Basic Principles and Calculations in Chemical Engineering
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Lecture # 14
Equilibrium Laws, Humidity and Saturation

Welcome to massive open online course on basic principles and calculations in chemical engineering. So, we are discussing about basic principles of multiple systems under, you know module 5. Now in this module we will discuss about that equilibrium laws, or humidity and saturation.

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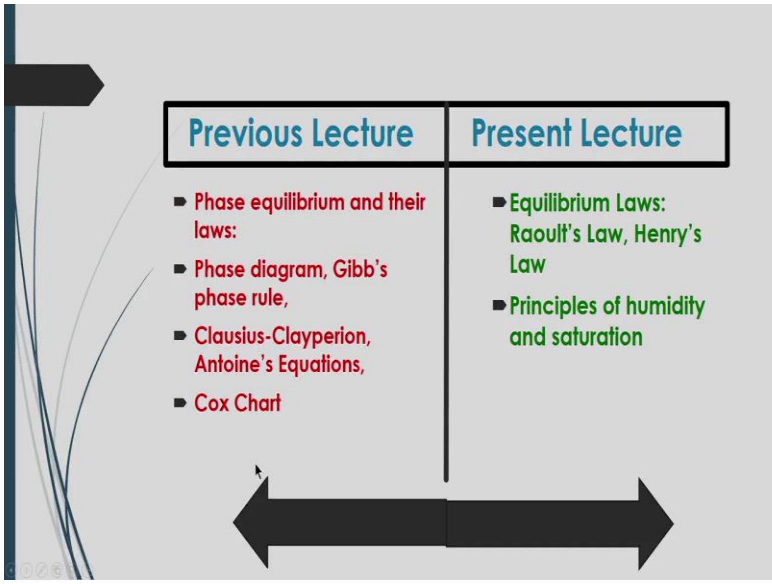

Previous Lecture	Present Lecture
Phase equilibrium and their laws: Phase diagram, Gibb's phase rule, Clausius-Clayperion, Antoine's Equations, Cox Chart	Equilibrium Laws: Raoult's Law, Henry's Law Principles of humidity and saturation

In the previous lecture we have described regarding that phase equilibrium and they are you know, different laws and also in phase diagram how we can read the different a state of the; you know substances at you know different temperature and pressure. And how that phase rule is applied to specified that is variables of the systems to you know identify any properties of the system and also we have described the vapour pressure of that you know equilibrium condition.

And also how that vapour pressure can be calculated by Clausius-Clapeyron equation with other equation like Antoine's equation and from the Cox Chart how it can be used to calculate that we have discussed there in this lecture will try to, you know describe mole about that equilibrium conditions of the systems. And how all that you know partial pressure and vapour pressure they are related to that euro liquid phase composition and vapour phase composition at its equilibrium condition with this partial pressure.

And also will try to describe something about that humidity and saturation, how that humidity criteria even what is the you know can see that moisture that is present in the atmosphere or in dry air how it can be calculated from a you know that psychometric salt that will try to you know learn something here in this lecture. Now, as we are talking about that multi-phase systems of course.

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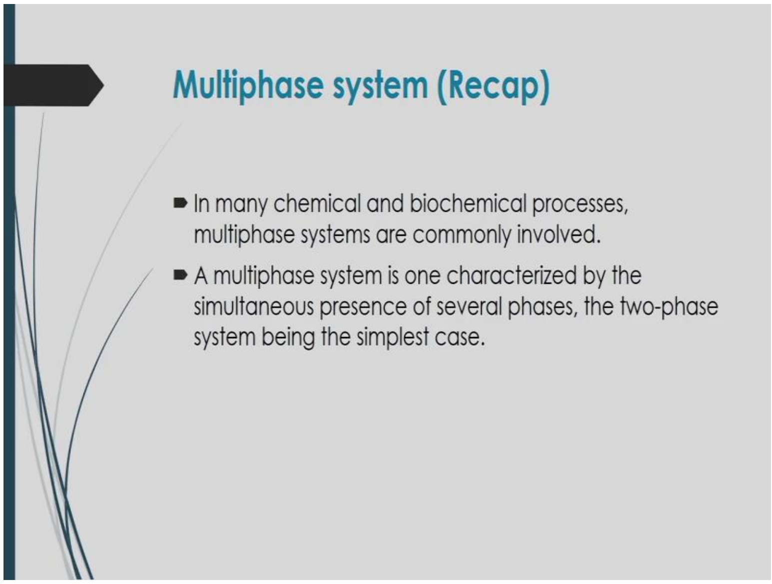

Multiphase system (Recap)

- In many chemical and biochemical processes, multiphase systems are commonly involved.
- A multiphase system is one characterized by the simultaneous presence of several phases, the two-phase system being the simplest case.

That in many chemical and biochemical you know that process systems you will see that mole than one phase will be involving for different you know, chemical a new process to you know, procure or you can sit to get the different products based on that, you know, processing of that multiple systems. Now, in that case, you will see that those phases may be sometimes in a particular condition at a certain temperature and pressure; they will be in equilibrium what we have described in our previous lecture.

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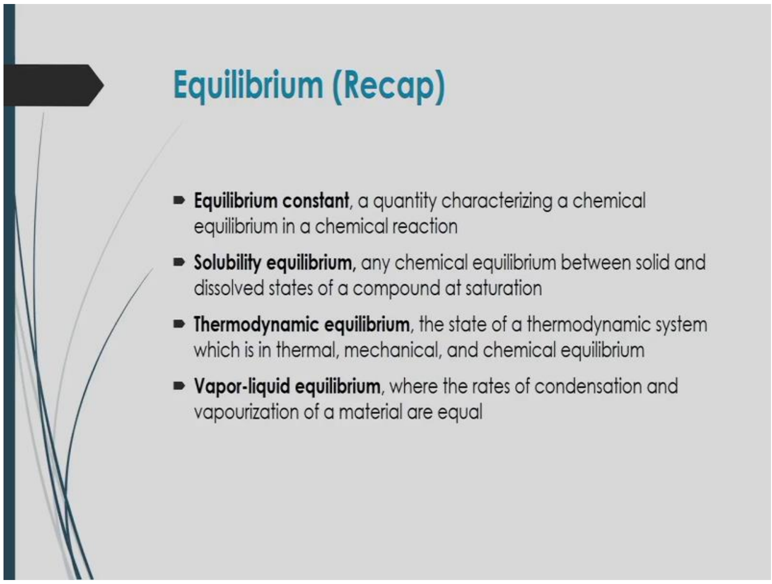

Equilibrium (Recap)

- **Equilibrium constant**, a quantity characterizing a chemical equilibrium in a chemical reaction
- **Solubility equilibrium**, any chemical equilibrium between solid and dissolved states of a compound at saturation
- **Thermodynamic equilibrium**, the state of a thermodynamic system which is in thermal, mechanical, and chemical equilibrium
- **Vapor-liquid equilibrium**, where the rates of condensation and vapourization of a material are equal

And also we have described that what are the different unit equilibrium condition like equilibrium constant solubility equilibrium thermodynamic equilibrium vapor liquid equilibrium and based on that before liquid equilibrium how we appreciate will be changing at that particular temperature and also how that diagonal partial pressure or moral composition can be calculated based on that you know that system pressure and also vapour pressure there.

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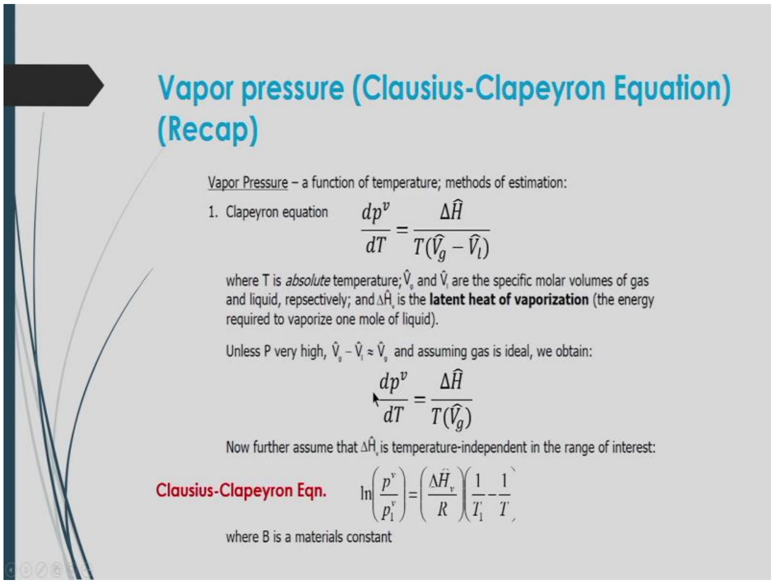

Vapor pressure (Clausius-Clapeyron Equation) (Recap)

Vapor Pressure – a function of temperature; methods of estimation:

1. Clapeyron equation $$\frac{dp^v}{dT} = \frac{\Delta\hat{H}}{T(\hat{V}_g - \hat{V}_l)}$$

where T is *absolute* temperature; $\hat{V}_g$ and $\hat{V}_l$ are the specific molar volumes of gas and liquid, repsectively; and $\Delta\hat{H}_v$ is the **latent heat of vaporization** (the energy required to vaporize one mole of liquid).

Unless P very high, $\hat{V}_g - \hat{V}_l \approx \hat{V}_g$ and assuming gas is ideal, we obtain:

$$\frac{dp^v}{dT} = \frac{\Delta\hat{H}}{T(\hat{V}_g)}$$

Now further assume that $\Delta\hat{H}_v$ is temperature-independent in the range of interest:

Clausius-Clapeyron Eqn. $$\ln\left(\frac{p^v}{p_1^v}\right) = \left(\frac{\Delta\hat{H}_v}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

where B is a materials constant

Now, we have you know that discuss about that Clausius-Clapeyron equation to calculate the vapour pressure and at different temperature if you know the consume that vapour pressure of the systems and then you will be able to calculate that you know latent heat of vaporization or if you know the latent heat of vaporization and it particular temperature of what should be the vapor pressure of the substance then based on that, you know quantity you will be able to calculate what should be the vapour pressure of other temperature for that particular substance based on this you know Clausius-Clapeyron equation.

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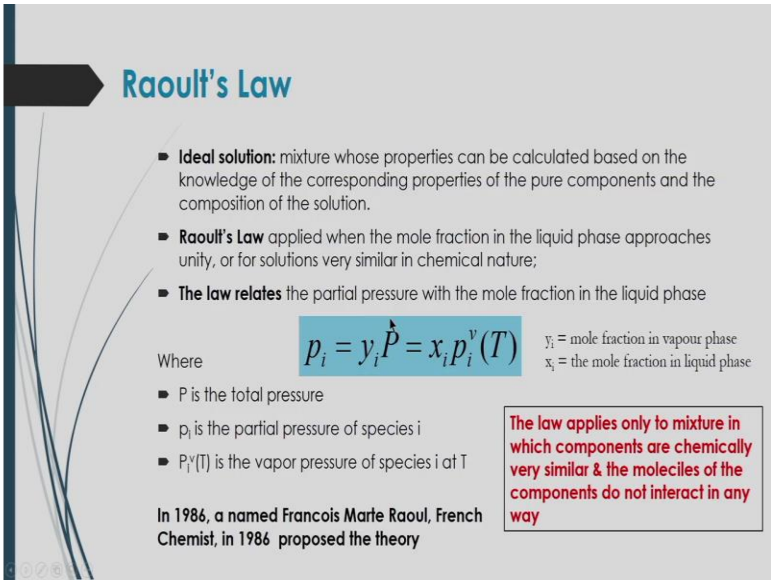

Raoult's Law

- **Ideal solution:** mixture whose properties can be calculated based on the knowledge of the corresponding properties of the pure components and the composition of the solution.
- **Raoult's Law** applied when the mole fraction in the liquid phase approaches unity, or for solutions very similar in chemical nature;
- **The law relates** the partial pressure with the mole fraction in the liquid phase

Where

$$p_i = y_i P = x_i p_i^v(T)$$

y_i = mole fraction in vapour phase
x_i = the mole fraction in liquid phase

- P is the total pressure
- p_i is the partial pressure of species i
- $P_i^v(T)$ is the vapor pressure of species i at T

In 1986, a named Francois Marte Raoul, French Chemist, in 1986 proposed the theory

The law applies only to mixture in which components are chemically very similar & the moleciles of the components do not interact in any way

Now, he had in this case, so, we will discuss another law that is called Raoult's law, who is actually will give you the you know, characteristics behavior of the you know ideal solution what is that ideal solution will be generally regarded as the mixture of you know components in a solution whose properties can be you know, calculated based on the knowledge of the corresponding properties of the pure components and the composition of the solution.

Now, in this case the Raoult's law will be applied when the mole fraction in the liquid phase that will process unity and, or pore solutions for you know, hit similar in chemical nature. Now, in this case, this law actually relates the partial pressure the mole fraction in the liquid phase. Suppose there is a you know substance like liquid is, you know becoming by its vapor at its particular you know equilibrium condition or it will see that in a particular solution, you will see that some components will be there and we need to be leveraging some components will be you know are going to the vapour phase and some components will be remaining in the liquid phase.

Now, what should be the component of that, what should be the unit concentration or mole fraction or you can say mass fraction in the liquid solution at a certain temperature and also pressure based on who is you will be able to calculate that, you know what should be the partial pressure there and also what should be vapour pressure at its equilibrium condition, that partial pressure also will be related to that.

So, know that this you know, Raoult’s law it generally relates the partial pressure we know that mole fraction in the liquid phase you can say that this partial pressure will be equal to you know mole fraction into you know a system total pressure and this partial pressure again it will be related to the you know, what will be the mole fraction of that components in the liquid phase that is denoted by xi and what should be the vapour pressure of that components at that particular temperature.

So, if you know that mole fraction of that particular component in the liquid phase and the vapour pressure of that, you know component at the particular temperature then the partial pressure. That you know that liquid phase will be all purpose particular pressure of that component, you know that will be related to this you know that mole fraction of that component in the liquid phase and vapour pressure of the component at that particular temperature.

So, this equation given in these slides is basically the mathematical expression for this Raoult’s Law. So, this is basically a relation between that partial pressure and the mole fraction of that you know component in the liquid phase and vapor pressure. So, here pi is the total pressure and P is the total pressure and pi is the partial pressure of this species i and Piv is the vapour pressure of the species i at temperature t and we will see that the law applies only to mixture in these components are, you know, chemically very similar, and the mole fraction of the components that will you know, do not interact in any way.

So, based on these you know, criteria this you know, Raoult’s Law will be applied. So, here we can say that by this Raoult’s Law will be able to know what from the partial pressure at a particular temperature once you know the mole fraction in the you know by equilibrium condition of that components and also system pressure, then you will be able to calculate What should be the partial pressure and also you can calculate that vapor pressure.

If you know the partial pressure and you know the mole fraction of the components in the liquid phase, then you can also calculate the vapour pressure there. Again, you can calculate the mole fraction of the liquid phase if you know the partial pressure and the vapor pressure they are. So, based on these Raoult's Law and based on this equation, you will be able to calculate the partial pressure or vapour pressure or you know mole fraction of the component of the liquid phase.

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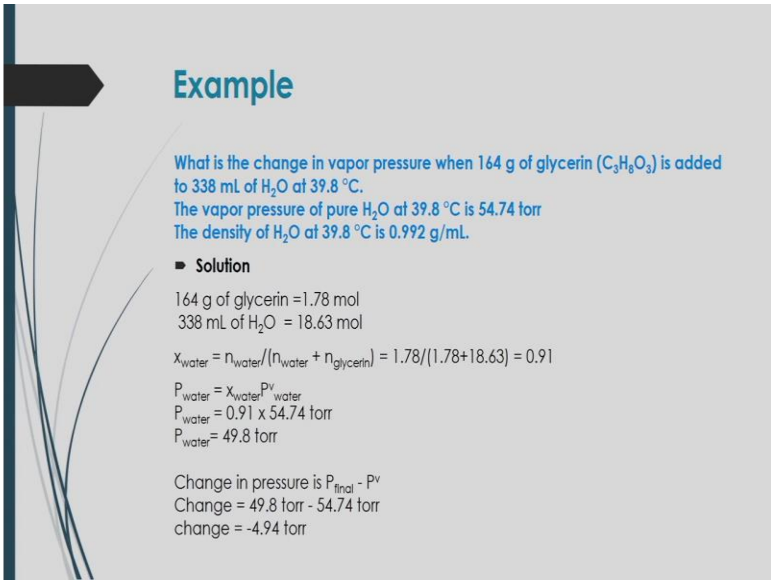

Example

What is the change in vapor pressure when 164 g of glycerin ($C_3H_8O_3$) is added to 338 mL of H_2O at 39.8 °C.
The vapor pressure of pure H_2O at 39.8 °C is 54.74 torr
The density of H_2O at 39.8 °C is 0.992 g/mL.

- Solution

164 g of glycerin =1.78 mol
338 mL of H_2O = 18.63 mol

$x_{water} = n_{water}/(n_{water} + n_{glycerin}) = 1.78/(1.78+18.63) = 0.91$

$P_{water} = x_{water} P^{v}_{water}$
$P_{water} = 0.91 \times 54.74$ torr
$P_{water} = 49.8$ torr

Change in pressure is $P_{final} - P^{v}$
Change = 49.8 torr - 54.74 torr
change = -4.94 torr

Now, let us do an example here. Now, what is the change in vapor pressure when 164 gram of glycerin is added to you know 338 milliliter of water at 39.8 degrees Celsius. In this case, the vapour pressure of the pure water at 39.8 degrees Celsius is 54.74 torr and the density of the water at this 39.8 degrees Celsius is even as 0.992 gram per milliliter. So, at this condition you have to calculate what should the change in vapor pressure of this amount of you know glycerin when it is added and added to this 338 milliliter of water at 39.8 degrees Celsius.

Now, in this case, first of all you have to calculate what should be the mole of the glycerin here. So, this glycerin, mole of glycerin can be calculated just by amount of that glycerin added divided by it is you know a molecular weight. So, simply you can get this mole of a glycerin individual to 1.78 mole and also what would be the volume of water it is given that is 338 milliliter of water and this 338 milliliter of the water that means, here how many moles of water will be there that will be just simply 18.63 mole just by having that you know one mole of you know components will add particular temperature and pressure that is at normal temperature and pressure will give you that 22.2 you know pore heater.

So, according to that we can see that how many moles of water will be there simply and after that, you have to calculate how much with a you know mole fraction of what are in the, you know solution of that glycerin. So, mole fraction of water if you know that mole of this individual component of glycerin and also what are then mole fraction will be equal to what that we saw here mole moles of water divided by total moles of you know mixture that is moles of water and moles of glycerin.

So, in this way we can say that mole fraction of you know what are will be equal to 0.91 according to this calculation. And then we know as per Raoult's law that partial pressure of the components will be able to you know mole fraction in the water into you know, mole fact partial pressure of water withdrawal mole fraction of water into you know vapour pressure of the water. So, according to that we can calculate what will the partial pressure of water it will be equal to you know x water is 0.91 and vapour pressure is 54.74 is given here.

So, ultimately this coming 49.8 torr, in this case, you will see that the change in pressure will be as what is the final pressure of that you know what are and also what will be the initial pressure of that water vapour. So, here in this case final you know that pressure is coming as what is that be final here as you know that water partial pressure at that particular condition, then it is coming 49.8 whereas, you know vapour pressure is at that particular temperature is you know 54.74 torr. So, if you subtract this, you will get that you know changing you know pressure when if you are adding these you know ugly certain of this amount. So, it will be coming as - 4.94 torr.

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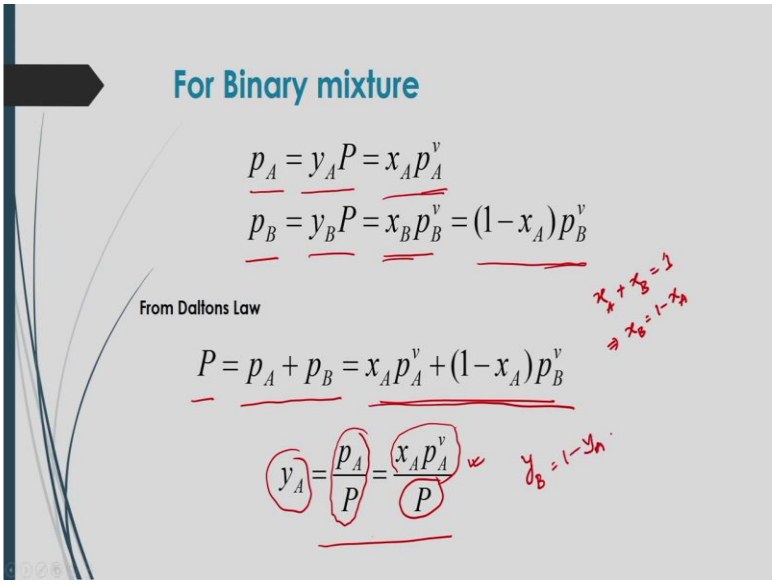

For Binary mixture

$$p_A = y_A P = x_A p_A^v$$

$$p_B = y_B P = x_B p_B^v = (1 - x_A) p_B^v$$

$x_A + x_B = 1$

$\Rightarrow x_B = 1 - x_A$

From Daltons Law

$$P = p_A + p_B = x_A p_A^v + (1 - x_A) p_B^v$$

$$y_A = \frac{p_A}{P} = \frac{x_A p_A^v}{P}$$

$y_B = 1 - y_A$

If we consider here a binary mixture for that Raoult's law, what will happen suppose there is a mixture of components A and B so, partial pressure of you know component A can be represented by yA into P, yA is the mole fraction of A and that will be equal to x A into PA into v, x is the mole fraction of component in the liquid and PA, P is the vapour pressure of the component.

Similarly, for component B that partial pressure of the component B will be equal to yB into P and that will be equal to what xB into PB into V that means here mole fraction of component B into partial you know pressure of component B. since we know that binary mixture that is xA + x B that will be equal to 1 that means summation of you know mole fraction of components or will be equals to 1. So, here xA + xB, will be close to 1 that implies that x B will be equal to 1 - xA.

So, if you substitute here 1 - x instead of xB then you can simply right here that 1 - xA into PBv. So, that is why these PB that means, partial pressure of the component B will be equal to 1 - x into PBv now, from Dalton's law that we have discussed in our earlier you know, lecture that Dalton's law basically says that the summation of partial pressures will give you that total system pressure.

So, here in this case our total pressure will be local to summation of this partial pressure of component A and B, then we can substitute that value of PA and PB here then we can write like this xA into PAv + 1 - xA into PvB. So, from these who can express here are what should be the mole fraction of you know a small fraction of A can be calculated as PA by P. So, this will be simply that xAPAv by p.

So, p can be calculated from this equation and then mole fraction of this component can be calculated by this equation. Once you know the vapour pressure of this component and also mole fraction of component A in the you know liquid and also total pressure then easily you can calculate for the mole fraction of A similarly mole fraction of B the vapour phase or that is you know, you can see that equilibrium condition in the vapour phase then yB that will be equal to 1 - yA. So, in this way you can calculate what would be a mole fraction of B there.

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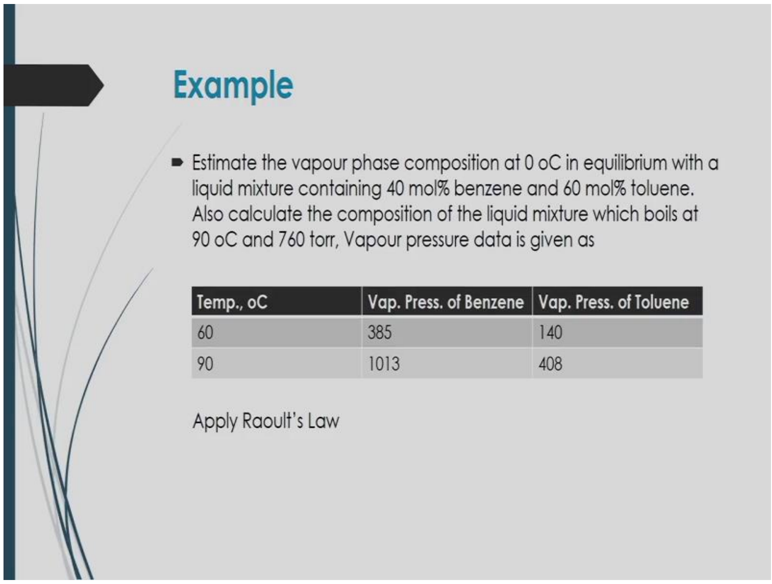

Example

- Estimate the vapour phase composition at 0 oC in equilibrium with a liquid mixture containing 40 mol% benzene and 60 mol% toluene. Also calculate the composition of the liquid mixture which boils at 90 oC and 760 torr, Vapour pressure data is given as

Temp., oC	Vap. Press. of Benzene	Vap. Press. of Toluene
60	385	140
90	1013	408

Apply Raoult's Law

Let us do an example based on these you know principles. Now, it is told you to that estimate the vapour phase composition at 0 degrees Celsius in equilibrium with a liquid mixture that contains 40 mole percent of benzene and 60 mole percent of toluene also have to calculate the composition of the liquid mixture who is boil set 90 degrees Celsius and 762 torr and vapour pressure data is given to you at 60 degrees Celsius.

This vapour pressure of the benzene is given 385 whereas vapour pressure of toluene is given a 140. They are at that 60 degree Celsius and that 90 degrees Celsius this vapour pressure of benzene 1013 and vapour pressure of toluene 408 torr.

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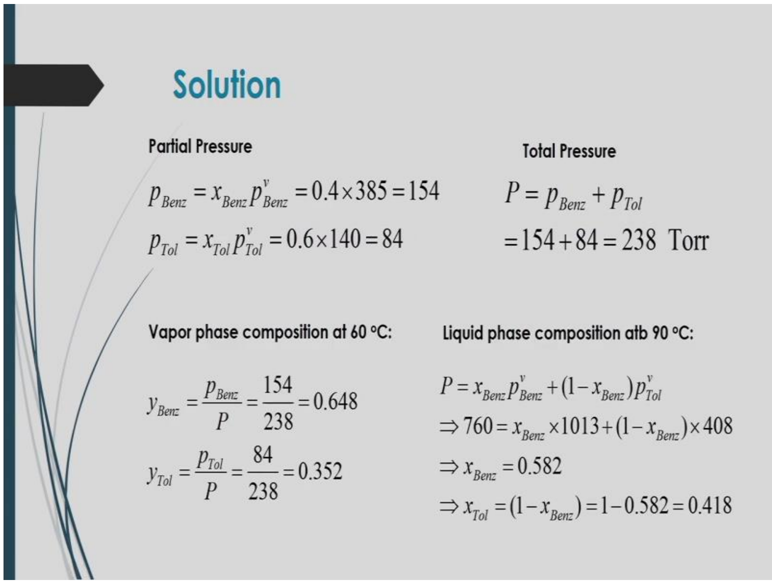

Solution

Partial Pressure

$$p_{Benz} = x_{Benz} p^{v}_{Benz} = 0.4 \times 385 = 154$$

$$p_{Tol} = x_{Tol} p^{v}_{Tol} = 0.6 \times 140 = 84$$

Total Pressure

$$P = p_{Benz} + p_{Tol}$$

$$= 154 + 84 = 238 \text{ Torr}$$

Vapor phase composition at 60 °C:

$$y_{Benz} = \frac{p_{Benz}}{P} = \frac{154}{238} = 0.648$$

$$y_{Tol} = \frac{p_{Tol}}{P} = \frac{84}{238} = 0.352$$

Liquid phase composition atb 90 °C:

$$P = x_{Benz} p^{v}_{Benz} + (1 - x_{Benz}) p^{v}_{Tol}$$

$$\Rightarrow 760 = x_{Benz} \times 1013 + (1 - x_{Benz}) \times 408$$

$$\Rightarrow x_{Benz} = 0.582$$

$$\Rightarrow x_{Tol} = (1 - x_{Benz}) = 1 - 0.582 = 0.418$$

Now, if you apply the Raoult’s law to solve this problem, we can write here, watching the partial pressure of the benzene that is based on that you know Raoult’s law we can write x benzene into you know that partial pressure of benzene vapor pressure of benzene. So, partial pressure of benzene that will be equal to mole fraction of benzene to vapor pressure of benzene that will be equal to what 0.4 into 385, what is that 0.4 it is given that 40% of the benzene will be in the mixture and vapour pressure of benzene is given as 385?

So, if you substitute this value and then multiply it you will get this 154 you know top of that benzene. So, similarly afford following that partial pressure will be equal to mole fraction of toluene into you know, vapour pressure up toluene. So, if you substitute that mole fraction of being toluene that is 0.6 and vapour pressure up toluene that is 140 after that if you multiply you will get that 84. Now, from this you can calculate what should be the total pressure. That total pressure will be equal to summation of that partial pressure of those components here.

So, it will be coming as 154 + 84 then it will give you that 238 torr now, you have to calculate what the vapor phase composition at 60 degrees Celsius. So, your vapor phase composition will be at that 60 degree Celsius that can be you know represented as y Benzene that will be equal to P Benzene partial pressure opinion out of total you know that the pressure then we can substitute this partial pressure of Benzene which is equal to 154 and this total pressure is 238.

So, it will be coming as 2.648 whereas, the same way we can calculate that toluene mole fraction and that can be you know expressed as you know ratio of that you know partial pressure up toluene into the total pressure of the system. So, it would be coming as 84 divided by 238 then it will give you 0.352. So, these are the mole fraction have been benzene and toluene in the vapor phase. Now, next problem is that you have to find out the liquid phase composition at you know that 90 degree Celsius.

Now, in this case again you have to you know, calculate what should be the total pressure at that 90 degree Celsius. Now, again that pressure will be, do you know that partial pressure of benzene and partial pressure up toluene. Now, that partial pressure of benzene as per Raoult's Law can be you know expressed as x Benzene into vapour pressure of you know that similarly, for toluene that is 1 minus Benzene into you know vapour pressure of toluene.

So, after the substitution of that composition, you know that you know Benzene and toluene we can obtain that you know that total pressure there, but here since that total pressure is not changing, so, we can write here this you know that 760 as given here, so, this 760 and also partial you know pressure spot that is what should be the vapour pressure they are also it is given.

So, that vapour pressure if you substitute here and then composition of that Benzene. It is not known to you so, finally, from this equation can calculate what is up the mole pressure of the Benzene in the liquid at that particular you know temperature here as a 90 degree Celsius. So, similarly x toluene that means mole fraction of toluene also you can calculate from this you know equation. So, it is coming finally, that mole fraction of Benzene is 58.2% whereas, mole fraction of toluene is coming here 41.8%.

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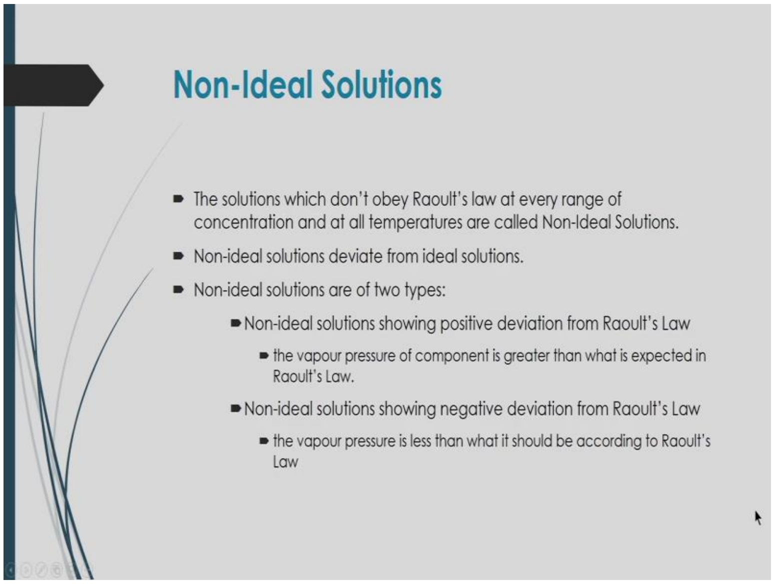

Non-Ideal Solutions

- The solutions which don't obey Raoult's law at every range of concentration and at all temperatures are called Non-Ideal Solutions.
- Non-ideal solutions deviate from ideal solutions.
- Non-ideal solutions are of two types:
    - Non-ideal solutions showing positive deviation from Raoult's Law
        - the vapour pressure of component is greater than what is expected in Raoult's Law.
    - Non-ideal solutions showing negative deviation from Raoult's Law
        - the vapour pressure is less than what it should be according to Raoult's Law

Now, we have by you know discuss about that ideal solution, where you can apply that Raoult's Law and if suppose any solution do not obey the Raoult's Law at every range your concentration and at all temperatures that will be called as non ideal solutions. Now, non ideal solutions actually deviate from that ideal solution in 2 way that is that non ideal solutions that will be showing positive deviation from the Raoult's Law be regarded as that you know, positive deviated, you know that non ideal solution.

And this case the vapour pressure of the component will be you know greater than what is expected in our Raoult's Law, whereas, some solutions will give you that negative deviation from that routes law and in that case the pressure that is vapor pressure will be less than what it actually should be for that system according to the Raoult's Law.

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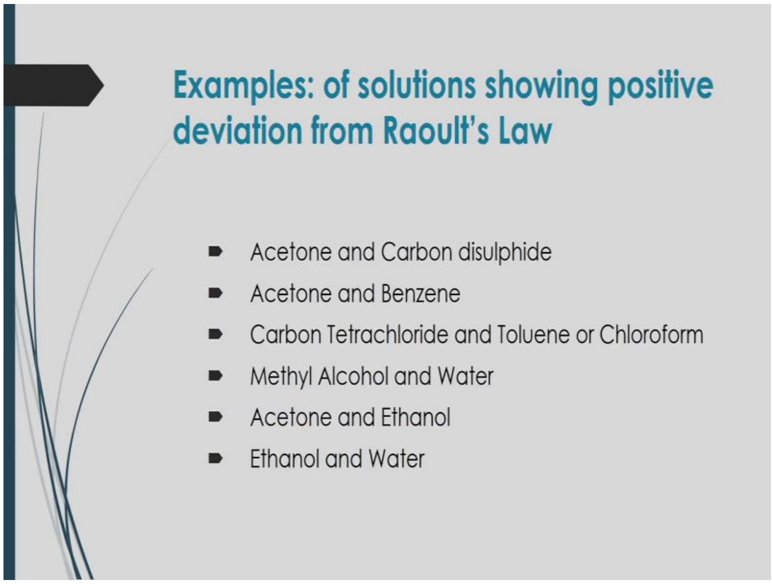

Examples: of solutions showing positive deviation from Raoult's Law

- Acetone and Carbon disulphide
- Acetone and Benzene
- Carbon Tetrachloride and Toluene or Chloroform
- Methyl Alcohol and Water
- Acetone and Ethanol
- Ethanol and Water

Now, some examples of that solution that will be showing positive deviation from the Raoult's Law like here, Acetone and Carbon disulphide, mixture Acetone and Benzene mixture Carbon Tetrachloride and Toluene or chloroform mixture, even Methyl Alcohol and Water, Acetone and Ethanol mixture. Ethanol and Water mixture that will be regarded as you know that not ideal solution of having positive deviation.

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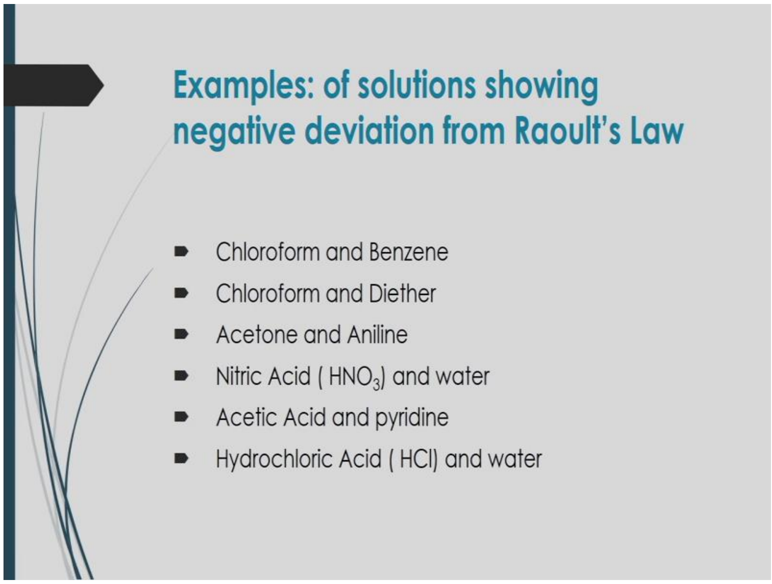

Examples: of solutions showing negative deviation from Raoult's Law

- Chloroform and Benzene
- Chloroform and Diether
- Acetone and Aniline
- Nitric Acid (HNO_3) and water
- Acetic Acid and pyridine
- Hydrochloric Acid (HCl) and water

From Raoult's Law similarly, some solutions will also showing negative deviation from the Raoult's Law like some examples here the mixture of chloroform and benzene mixture of chloroform and diether mixture of acetone aniline. Mixture of nitric acid and water and mixture of you know that acidic acid and you know pyridine and also mixture of you know hydrochloric acid and water. So, this combination of this solution you can call that are you know, non-ideal solution, which will show you the negative deviation from the Raoult's law.

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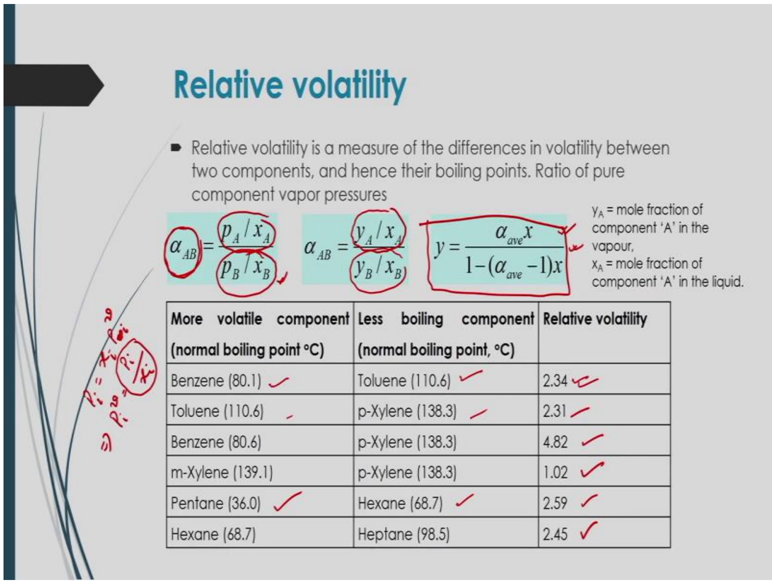

Relative volatility

- Relative volatility is a measure of the differences in volatility between two components, and hence their boiling points. Ratio of pure component vapor pressures

$$\alpha_{AB} = \frac{p_A/x_A}{p_B/x_B} \qquad \alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} \qquad y = \frac{\alpha_{ave}x}{1-(\alpha_{ave}-1)x}$$

y_A = mole fraction of component 'A' in the vapour,
x_A = mole fraction of component 'A' in the liquid.

$P_i = x_i P_i^0$

$P_i^0 = P_i / x_i$

More volatile component (normal boiling point °C)	Less boiling component (normal boiling point, °C)	Relative volatility
Benzene (80.1)	Toluene (110.6)	2.34
Toluene (110.6)	p-Xylene (138.3)	2.31
Benzene (80.6)	p-Xylene (138.3)	4.82
m-Xylene (139.1)	p-Xylene (138.3)	1.02
Pentane (36.0)	Hexane (68.7)	2.59
Hexane (68.7)	Heptane (98.5)	2.45

And other important properties of this you know, solution it is called that relative volatility. You will see that this relative volatility will measure the difference in volatility between 2 components and hence their boiling points. And in this case ratio of pure component vapor pressure will give you that you know that relative volatility and it will be represented by that alpha AB, this alpha AB then will be defined as that what is that this is your what is that vapor pressure of that pure component and A and this is a vapor pressure of component B.

So, this is your this is called vapor pressure because we know that from the Raoult's Law that partial pressure that will to you know that xi into you know that we get on vapour pressure of that component. So, in this case we can write then vapour pressure of that component will be equal to simply you know that by partial pressure by it is mole fraction. So, from this we can say that for component A that you can write that you know vapor pressure of component will be PA by xA.

And similarly for component B it will be able to you know that PB by x B. So, this relative volatility will be defined as this ratio of this you know vapour pressure of component A to the vapour pressure of component B and it is denoted by you know alpha AB and this alpha AB also her can be you know defined as these you know mole fraction of component in the vapour phase to it liquid phase for the component A.

Similarly, what should be that you know that mole ratio of the mole fraction of that component B in the vapor phase to the; you know liquid phase. So, in this way also you can you know calculate that relative volatility and if we you know that substitute that value of this you know why in terms of you know xA then you can finally calculate that part should be that or mole equation of that mole fraction in the vapor phase in terms of you know that liquid phase come mole fraction.

So, this equation will give you that you know that some equilibrium equation based on each you know relative volatility. Now, mole volatile components that is at normal boiling point degree Celsius and some will be some less boiling component normal boiling point and their relative volatility here given as yet. Suppose, there is a mixture of Benzene and Toluene here in this case, mole volatile component is Benzene whereas, less boiling point component is Toluene. In that case, this relative volatility will be equal to 2.34 as part that you know that condition.

Similarly, for following m-Xylene mixture, this latest volatility is 2.31 Benzene and m-Xylene mixture it will give you a 4.8 to m-Xylene and p-Xylene, which will give you that relative volatility will be doubled 1.02 Pentane and Hexane it will give you that relative volatility as a 2.59 whereas the mixture of Hexane and Heptane will give you the relative volatility as 2.2 you know, 45. So, this you can calculate, how to assess that the components whether it will be you know, volatile and how it will be relatively, you know, mole volatile than other components there.

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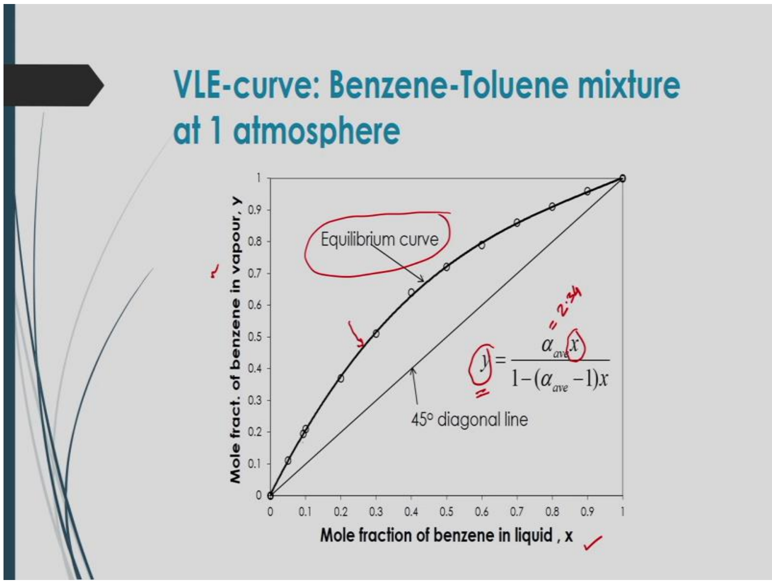

VLE-curve: Benzene-Toluene mixture at 1 atmosphere

$$y = \frac{\alpha_{ave} x}{1-(\alpha_{ave}-1)x}$$

= 2.34

Now, vapour liquid equilibrium also can be made, you know, based on that, you know, relative volatility, and also you know, composition of that, you know, mixture. Now, as we told that this, here from this relative volatility we can form this you know equation y is equal to alpha AB into x divided by 1 - alpha A B minus one into x, what is alpha A B just average you know volatility at the range of temperature and also you know, this x is the mole fraction in the liquid phase and why is the mole fraction in the you know, vapor phase.

Now, if we consider any components, then we can say that suppose A so, why you will be called to alpha AB into you know that x A divided by 1 - you know that alpha AB -1 2 x A. So, similarly for a cam component we can represent these you know that y and x our relationship in a graphical form like in that case suppose, if we consider that benzene now mole fraction of benzene in the liquid can be represented as x and mole fraction of benzene in refer as y.

So, as per that equation of y = alpha x by 1 - alpha -1 into ax then we can you know get this if you consider that that mole fraction will be 0 to 1, and if you change that mole fraction of x in the liquid phase accordingly, then it will come as you know that y value he had in this case alpha av value is you know, given as possible here, suppose, if there is a billion dollar mixture, then you have to consider that relative volatility will be equal to 2.34.

So, if you write here alpha as 2 point you know, 3, 4, and if you change the value of x accordingly you will get that y value. So, if you plot this you will get that 2 different values of you know that y value based on these different value of x. So, this line will be represented as you know that equilibrium line, this is equilibrium line. So, this equilibrium line will actually be calculated when that happens. Actually that you know benzene will be relatively higher volatile or less volatile relative to that other component and it will be useful for you know basically for you know distillation operation in chemical engineering process.

So, in that case this you know that vapor liquid equilibrium cap to be generated and also based on this vapor liquid equilibrium cap, you have you will be able to assess what should be the different mole fraction of components in different you know temperature as well as at different stages. And also what should be the mole fraction in that liquid phase of that component at different temperature and it can different stages of that you know distillation processes. Now, another important equilibrium law it is called Henry's law.

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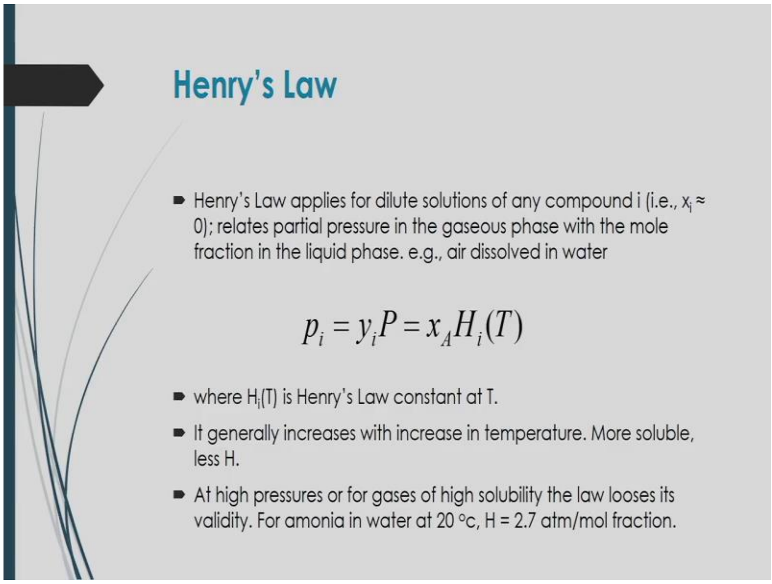

Henry's Law

- Henry's Law applies for dilute solutions of any compound i (i.e., $x_i \approx 0$); relates partial pressure in the gaseous phase with the mole fraction in the liquid phase. e.g., air dissolved in water

$$p_i = y_i P = x_A H_i(T)$$

- where $H_i(T)$ is Henry's Law constant at T.
- It generally increases with increase in temperature. More soluble, less H.
- At high pressures or for gases of high solubility the law looses its validity. For amonia in water at 20 °c, H = 2.7 atm/mol fraction.

Here in this case, listen this law will apply for dilute solutions of any compound like it here that is xA that almost will be close to you know 0 because it is dilute you can see that will release that partial pressure in the gaseous phase with the mole fraction in the liquid phase that is air dissolved in water like this so, in that case this partial pressure of that component will physical to you know that will be you know professional to that you know that mole fraction in the liquid phase.

And then professionally constant will be regarded as in this law constant at that particular time presets and it is generally increases with increasing temperature and you can say that, if you have you know values of you know in this constant you can expect that solubility will be higher at higher pressures for gases of high solubility. The law actually will not actually valid. So, in that case this law loses it is validity and for ammonia in water at 20 degrees Celsius.

In that case Henry's law constant will be equal to 2.7 atmosphere per mole fraction there so, we can see that these for dilute solutions of any compound that is partial pressure will be related to again that mole fraction of components in the liquid phase, but, this air the proportionality constant will be you know Henry’s law constant and this Henry’s law constant will give you without this you know components will be soluble or not.

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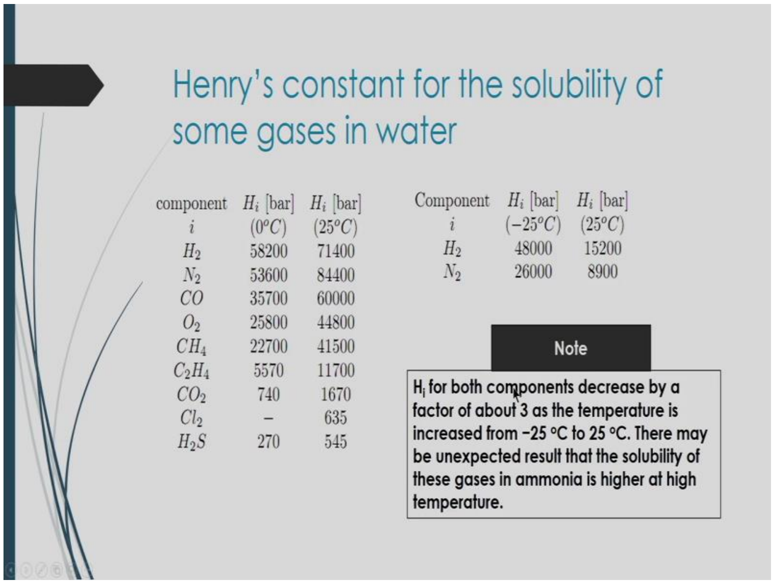

Henry’s constant for the solubility of some gases in water

component i	H_i [bar] (0^oC)	H_i [bar] (25^oC)
H_2	58200	71400
N_2	53600	84400
CO	35700	60000
O_2	25800	44800
CH_4	22700	41500
C_2H_4	5570	11700
CO_2	740	1670
Cl_2	–	635
H_2S	270	545

Component i	H_i [bar] (-25^oC)	H_i [bar] (25^oC)
H_2	48000	15200
N_2	26000	8900

Note

H_i for both components decrease by a factor of about 3 as the temperature is increased from −25 °C to 25 °C. There may be unexpected result that the solubility of these gases in ammonia is higher at high temperature.

Now, some hint is constant for the solubility of some gases in water is given like here is some components that have shown here in the slides like hydrogen nitrogen carbon monoxide, oxygen methane unit in you know, ethane, carbon dioxide, chlorine hydrogen sulphide and their respective you know that Henry's constants are given the slides at a different temperature, 0 degree Celsius and 25 degrees Celsius at constant pressure.

So, in that case, how this Henry’s law constant will be heading to temperature soon, but you have to you know, give a special attention to that hot gases nitrogen and hydrogen in that case, both components you know, henry’s law is constant decreases by a factor of about 3 as the temperature is increased from minus 25 degrees Celsius to 25 degrees Celsius, there may be unexpected result that the solubility of these gases in you know ammonia is higher at high temperatures there so, you have to you know, see these changes of this, you know, Henry’s law constant at this, you know hydrogen and nitrogen gases.

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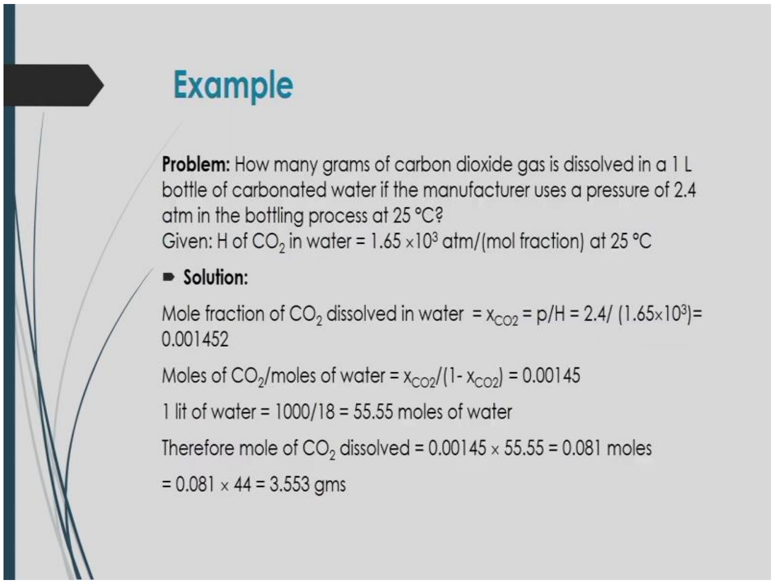

Example

Problem: How many grams of carbon dioxide gas is dissolved in a 1 L bottle of carbonated water if the manufacturer uses a pressure of 2.4 atm in the bottling process at 25 °C?
Given: H of CO_2 in water = 1.65×10^3 atm/(mol fraction) at 25 °C

- **Solution:**

Mole fraction of CO_2 dissolved in water $= x_{CO2} = p/H = 2.4/\ (1.65 \times 10^3) = 0.001452$

Moles of CO_2/moles of water = $x_{CO2}/(1 - x_{CO2}) = 0.00145$

1 lit of water = 1000/18 = 55.55 moles of water

Therefore mole of CO_2 dissolved = $0.00145 \times 55.55 = 0.081$ moles

$= 0.081 \times 44 = 3.553$ gms

Now, let us do an example based on this Henry’s law. Here, how many grams of carbon dioxide gas is dissolved in a 1 liter bottle of carbonated water, if the manufacturer uses a pressure of 2.4 atmosphere in the bottling process at 25 degree Celsius in this case Henry's constant of carbon dioxide in water is given as 1.65 into 10 to 2 or 3 atmosphere by mole fraction at 25 degrees Celsius.

Now, mole fraction of carbon dioxide dissolved in water to first find out that we Xco2 that can be you know calculated based on that Henry's law it will be coming as simply you know that what is the law here this p = x into Ace that means x will be equal to pi, pi is that when p is the partial pressure of that carbon dioxide and here this is Henry's law constant. So, here partial pressure is given to you that is 2.4 atmosphere and hinders law constant is given 1.65 into 10 to the power 3 and then finally coming 0.001452.

This is the mole fraction of carbon dioxide. Similarly, most of carbon dioxide for moles of water how to be calculated. So, here moles of carbon dioxide divided by then moles of water, so, moles of our water will be coming becoming as one minus that is moles of carbon dioxide, then, after calculation, it is coming at 0.00145. Now, 1 liter of water we can see that, that 55.55 moles of water this is in liter of water then you have to you know calculate in terms of you know moles of water because 1 bowl of water is equivalent to 22.4 liter of you know water. So, based on that you can calculate what should be the most of water in this 1 liter of water.

Therefore, moles of carbon dioxide dissolved that will be equal to what because one moles of water will dissolve this mass of 0.00145 moles of carbon dioxide. So, if you have this you know these 55.55 miles of water then you can easily calculate what should be the most of carbon dioxide will be dissolved in the water then it will be equal to 0.00145 into 55.55. So, this will give you that we are 0.081 moles of carbon dioxide, you know that will be dissolved in 1 liter of water. So, these moles of carbon dioxide simply it will give you 3.553 grams of carbon dioxide if you multiply it by its molecular wage.

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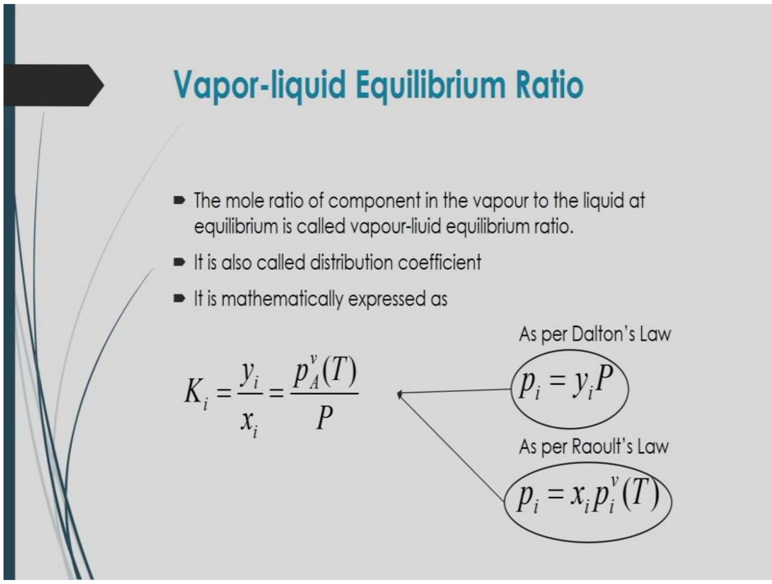

Vapor-liquid Equilibrium Ratio

- The mole ratio of component in the vapour to the liquid at equilibrium is called vapour-liuid equilibrium ratio.
- It is also called distribution coefficient
- It is mathematically expressed as

$$K_i = \frac{y_i}{x_i} = \frac{p_A^v(T)}{P}$$

As per Dalton's Law

$$p_i = y_i P$$

As per Raoult's Law

$$p_i = x_i p_i^v(T)$$

Now, then vapor liquid equilibrium ratio and other important properties have discussed liquid mixture at its equilibrium condition, in that case the mole ratio of the component in the vapor to the liquid at equilibrium is called the vapor liquid equilibrium ratio. And it is also called that distribution coefficient. How you know most will be you know distributed in the vapor from its liquid phase and it can be mathematically expressed by this you know that Ki will be equal to y i by x i is this k i will be called as that equilibrium constant or sometimes it is called distribution coefficient.

And it is simply that what is the most of you know that component in the vapor phase and most of component in the liquid phase and what is the ratio of these 2. And if you substitute that, you know, if we apply that, you know, Raoult's law, then we can say that this will be basically as you know that ratio of vapour pressure to that, you know, to partial pressure of the system. Now, as per Dalton's Law we can have that partial pressure will be triggered to y i into p.

As per Raoult's Law it p i will be equal x i into p iv into T that means, here mole fraction of that component into vapour pressure of that component. So, according to that, if we substitute here you can simply say that this k i will be difficult to here p Av that will be a ratio of vapour pressure of the component to it is you know, total pressure.

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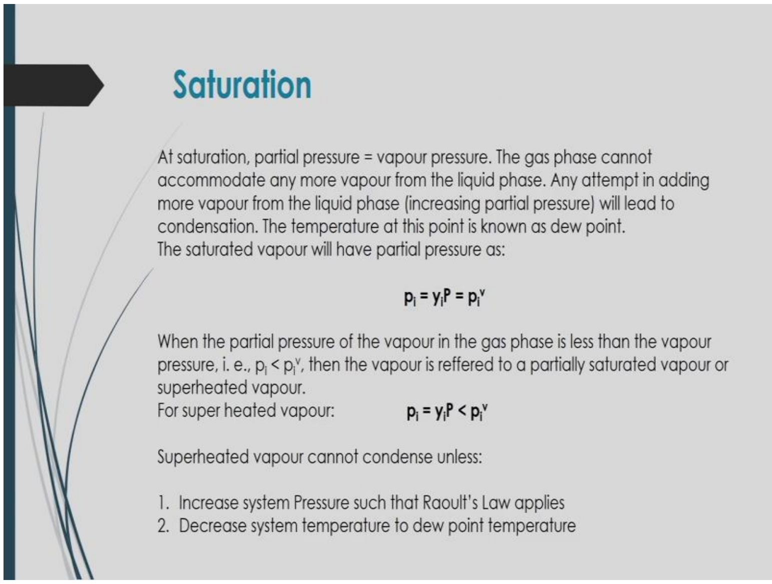

Saturation

At saturation, partial pressure = vapour pressure. The gas phase cannot accommodate any more vapour from the liquid phase. Any attempt in adding more vapour from the liquid phase (increasing partial pressure) will lead to condensation. The temperature at this point is known as dew point.
The saturated vapour will have partial pressure as:

$$p_i = y_i P = p_i^v$$

When the partial pressure of the vapour in the gas phase is less than the vapour pressure, i. e., $p_i < p_i^v$, then the vapour is reffered to a partially saturated vapour or superheated vapour.
For super heated vapour: $p_i = y_i P < p_i^v$

Superheated vapour cannot condense unless:

1. Increase system Pressure such that Raoult's Law applies
2. Decrease system temperature to dew point temperature

Now, saturation what is saturation you know, you will see that the gas phase sometimes cannot accommodate at any mole vapor from the liquid phase at particular you temperature and pressure. Now, any attempt in adding mole vapor from the liquid phase, if you increase the partial pressure there or you can see if you add mole vapor there, there will be no increase in partial pressure that may lead to the condensation.

Now, you will see that if you add mole vapor up from the liquid phase and you will see that the partial pressure will keep on increasing there. So, when you will see it condition, when you will see that partial pressure will be almost will be close to vapor pressure, you will see that that solution will be you know that necessitated with that you know vapor component. So, we can see that at a saturation condition, partial pressure will be equal to vapor pressure.

So, we can see that temperature at this point of this saturation. If you know vapor phases, you know that tries to you know be condense it at that saturated temperature. So, that temperature will be called as dew point temperature. So, we can say that when a bar you know that any you know gas or you can see mole vapor from the liquid phase tries to you know condense it higher the partial pressure will be equal to vapour pressure the respective temperature will be called as dew point temperature.

And at that condition the saturated vapor will have that partial pressure as you know that here P i will be equal to what is that y iP you know if you know that total system pressure and two components of that component in that vapor phase, then you can calculate what without partial pressure and the partial pressure will be equal to their vapour pressure of that particular components. So, when the partial pressure of this vapor in the gas phase is less than the vapor pressure, that is you know p i less than piv here has for notation.

Then the vapor phase is report to a partially saturated vapor or you can see that it will be superheated vapor and then you can see that P i will be no less than piv. Now, superheated vapor cannot condense unless that in phase system pressure says that Raoult’s law applies and also decrease the system temperature to the dew point temperature there so, these are the conditions they are to you know the superheated vapor who is may not be condensate at this condition.

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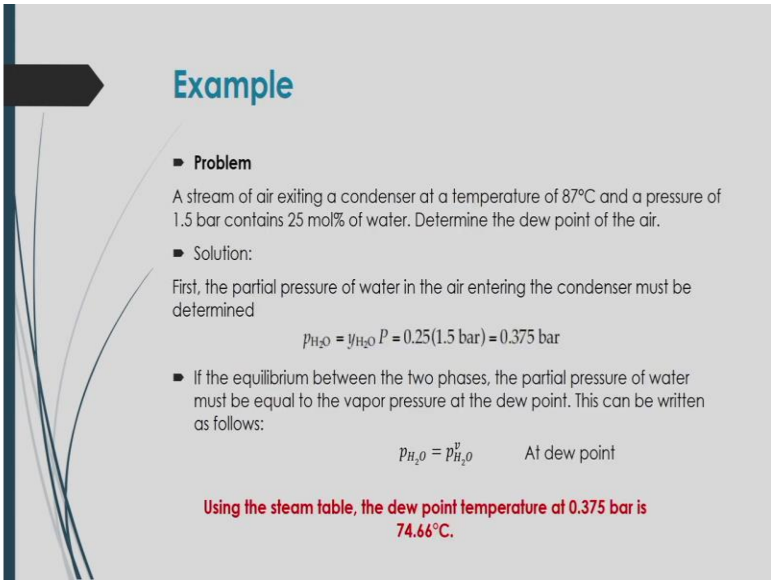

Example

- **Problem**

A stream of air exiting a condenser at a temperature of 87°C and a pressure of 1.5 bar contains 25 mol% of water. Determine the dew point of the air.

- Solution:

First, the partial pressure of water in the air entering the condenser must be determined

$$p_{H_2O} = y_{H_2O} P = 0.25(1.5\ \text{bar}) = 0.375\ \text{bar}$$

- If the equilibrium between the two phases, the partial pressure of water must be equal to the vapor pressure at the dew point. This can be written as follows:

$$p_{H_2O} = p^v_{H_2O} \qquad \text{At dew point}$$

Using the steam table, the dew point temperature at 0.375 bar is 74.66°C.

Now, let us do an example here let us say that a stream of air exiting a condenser at a temperature of 87 degrees Celsius and a pressure of 1.5 bar contains 25 mole percent of water. Now, in this case you have to know calculate to what should be the dew point of the air. Now, in this case you have to first calculate the partial pressure of the water in the air that is entering to the condenser and it can be calculated as that you know by you know that either by Raoult’s law or by you know that simply you know the Dalton’s law that will be able to partial pressure will be able to you know that mole fraction of that components into each start to temperature.

Then it will be coming as here 0.37 pipe bar. Now, if the equilibrium between the 2 phases against the partial pressure of that water must be equal to the vapor pressure at that dew point. Now, this can be written as here, partial pressure will be equal to vapor pressure. Now, using that steam double the dew point temperature at that particular condition of that equality of that partial pressure to each you know vapor pressure at a particular temperature and pressure that temperature will be as you know 74.66 degrees Celsius that you can get it from the steam table and pressure will be as you know 0.375 bar.

So, we can say that simply here that dew point will be that temperature, when this you know moisture partial pressure in the air will be you know equal to the pressure of that moisture in the air.

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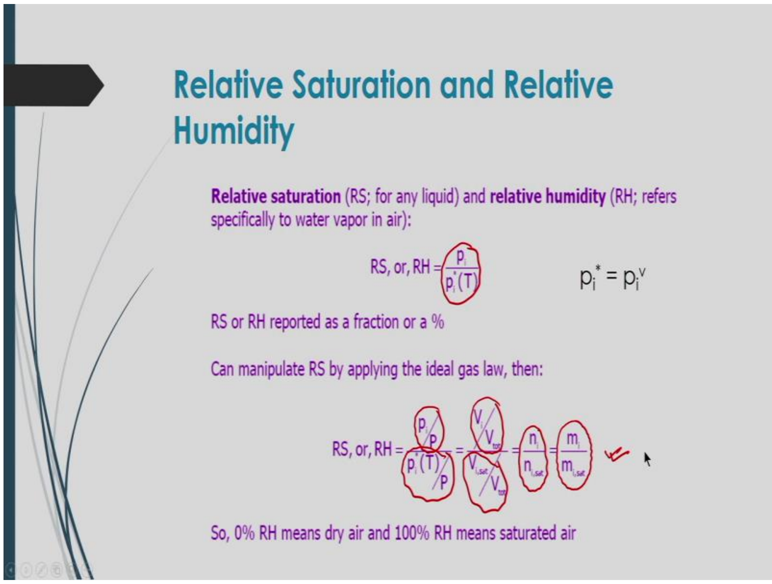

Relative Saturation and Relative Humidity

Relative saturation (RS; for any liquid) and **relative humidity** (RH; refers specifically to water vapor in air):

$$\text{RS, or, RH} = \boxed{\frac{p_i}{p_i^*(T)}} \qquad p_i^* = p_i^v$$

RS or RH reported as a fraction or a %

Can manipulate RS by applying the ideal gas law, then:

$$\text{RS, or, RH} = \frac{\boxed{p_i/P}}{\boxed{p_i^*(T)/P}} = \frac{\boxed{V_i/V_{tot}}}{\boxed{V_{i,sat}/V_{tot}}} = \boxed{\frac{n_i}{n_{i,sat}}} = \boxed{\frac{m_i}{m_{i,sat}}} \checkmark$$

So, 0% RH means dry air and 100% RH means saturated air

What is that relative saturation and relative humidity that is also important in this case, relative saturation and relative humidity can be defined as what should be the partial pressure of the moisture in the air and what will be the vapor pressure of the moisture in the air at that particular temperature, the ratio will be regarded as relative saturation or it is sometimes called relative humidity.

And also you can say that, if you apply the ideal gas law, the relative saturation or relative humidity can be defined as here you can see that what is the ratio of you know partial pressure to the total pressure it would be regarded as simply you know that mole fraction of that components in the vapor or you can see they are here in itself for the humidity consideration or in a system of gas liquid mixture, they are. So, relative saturation to be you know; defined as Pi by P divided by again the ratio of that you know vapor pressure to that total pressure.

So, here basically the ratio of you know partial pressure to the total pressure to the vapour pressure to you know total pressure. So, in this way you can write it seems here you can say that most ratio is equal to pressure issue is equal to volume ratio. So, you can represent it as volume ratio also here like this and also you can represent it as you know that mass ratio here and from that mass ratio, if you multiply it by you know molecular weight then you can represent it as mass ratio at that particular solution condition.

Now, from this, you know, principle you can say that suppose relative humidity or relative saturation, it is a carbon zero percent that means, the air will be totally dry, harassed 100% relative humidity means that it will be saturated with moisture.

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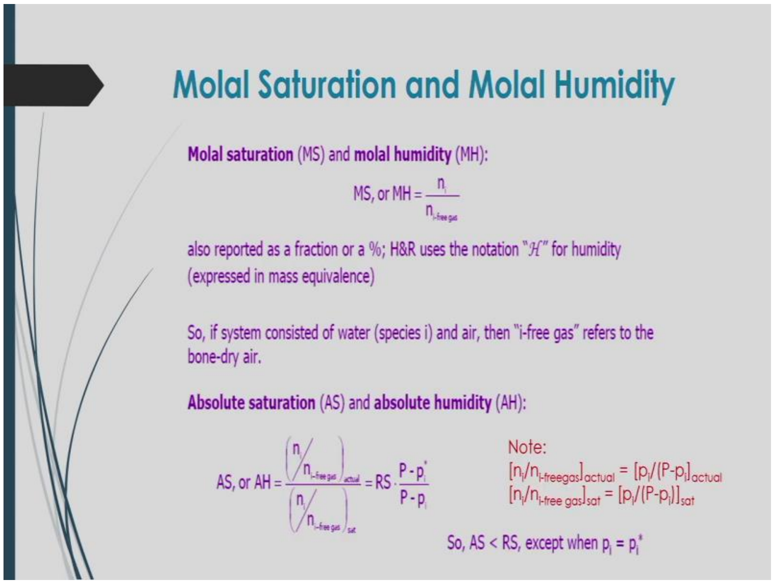

Molal Saturation and Molal Humidity

Molal saturation (MS) and **molal humidity** (MH):

$$\text{MS, or MH} = \frac{n_i}{n_{i\text{-free gas}}}$$

also reported as a fraction or a %; H&R uses the notation "$\mathcal{H}$" for humidity (expressed in mass equivalence)

So, if system consisted of water (species i) and air, then "i-free gas" refers to the bone-dry air.

Absolute saturation (AS) and **absolute humidity** (AH):

$$\text{AS, or AH} = \frac{\left(n_i / n_{i\text{-free gas}}\right)_{actual}}{\left(n_i / n_{i\text{-free gas}}\right)_{sat}} = \text{RS} \cdot \frac{P - p_i^*}{P - p_i}$$

Note:

$[n_i/n_{i\text{-freegas}}]_{actual} = [p_i/(P-p_i]_{actual}$

$[n_i/n_{i\text{-free gas}}]_{sat} = [p_i/(P-p_i)]_{sat}$

So, $\text{AS} < \text{RS}$, except when $p_i = p_i^*$

There is another representation of that saturation called that Molal saturation and also humidity respective which is called Molal Humidity. Molal Saturation or Molal Humidity is defined as similarly by that mole ratio here and also it is sometimes you put it as a fraction or a suppose a percent here sometimes some books they are using as humidity representation like this and also sometimes, if the system consisted of water species i and air.

Then i-free gas refers to the bone-dry air here for the presentation of this Molal saturation or Molal Humidity. Now, what is the absolute saturation or absolute humidity that is also defined as like here given in this equation here so, this is basically the ratio of you know most of that component i to the moles of its you know, in the, you know, free gas they are in excellent condition and also that ratio will be in the you know saturated condition, how it will be there and based on that excellent saturation condition if you make it ratio they need to be called as you know absolute saturation or absolute humidity and it is defined as by this equation.

Now, in this case, you have to remember that, if suppose absolute saturation is less than relative saturation, then you can say that P i that means partial pressure will not be close to that vapor pressure, but this will come only when then if this partial pressure is you know that changing or deviated from the vapor pressure so, this absolute pressure will be you know, then defined in terms of relative saturation and also that ratio of that you know, vapor pressure to the partial pressure deviated from the total pressure. So, in this case of course, that this you know absolute pressure will be you know less than saturated pressure.

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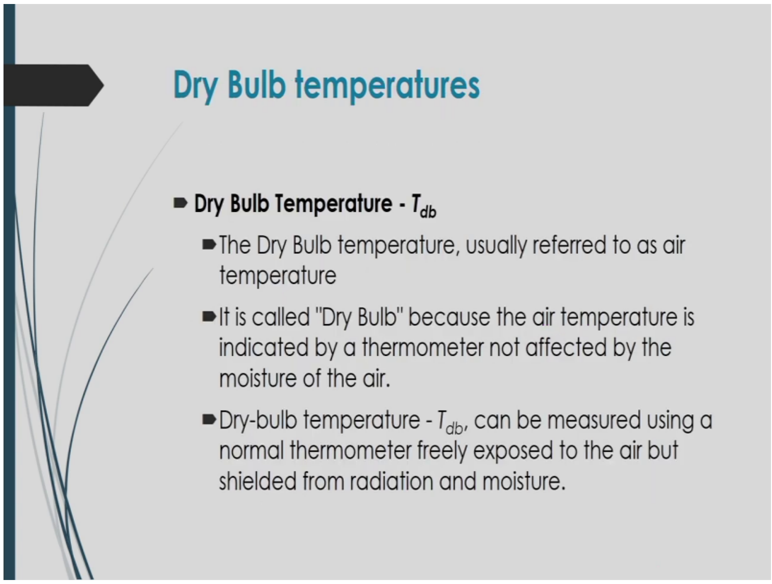

Dry Bulb temperatures

- **Dry Bulb Temperature - T_{db}**
  - The Dry Bulb temperature, usually referred to as air temperature
  - It is called "Dry Bulb" because the air temperature is indicated by a thermometer not affected by the moisture of the air.
  - Dry-bulb temperature - T_{db}, can be measured using a normal thermometer freely exposed to the air but shielded from radiation and moisture.

Now, another important point is dry bulb temperature in the gas liquid equilibrium condition. In this case, the dry bulb temperatures are usually referred to as the air temperature that will indicate by thermometer not affected by the moisture of the air and dry bulb temperature is denoted by T db generally, and it can be measured using a normal thermometer freely exposed to the air but shielded from radiation and moisture.

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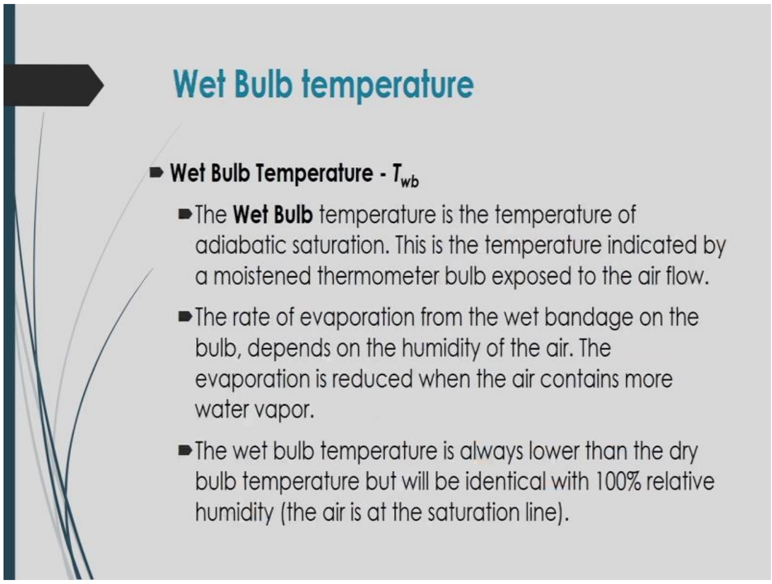

Wet Bulb temperature

- **Wet Bulb Temperature - T_{wb}**
  - The **Wet Bulb** temperature is the temperature of adiabatic saturation. This is the temperature indicated by a moistened thermometer bulb exposed to the air flow.
  - The rate of evaporation from the wet bandage on the bulb, depends on the humidity of the air. The evaporation is reduced when the air contains more water vapor.
  - The wet bulb temperature is always lower than the dry bulb temperature but will be identical with 100% relative humidity (the air is at the saturation line).

As wet bulb temperature is the temperature set of adiabatic saturation, this is the temperature that is indicated by moistened thermometer bulb exposed to the air flow and the rate of evaporation from that weight you know on about depends on the humidity of the air and that the evaporation is reduced when the air contains mole water vapor and the wet bulb temperatures are always lower than the dry bulb temperature. And you have to remember that it will be identical to the 100 percent relative humidity they are if they get to the saturation condition.

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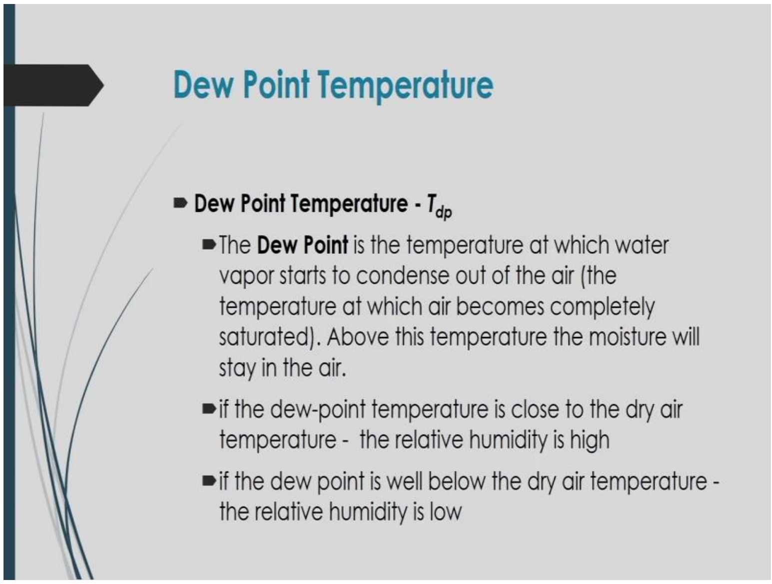

Dew Point Temperature

- **Dew Point Temperature - T_{dp}**
  - The **Dew Point** is the temperature at which water vapor starts to condense out of the air (the temperature at which air becomes completely saturated). Above this temperature the moisture will stay in the air.
  - if the dew-point temperature is close to the dry air temperature - the relative humidity is high
  - if the dew point is well below the dry air temperature - the relative humidity is low

Now, dew point we have already discussed that what is the dew point temperature they are it is basically the temperature at which water vapor starts to condense it out of the air that is the temperature at which that air becomes completely saturated. And above this temperature the moisture will stay in the air and if the dew point temperature is close to the dry air temperature then the relative humidity will be high whereas the dew point is well below the dry air temperature you can see that relative humidity will be low.

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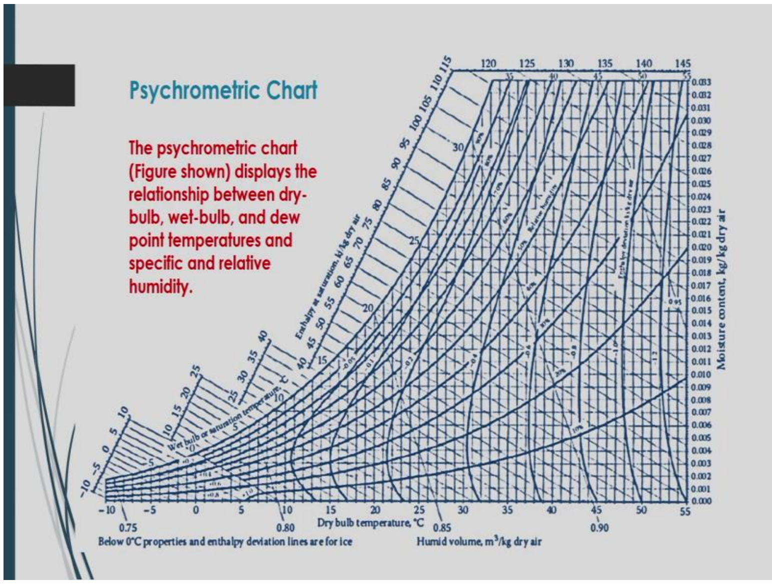

Psychrometric Chart

The psychrometric chart (Figure shown) displays the relationship between dry-bulb, wet-bulb, and dew point temperatures and specific and relative humidity.

Now here on Psychrometric chart is given to calculate that you know humidity chart and also what is that different components what is the dry air temperature what is the you know dew point temperature how that enthalpy access solution condition can be calculated, what should be the word but or saturated saturation temperature, how to calculate that you know absolute you know moisture content and also what should be the you know humid volume they are how it is defined. And also there are other properties like you know, what would be the enthalpy deviation, what is the relative humidity how to calculate. So, I will discuss these things are in the next lecture.

How to you know use that Psychrometric chart to you know calculate the relative humidity and also dew point temperature, dry air temperature are enthalpy even you know that towards the humid volume and also relative saturation, absolute, you know, moisture content in the air based on phase. So, we will discuss more about that you know this humidity and condensation and also what is that you know when saturation problem, condensation problem, evaporation problem we will discuss more about that in the next lecture. So, thank you for your attention for this lecture.