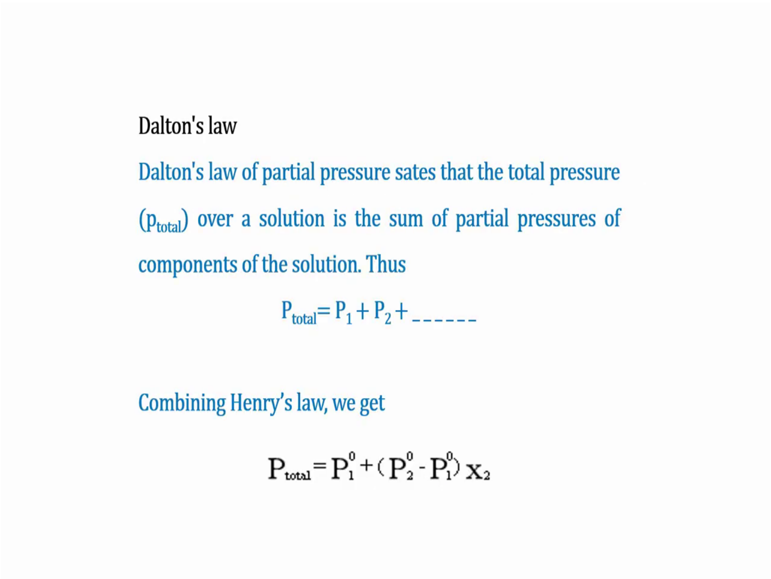

Dalton's law

Dalton's law of partial pressure sates that the total pressure (p_{total}) over a solution is the sum of partial pressures of components of the solution. Thus

$$P_{total} = P_1 + P_2 + \_\_\_\_\_\_$$

Combining Henry's law, we get

$$P_{total} = P_1^0 + (P_2^0 - P_1^0) x_2$$

So, I will try to correct that also and Dalton's law next comes Dalton's law this is another high school pre university syllabus. Dalton's law of partial pressure states that the total pressure over a solution is the sum of the partial pressures of the components of the solution.

So, what we have here in Dalton's law, we want to say that the I have a system here containing a solution I have a system here containing a solution and then there are lot of gases dissolved in that and the there is corresponding vapor pressure above every solution there is vapor pressure of the solvent we have to live with that above the sea there is lot of humidity is not it. So, wherever there are large water bodies the atmosphere becomes humid you know we do not feel comfortable. So, above every solution whether it is in a beaker or in test tube or it is just lying there will be vapor pressure above that.

So, suppose you have a system containing a solution containing number of gases each gas will exert pressure above the component of the vapor pressure is the sum of each component that is total pressure is the sum of each component that is Dalton's law. So, mathematically how do we express, we express P total is equal to P 1 plus P 2 plus P 3 etcetera depending upon how we are how many substances have been dissolved.

So, look at the slide now I have put it in the equation form that is P 1 plus P 2 plus P 3 plus so on etcetera and we can combine Henrys law and Daltons law we say total pressure is sum of P 1 0 plus P 2 naught minus P 1 naught into X 2. So, they say other thing this P 2 naught P 1 naught X 2 naught I have defined in the previous slide ok.

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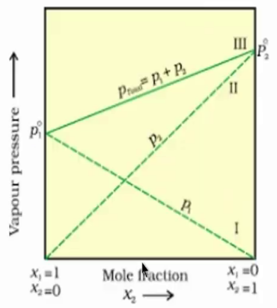

So, here I am plotting mole fraction versus pressure vapor pressure. So, the pressure here is X 1 that is pure component of X X component and when it is 100 percent pure naturally X 2 should be 0 is not it. So, here X 2 should be 0. So, it keeps on increasing here. So, I keep on in adding X 2 to the pure solution of X 1 and then it keeps on increasing when it becomes a 0 now when X 2 becomes 100 X 1 becomes 0.

So, maximum ratio mole fraction would be 0 to 1 on these cases. So, if this will be 0.2 0.6 0.5 0.8 like that up to 1. So, the here I am plotting vapor pressure versus mole fraction ok. So, total pressure P 1 is for pure component it is here that is P 1 naught and for P 2 naught vapor pressure is like this ok. So, in between any composition it will be the sum of this plus this P 1 and P 2. So, the total pressure can be represented like this.

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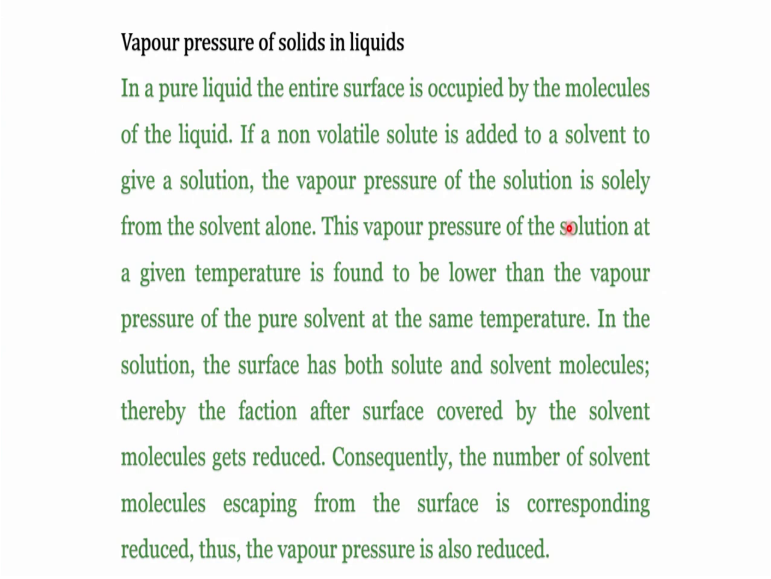

Vapour pressure of solids in liquids

In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non volatile solute is added to a solvent to give a solution, the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. In the solution, the surface has both solute and solvent molecules; thereby the faction after surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is corresponding reduced, thus, the vapour pressure is also reduced.

So, vapor pressure of solids in liquids. So, in a pure liquid the entire surface is occupied by the molecules of the liquid, is not it? If a non volatile solute is added to a solvent to give a solution the vapor pressure of the solution is only from the solvent alone. This vapor pressure of the solution at a given temperature is found to be lower than the vapor pressure of the pure solvent at the same temperature that is understood.

In the solution the surface has both solute and solvent molecules. So, molecules there by the fraction of the surface covered by the solvent molecules get reduced. Consequently the number of solvent molecules escaping from the surface will be correspondingly reduced. So, the vapor pressure also gets reduced this is only an explanation of the previous diagram ok.

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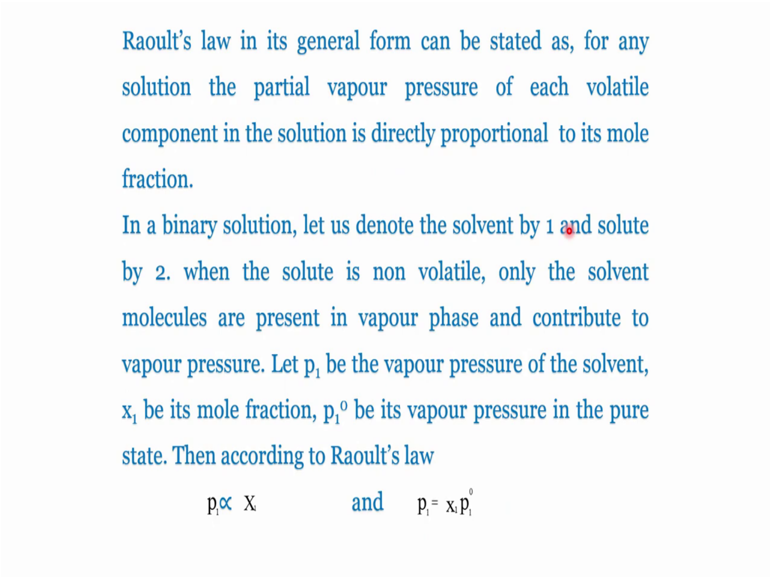

Raoult's law in its general form can be stated as, for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

In a binary solution, let us denote the solvent by 1 and solute by 2. when the solute is non volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let p_1 be the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto X_1 \quad \text{and} \quad p_1 = x_1 p_1^0$$

So, Rault's law in general in it is general form can be stated that for any solution the partial vapor pressure of each volatile component is directly proportional to it is mole fraction. So, suppose I have 2 2 solvents 2 solutions it is known as binary solution then solvent let us denote solvent 1 here and solute by 2. So, when the solute is non volatile only the solvent molecules are present in the vapor phase and they contribute to the vapor pressure because the solute does not have vapor pressure, it is a solid, solids have very little vapor pressure.

So, if the solute is a solid it will have very less vapor pressure. So, let P 1 be the vapor pressure of the solvent like X 1 be it is mole fraction P 1 naught will be it is vapor pressure then according to Rault's law you can say P 1 is proportional to X 1 and P 1 would be equal to X 1 and P 1 naught multiplication a very simple mathematics here this thing.

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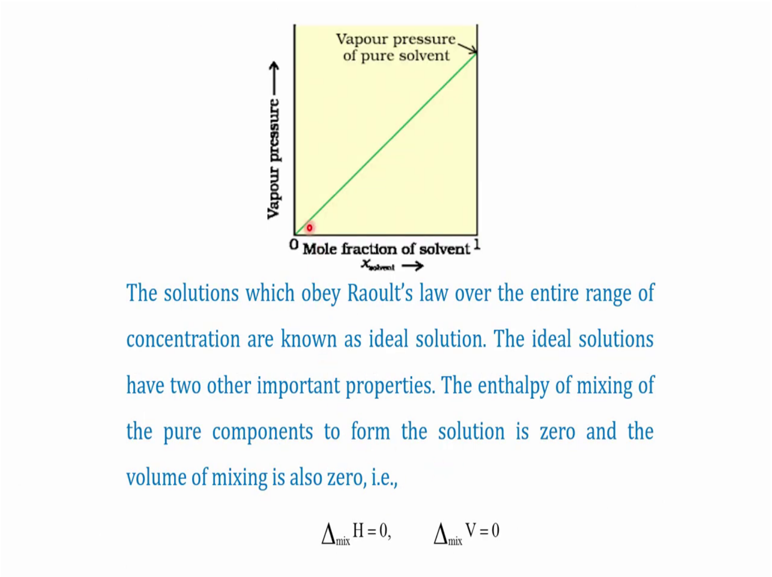

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solution. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{mix}H = 0, \qquad \Delta_{mix}V = 0$$

So, vapor pressure of the pure solvent keeps on increasing as the mole fraction keeps on increasing when it is 0 vapor pressure is 0, when the solvent is 100 percent it will reach up to a maximum this is the characteristic of the of each solvent. So, this curve may have different slopes for different solvents for solvent 1 it may go like this, for solvent 2 it may go like this, for solvent 3 it may go like this and somewhere. So, the solutions which obey Rault’s law over the entire range of concentrations are known as ideal solutions entire range that is from 0 mole fraction to 1 mole fraction. So, if it obeys Rault’s law then it is known as ideal solution.

Ideal solutions have 2 important properties what are they the enthalpy of mixing of the pure components to form the solution is 0; that means, almost no heat is generated during mixing and the volume of mixing is also 0; that means, when I take a substance add a little solute the and temperature does not increase that is number 1, number 2 is the volume of mixing after sometimes if you add 2 solutions of solvents the volume will increase here if you take a solid and try to dissolve it in liquid the volume will not increase. So, delta H is equal to 0, delta H of mixing heat of the mixing is 0 and I have volume mixing volume delta change in the mixing volume is also 0 here ok.

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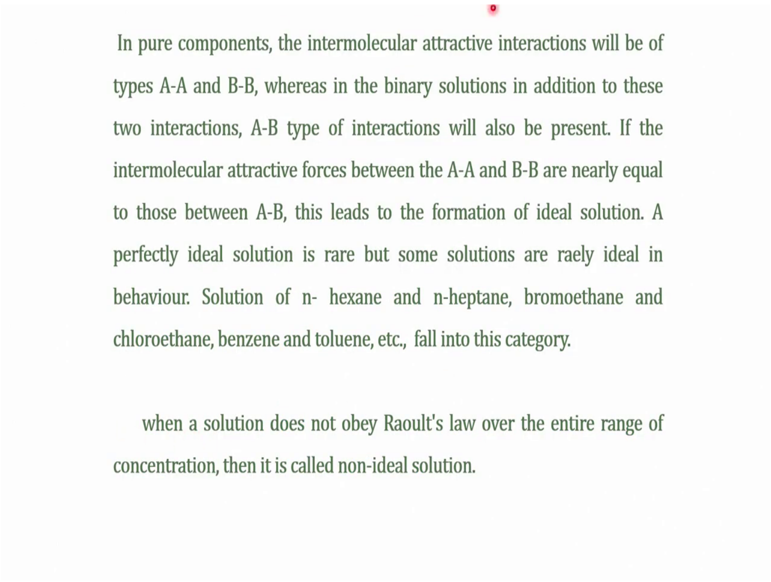

In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are raely ideal in behaviour. Solution of n- hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc., fall into this category.

when a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution.

So, this is a very important concept in pure components the intermolecular interactions attractive interactions will be of A-A and B-B whereas, in binary solutions in addition to this A-A and B-B we have A-B type of interaction molecules of a may react with molecules of b attract attractive interaction. So, if the interact molecular attractive forces between A-A and B-B are nearly equal to that of A-B this leads to the formation of ideal solutions.

So, the what is the definition of ideal solution now, the there is no change in the heat of mixing whether it is A-A or B-B or A-B, a perfectly ideal solution is rare, but some solutions are rarely ideal in behavior. Solution of n – hexane, n – heptanes, bromoethane, chloroethane, benzene and toluene they all fall into this category they are rarely ideal in behavior.

So, when a solution does not obey Rault's law over the entire range of concentration then it is called non ideal solutions is not it, if it follows Rault's law ideal solution, if it does not follow Rault's law non ideal solution. On what range it may follow Rault's law in particular range, but it may not follow the Rault's law in the whole range of mole fraction that is 0 to 1. So, in case of so, from the Rault's law they assume that the figure is like this ok.

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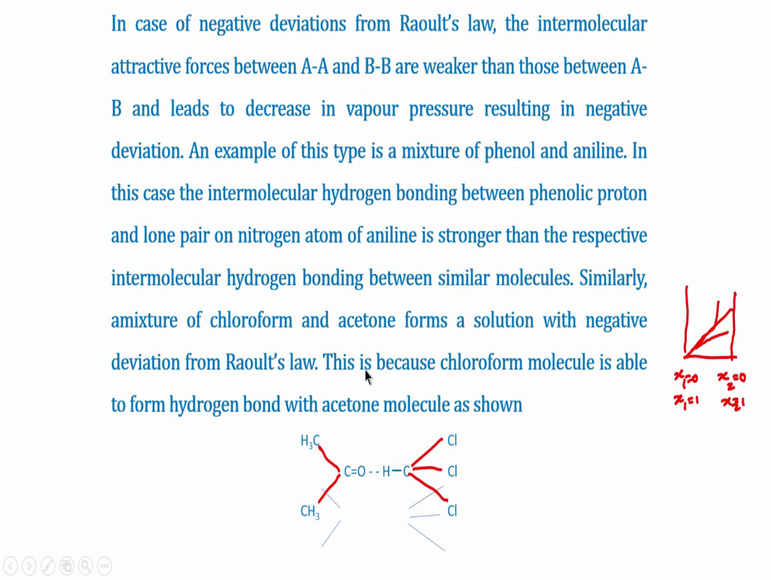

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviation. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, amixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown

If the vapor pressure is a standard that is A-A and B- B are all same and the there is no change in the enthalpy or volume delta H mixing, then it is possible that intermolecular attractive co forces of A-A and B-B are weaker than those of A and B. For example, here I have ideal Rault's law X 1 is equal to 0, here it is X 2 is equal to 1 0, X 1 is 1 X 2 is 1 here ok.

So, if it is it may follow Rault's law only after this and then go off like this or it may follow only over like this and form the go away from the ideality, ideality is what is drawn in the center. So, the non ideal this is known as negative when it is goes below this curve it is negative when it goes above this it is positive deviation from Rault's law ok. So, in this case an example of this type is a mixture of phenol and aniline.

So, what happens, in this case the intermolecular hydrogen bonding between phenolic proton and lone pair of electrons on the nitrogen atom is stronger than the respective intermolecular hydrogen bonding between similar molecules. This is slightly more technically put, but what you can say is intermolecular hydrogen bonding between phenol and nitrogen is greater than the nitrogen at the aniline.

So, here we have mixture of if I take chloroform CH 3 Cl and this is how it is represented CH 3 carbons Cl Cl and the acetone similarly chloroform and acetone CH 3 CO CH 3 is acetone and here I have CH Cl 3 there is some sort of a hydrogen bond between ketonic group and H group and with the negative deviation.

So, such molecules will show negative deviation from Rault's law that is it will bend towards y axis towards x axis, if it bends towards y axis then it is we have a positive deviation. So, this is because my chloroform molecule is able to form a hydrogen bond this molecule CH Cl 3 will react with CH 3 CO CH 3 actually this curve should have been here like this ok, it should have been this is CH 3 CO CH 3, this is CH Cl Cl the there is the interaction between these 2 ok. So, here because of this hydrogen bond there is stronger interaction and that is why it shows negative deviation from Rault's law.

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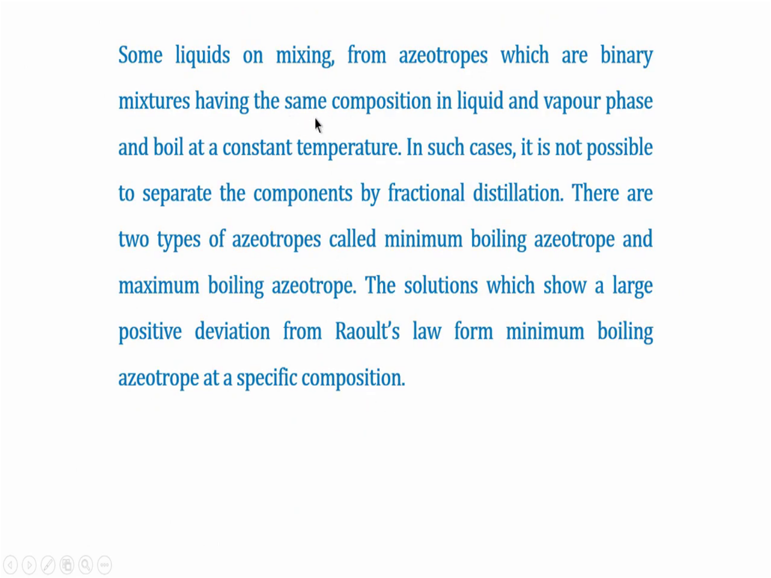

Some liquids on mixing, from azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

So, some liquids are there which are mixing form azeotropes which are binary mixtures having same composition and in liquid and vapor phase. So, substances which have got same composition; same composition within the liquid form mixture and vapor pressure same composition. So, there is no difference between the pressure expected and pressure calculated composition, you condense the vapor you will get the same solution that is such as mixture is known as azeotrope.

So, in such cases it is not possible to separate the components by distillation at all, if the vapor pressures are different then I can heat one one component heat the whole solution take out one component because we have the one with the minimum vapor maximum vapor pressure comes out first, then comes second, then comes third like that, but in the case of azeotropes vapor also is same and liquid also is same.

So, if I condense the vapor I get the same liquid. So, it is almost impossible to separate the components by fractional distillation because fractional distillation is a sort of physical separation. There are 2 types of a azeotropes called as minimum boiling azeotrope and maximum boiling azeotrope. So, the solutions which show a large positive deviation from Rault's law form minimum boiling azeotrope at a specific composition.

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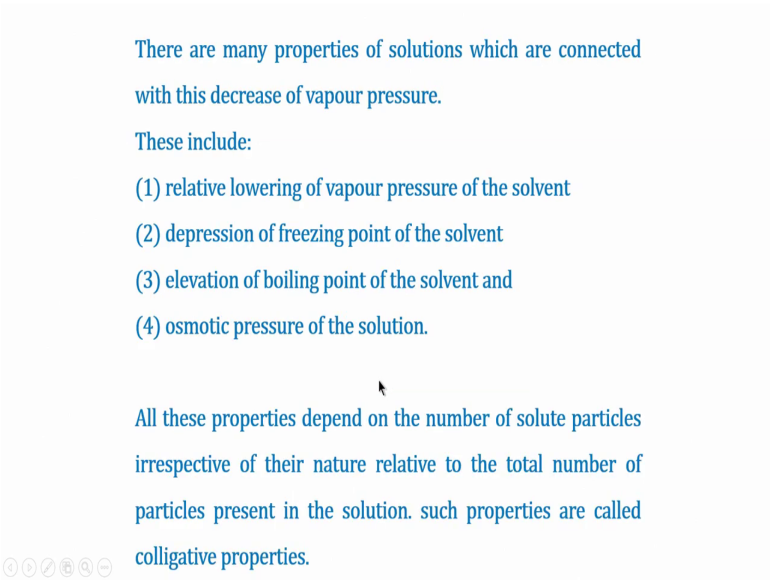

There are many properties of solutions which are connected with this decrease of vapour pressure.

These include:

(1) relative lowering of vapour pressure of the solvent

(2) depression of freezing point of the solvent

(3) elevation of boiling point of the solvent and

(4) osmotic pressure of the solution.

All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. such properties are called colligative properties.

So, we will stop here and continue our class in the next session.

Thank you.