Basic Principles and Calculations in Chemical Engineering

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Lecture # 13

Phase Equilibrium

Welcome to massive open online course on basic principles and calculations in chemical engineering we discuss basic you know material balance principles and also their applications by you know discussing with several, you know, examples and up to module 4 we have discussed these things. Now, we will start here module 5, where we will discuss about the business principles of multi-phase systems and also the application of this multiple systems for the engineering calculations. And in this module has a first lecture we will discuss about that phase equilibrium in that you know that this lecture will you know cover that.

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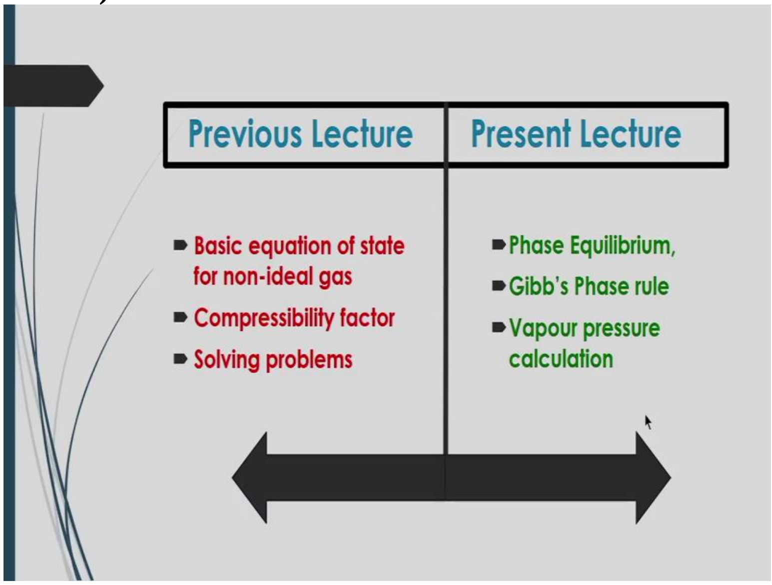

Previous Lecture

- Basic equation of state for non-ideal gas
- Compressibility factor
- Solving problems

Present Lecture

- Phase Equilibrium,
- Gibb's Phase rule
- Vapour pressure calculation

you know what is the phase rules and also how to calculate the vapour pressure many chemical engineering processes are actually being involved with you know, multi-phase systems, what is actually that multi-phase systems we have already talked about that you know, only single phase systems like you know that liquid gash or solid these are you know that when you know that we will be using has the you know single entity.

Then it will be considered as a single phase even its you know principles will be for that single phase principles and also whenever it would be flowing for a particular process that will be you know single phase flow. Now, when any chemical engineering operation or biochemical any other engineering operations, there are if more than 1 phase will be involving, then the system will be you know, regarded as the multi-phase systems.

Like, you know that gas and liquid both to be flowing through the system, even gas liquid solid to be you know, simultaneously will be flowing through the system for a particular chemical engineer operation. Let us have an example for that suppose, if there is a flow of gas and liquid in a you know in a particular reactor or in a particular column you will see that there may be used for chemical engineering operation like absorption process.

If suppose if you want to you know remove carbon dioxide gas from you know atmospheric air then what do you have to do that mixture of air and carbon dioxide to be passed through that you know liquid medium like if it is sodium hydroxide or some Ambien solution, you will see that carbon dioxide gas will be absorbed by that you know by that liquid medium like you know alcoholic or you know that mean solution the this type of operation is called that 2 phase system even you will see that.

Other chemical engineering operations are not only these 2 phases, they are maybe you know involving another phases like solid phase will be also involving for a particular Chemical Engineer operation like in a slurry, you know, bubble column reactor where you will see that synthesis gas like you know that carbon monoxide and hydrogen gas will be you know supplied to that you know by liquid medium in presence of catalyst particles to you know synthesize that you know different you know, valuable products like gasoline, even elfin and also other different types of hydrocarbons.

Just by you know that processing of that gas liquid mixture in a liquid medium in prison sub catalyst particle. So, this type of operation actually scored that the pitcher drops the synthesis or this gas liquid solid 3 phases are important. So, this is called multi-phase systems when you will see sometimes from a you know single phase you can have different you know, form of it is a change of state like liquid may be converting into solid or solid may be converting into liquid or gas may be converting into liquid or liquid may be converting into gas or gas will be converting to solid.

So, these are change of state from 1 phase to another phase, you will see, we possible if you know change the pressure or temporary set there. So, by changing the pressure and temperature of the system you can change the state particular state from either by liquid or either by you know either from gas for space or either from solid phase to the other phases. Now, you will see at a particular pressure and temperature there will be you know starting change of these phases.

Now, you have to you know notice down where that particular temperature and pressure by who is you can get that you know that change of this liquid like here at a particular pressure like 1 atmospheric pressure and 100 degrees Celsius, you will see that water is converting into you know vapour. So, this type of change of this state like you know that some other sometimes this liquid will be converting into solid or you will see that a solid may be converting into liquid state like this.

So, there will be a certain change or pressure and temperature by which you can get Now, what will be that equilibrium you know that temperature and pressure at who is that just the phase will be changing from that its initial to the final state. So, that you know that transition or equilibrium condition can be represented by you know diagram. So, this diagram will be you know referred as a phase diagram.

So, we will be discussing that phase diagram on which you will see that how equilibrium condition of this you know, pressure and temperatures based on who is that the state will be changing here before going to that representation of that equilibrium you know condition of pressure and temperature for compassion of you know, that 1 state to another state, we have to discuss that other different types of equilibrium maybe you know, they are in the, you know, different chemical engineering processes, that also you have to know some extent.

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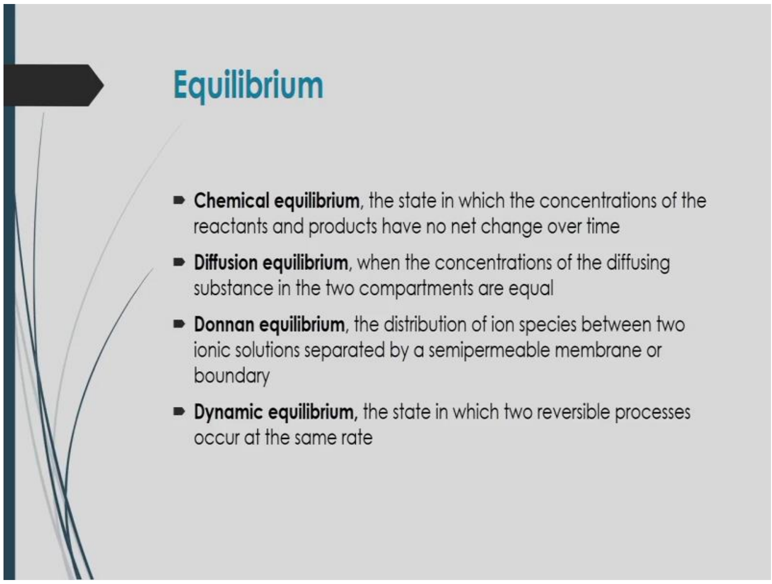

Equilibrium

- **Chemical equilibrium**, the state in which the concentrations of the reactants and products have no net change over time
- **Diffusion equilibrium**, when the concentrations of the diffusing substance in the two compartments are equal
- **Donnan equilibrium**, the distribution of ion species between two ionic solutions separated by a semipermeable membrane or boundary
- **Dynamic equilibrium**, the state in which two reversible processes occur at the same rate

So, let us have that different types of chemical, you know, processing equilibrium like here, 1 is called chemical equilibrium. This is basically a state in which you concentration of the reactants and you know that products have you know no net change over time. So, this will be called as chemical equilibrium. Even sometimes you will see that there will be a certain change of you know that concentrations just by diffusion.

So, when the concentrations of the diffusing substance in the 2 components will be equal then that the you know equilibrium condition or equal condition will be represented by diffusion equilibrium another you will see sometimes in a certain process will see sometimes that ionic processes there the distribution of ion species between 2 ionic solutions that will be separated by a semi permeable membrane or boundary.

So, they are that when this you know ionic you know species will be equilibrium in condition for its distribution, then it will be called as Donnan you know equilibrium, another important aspect of equilibrium It is called dynamic equilibrium. In this case, you will see that the state in Greece, the 2 reversible processes will be occur at the same time rate, the same rate that is called dynamic equilibrium.

Now, you will see that, you know sometimes that chemical equilibrium will be represented by a certain constant that will be called chemical equilibrium constant. This is basically a quantity that will be characterized a chemical equilibrium in a chemical reaction and other important equilibrium it is called solubility equilibrium. Now, if any chemical equilibrium between solid and dissolve states of the compound at saturation will happen to be called a solubility equilibrium

And if support any state of thermodynamics system which is you know in thermal or mechanical or chemical equilibrium exists then it will be actually referred as thermodynamic equilibrium. You will see a for you know when a bar liquid will be you know converting into each vapour, there will be a certain equilibrium condition at a certain temperature and pressure, so, that when our liquid will be converting into vapour and the vapour liquid equilibrium will be there.

So, it you know may you know happened when that you know liquid be converting into vapour that we said before vaporization process and sometimes you will see that vapour will be again converting into a liquid since then it will be called as conversation process. So, when the rates of condensation and vaporization of the material will be you know equal then there will be an equilibrium Augusta. We in this vapour and liquid.

So, that equilibrium will be called as vapour liquid equilibrium. Now, what we actually talked about that there will be a phase diagram. So, this is basically a you know graphical representation of pressure.

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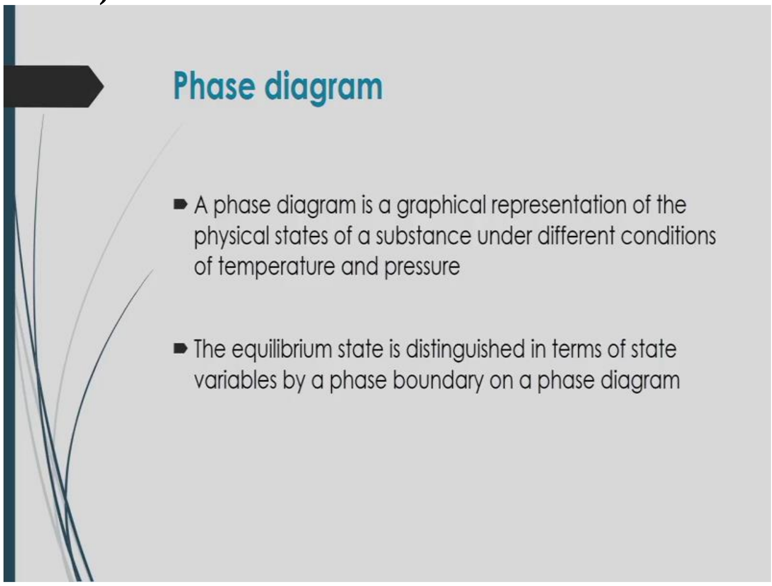

Phase diagram

- A phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure
- The equilibrium state is distinguished in terms of state variables by a phase boundary on a phase diagram

And temperature you know, at we saw you can say that this you know vapour and liquid will be coming into equilibrium condition and to be represented in that you know graphical you know diagram so, it will be called as phase diagram. So, a phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure. Now, this equilibrium can be actually you know, differentiated in terms of you know state variables by a you know phase boundary or it is called that transition you know boundary or transition condition or you can say transition points on a phase diagram.

So, this you know if you have different you know condition point or equilibrium point and if you add those equilibrium points and represented by a profile or line that will be regarded as condition blind or it can be considered as a page diagram. So, the equilibrium state is distinguished in terms of you know state variables by a phase boundary on a phase diagram. Now, here see 1 phase diagram is shown by in the slides, you will see that.

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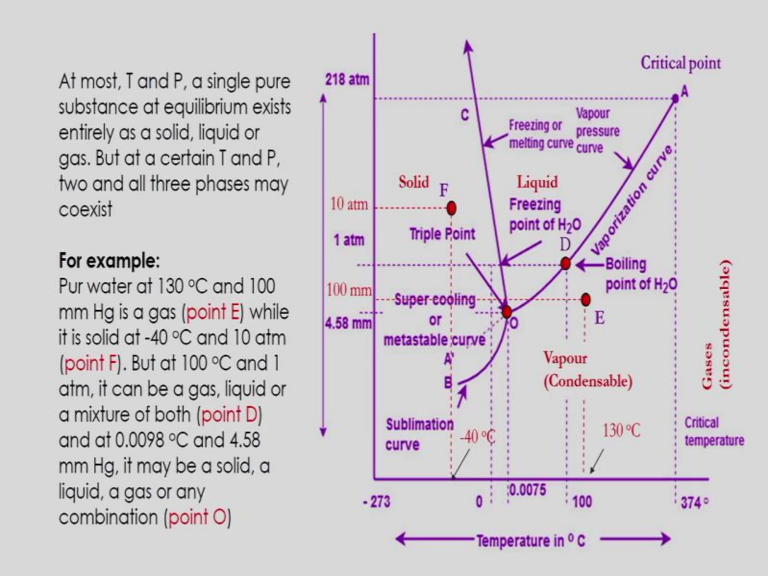

At most, T and P, a single pure substance at equilibrium exists entirely as a solid, liquid or gas. But at a certain T and P, two and all three phases may coexist

For example:
Pur water at 130 °C and 100 mm Hg is a gas (point E) while it is solid at -40 °C and 10 atm (point F). But at 100 °C and 1 atm, it can be a gas, liquid or a mixture of both (point D) and at 0.0098 °C and 4.58 mm Hg, it may be a solid, a liquid, a gas or any combination (point O)

This phase diagram if you look into this space diagram you will see that in X axis, there will be a temperature in degrees Celsius and Y axis there will be you know pressure in atmosphere and you will see that there is some profiles that is here passion like here be here that BO then D A and also here OC and O like here like this will OB an O dash or OA dash. So, and you will see that this line will be representing here as a you know phase boundary or you can see that condition you know line or boundary line.

Which will you know that distinguish that you know different phases. Now, if we see that, you know that different points on this you know, phase boundary what we can see here before going to that we have to identify for is that other things are there like you will see some vapour you know it is written here it is written solid here it is retained what is that liquid. Now, see there are some regions here that will be denoted by this here vapour you know region and there is some regions to be you know liquid solid region and where you will see that some other region which will be you know that regarded as liquid region.

Now, that phase boundary will segregate that region by each you know transition points. Now, interestingly you will see that this equilibrium points are actually plotted based on that different you know temperature and pressure change. If you change the system temperature and pressure and accordingly you will see that there will be an equilibrium condition equilibrium, you know temperature and pressure at ease.

Just you know that the phrase will be you know, changing from its initial state to another state. Now, if we consider these you know boundary line here, that is BO what exactly it means, that you know that any point here under this you know that this boundary layer or boundary you know line you will see that at this point there will be a certain temperature and there will be a certain pressure.

At this point the water bar it is that the state will be you are not the vapour stage or vapour phase. And here, ever this line there will be you know that solid phase like other point if you consider here E point you will see that this is the vapour phase at this temperature of 100 degrees Celsius and pressure is at 100 you know millimeter marking. Now, you will see here again if we consider that point D here at this equilibrium condition at a certain temperature and pressure and this is the you know boundary of these 2 phases of 2 phases.

Similarly, here at F there will be a you know that point at which certain temperature and pressure also this point will be represented by a solid state. Now, if we represent the you know phase diagram of water, you know that and it is vapour system, what will happen? Now, if you consider that liquid phase is converting into its solid and liquid phase is converting into vapour and vice versa, then how it can be represented.

Now if we consider that Water, you will see that if we consider this point F what will happen at this point we are getting here - 40 degrees Celsius whereas, pressure is 10 atmosphere, what does it mean at this temperature of - 40 degrees Celsius and 10 atmospheric be sharp the water will become a solid edge and at an equilibrium condition of any via here in the slide you will see that this is vapour to solid.

So, it will be you know that vapour to solid AB is actually at - 40 degrees centigrade, this vapour will be what our vapour will be converting into solid now, if we consider here you know that point A you will see that if we you know that a change the temperature from each you know that 100 degrees Celsius or any suppose that 30 degrees Celsius to you know that - 40 degrees Celsius, what will happen at the same temperature at the same pressure obtain atmospheric pressure you will see that liquid water will be converted into solid.

So, here this how at a particular you know pressure if you change the temperature this liquid will be converting into solid and at this boundary, you will see that at a particular temperature and pressure this liquid just changing its you know state 2 it is solid similarly, at this point E what does it mean that if you know change the temperature from 0 degree Celsius to you know that 100 degrees Celsius, what will happen? You will see that this liquid will be converting into vapour at a constant you know pressure.

Similarly, you can see that if you fixed your temperature and if you lower its pressure you will see that liquid also will be converting into vapour. So, at a certain temperature appeal, you know decrease the temperature that liquid water maintains to converting into a vapour. Similarly, at a particular temperature if you decrease, if you know, if you increase that, you know pressure you will see that vapour will be converting into liquid again at the particular you know that pressure if you change the liquid from you know 0 degree to you know - 40 degrees Celsius.

You will see that or even you know - 1 degree or less than 0 degree Celsius you will see that liquid will be converting into a solid state. So, this pace diagram you will see very interesting that, from this phase diagram, you did be able to save that how or what extent of pressure can be changed to get you know that the liquid to vapour or you can say that solid to vapour or you can say that just by changing up it is temperature.

How you can change the solid to liquid or you can say that from liquid to vapour also. Now, at 1 atmospheric pressure if you change the temperature from 0 to 100 degrees Celsius, you will see that liquid automatically will be a change to you know vapour. So, in this way this space diagram if you know to read then from this you know pressure and temperature data, you will be able to say what extent of pressure and what extent of temperature, you can change to get it change of phases.

Now, one important interesting point here this is O point. Now, at this point you will see if you consider water you will see that this point this is that 0.0075 degrees Celsius and pressure is 4.58 millimeter micrometer at this temperature and pressure this water will be either solid or liquid or vapour there will be you know that 1 point that you cannot say that will be solid or liquid or vapour. So, that is a state what is called that triple point state of water.

So, this triple point is basically refer that this water cannot be regarded as either solid or liquid or gas all the 3 phases will be you know considered as this point here. So, here in this case this temperature and pressure will be called as triple point of water and this cannot be changed. You cannot get another value up triple point of water, this will be you know that always will be a distance at this particular temperature and pressure.

So, pure water if we consider that here at 130 degrees Celsius and hundred millimeter mercury that will be a gash that is point E while it is solid at - 40 degrees Celsius and in an atmosphere but at 100 degrees Celsius and 1 atmosphere it can be a gas liquid or a mixture of both. So that will be pointed D and at 0.0098 degrees Celsius and 4.58 millimeter mercury. It may be a solid, a liquid or a gas any combination there.

So, it will be regarded as point O and it is called triple point of water. So, at moles, you know temperature and pressure a single pure substance at equilibrium, it will exist entirely as a solid, liquid or gas, but at a certain temperature and pressure 2 and all 3 phases may, were exist. So, this way this by the start you know phase diagram, you can assess whether at that particular temperature and pressure this you know, the what will be the state of that substances.

Now, beyond these you know certain temperature and pressure you will see that the properties of that substances will drastically change that will be called as you know, critical point. Now, beyond that critical point of that temperature and pressure, you will see that there will be a change of properties of the substances but as you will see that some you know substances were supposed gases.

You will see that above 374 degrees Celsius and pressure of you know at pressure 218 atmosphere uses some gases will be you know that in condensable that gases cannot be you know converting into you know solid states so, that temperature will be called as critical temperature. So, the critical temperature or critical point will be regarded as a condition higher, the gas cannot be changed into a solid state or it cannot be condensable.

So, this is the state of you know phase and how that state of phase can be you know that you know represented in a diagram that would be called phase diagram. Now, as for that phase diagram we can say that along vapour liquid equilibrium.

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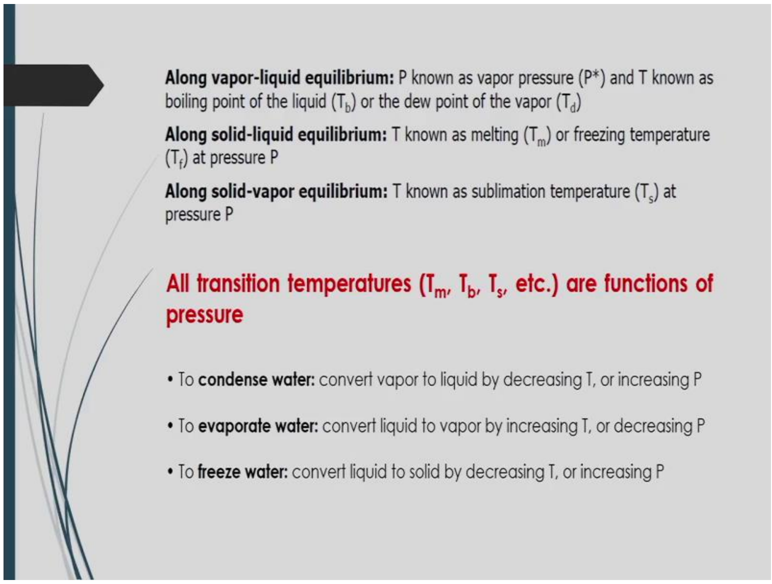

Along vapor-liquid equilibrium: P known as vapor pressure (P*) and T known as boiling point of the liquid (T_b) or the dew point of the vapor (T_d)

Along solid-liquid equilibrium: T known as melting (T_m) or freezing temperature (T_f) at pressure P

Along solid-vapor equilibrium: T known as sublimation temperature (T_s) at pressure P

All transition temperatures (T_m, T_b, T_s, etc.) are functions of pressure

- To **condense water:** convert vapor to liquid by decreasing T, or increasing P
- To **evaporate water:** convert liquid to vapor by increasing T, or decreasing P
- To **freeze water:** convert liquid to solid by decreasing T, or increasing P

Pressure known as vapour pressure sometimes to be denoted by P star or sometimes it will be denoted by P V and T at that equilibrium line temperature will be known as boiling point of the liquid or new point of the vapour. Along the solid liquid equilibrium this temperature will be known as melting point temperature or freezing temperature at particular pressure along this solid vapor equilibrium t known as sublimation temperature that is regarded as Ts at pressure p or transition temperatures like Tm, Tb, Ts etcetera are functions of pressure.

Now, to condense it water you have to convert the vapour to liquid by decreasing the temperature or increasing the pressure to evaporate water what you have to do you have to convert the liquid to vapor by increasing temperature or decreasing the pressure to freeze the water you have to convert the liquid to solid by decreasing temperature or increasing the pressure. So, this is that you know phase diagram will give you.

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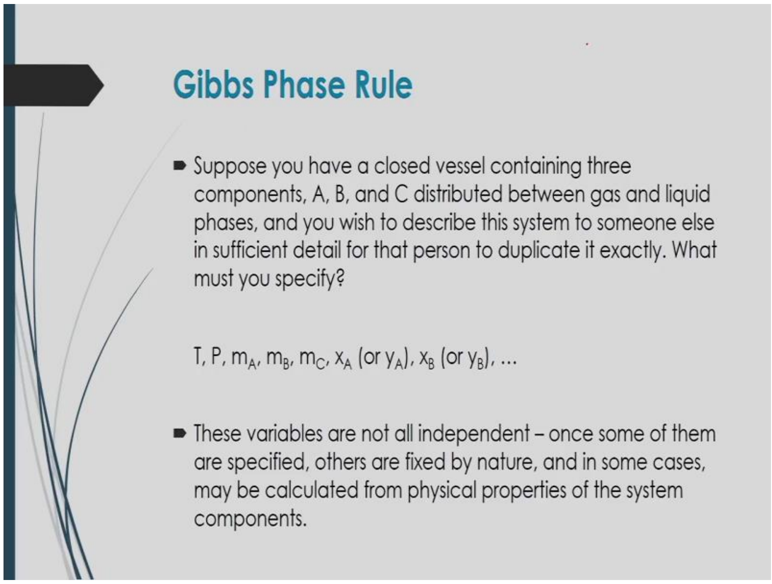

Gibbs Phase Rule

- Suppose you have a closed vessel containing three components, A, B, and C distributed between gas and liquid phases, and you wish to describe this system to someone else in sufficient detail for that person to duplicate it exactly. What must you specify?

$T, P, m_A, m_B, m_C, x_A \text{ (or } y_A), x_B \text{ (or } y_B), \ldots$

- These variables are not all independent – once some of them are specified, others are fixed by nature, and in some cases, may be calculated from physical properties of the system components.

All this information from each transition point. Now, what I told that to convert this liquid water into each vapour so, you have to you know specify certain things that what is that temperature and pressure. So, these temperature and pressures will be integrated as variables. Now, there are other so many variables will be there. So, for a particular you know representation of the state of a stance you have to specify certain variables. Now, how many specified variables to be there or how many variables to be specified that should be you know known to you.

Now, that specification number of that variables can be estimated by a certain rule. So, that rule is called Gibbs phase rule. Suppose, you have a close to vessel that contains 3 components like ABC that is distributed between gas and liquid phases. And you wish to describe this system to someone else that is in sufficient detail for that person to duplicate it exactly what must you specify there you have to specify that system either by temperature or by pressure or by moles of that components or by more fraction of that components or by mass production of that components or combination of these things.

Now, these variables are not all independent in this case, one some of them are specified, others are fixed by the necessary and in some cases you will see that, it may be required to calculate from physical properties of the system components there. So, according to these are system variables to specify the state of that particular you know substance, you need to specify some variables out of these variables. Now that how many variables to be specified to calculate that you have to follow that Gibbs phase rule what that the Gibbs phase rule actually, you know says.

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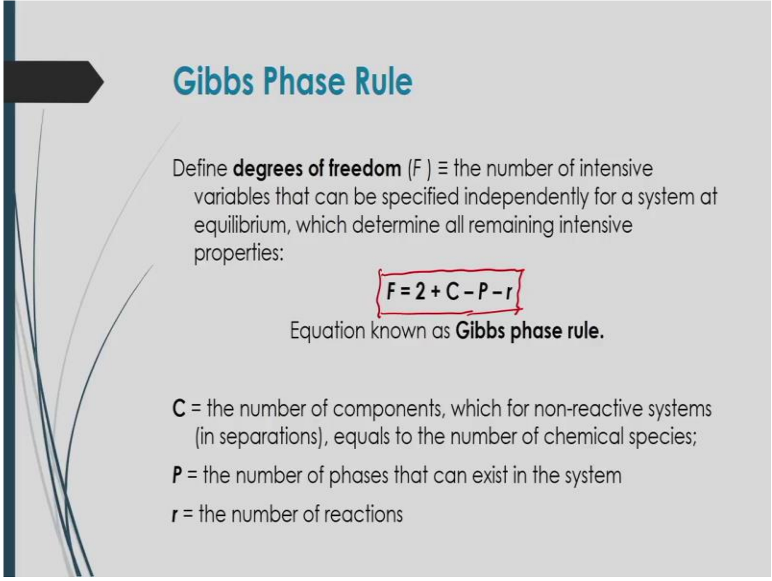

Gibbs Phase Rule

Define **degrees of freedom** (F) ≡ the number of intensive variables that can be specified independently for a system at equilibrium, which determine all remaining intensive properties:

$$\boxed{F = 2 + C - P - r}$$

Equation known as **Gibbs phase rule.**

C = the number of components, which for non-reactive systems (in separations), equals to the number of chemical species;

P = the number of phases that can exist in the system

r = the number of reactions

Here, in this case this rule is defined as a degrees of freedom, which is basically number of intensive variables that can be specified independently for a system at its equilibrium condition, whose determine my all remaining intensive properties. So, by that degrees of freedom, you will be able to say that how many number of variables will be specified to represent it is intense properties according to this Gibbs phase rule, the equation here given in the slides as if that will be equal to 2 + C - P - r.

So, this is your you know mathematical expression for the Gibbs phase rule in this case F is called degrees of freedom C is called number of components of phases in the system or number of species are present in the systems and P is called how many phases are they are in the system and also R is called the number of reactions are going on the system. So, according to these you will be able to calculate what should be the degrees of freedom based on this Gibbs phase rule and also you will be able to specify that system variables.

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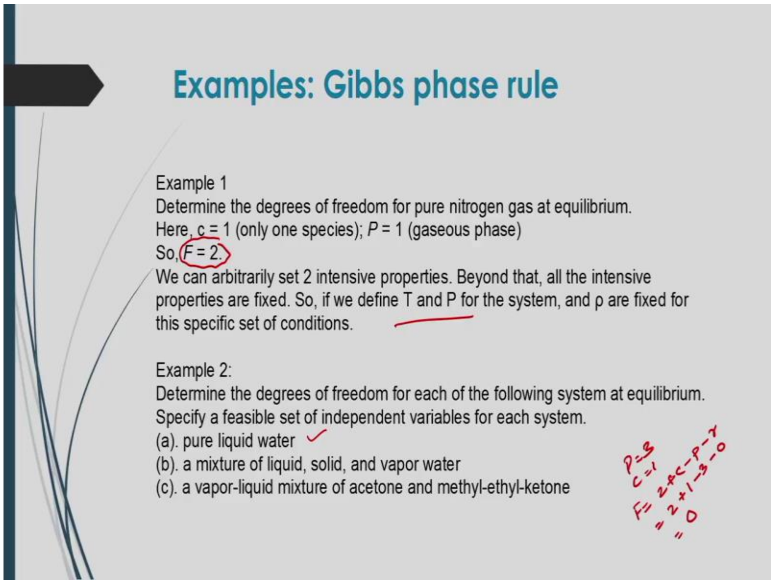

Examples: Gibbs phase rule

Example 1
Determine the degrees of freedom for pure nitrogen gas at equilibrium.
Here, $c = 1$ (only one species); $P = 1$ (gaseous phase)
So, $F = 2$.
We can arbitrarily set 2 intensive properties. Beyond that, all the intensive properties are fixed. So, if we define T and P for the system, and ρ are fixed for this specific set of conditions.

Example 2:
Determine the degrees of freedom for each of the following system at equilibrium.
Specify a feasible set of independent variables for each system.
(a). pure liquid water ✓
(b). a mixture of liquid, solid, and vapor water
(c). a vapor-liquid mixture of acetone and methyl-ethyl-ketone

$P = 3$
$C = 1$
$F = 2 + C - P - r$
$= 2 + 1 - 3 - 0$
$= 0$

To the present its properties let us have an example for this now, in this case what should be the degrees of freedom for pure nitrogen gas at equilibrium condition in this case the system here will consist only component 1 that is nitrogen gas 1 species phase is 1 because only gas was phase then according to this phase rule, since there is no reaction is going on with this you know gas phase single gas space then the you know degrees of freedom will be they are F = 2.

Then we can say that to represent says you know that intensive properties of this nitrogen then you have to specify 2 variables to represent this properties that you know that arbitrary to you know intense properties you can represent in this case, all the intensive properties are here fixed. Now. So, if we define temperature and pressure for the system and row are fixed for this specific set of conditions, then you can say that only degrees of freedom will be 2 and accordingly this only temperature and pressure will be specified there.

Similarly, determine the degrees of freedom for ease of the falling system at equilibrium to specify a feasible set of independent variables for the system like pure liquid water here also you see that degrees of freedom will be you know 2 for this you know that you know nonreactive system because age is 1 component is 1. So, simply F = 2 similarly a mixture of liquid solid and vapour water in this case you will see that liquid solid and vapour 3 phase will be there. P = 3 here and you know component will be only what is that component is if it is coming from only water phase and C will be = 1.

And then what we can say that F will be = 2 + here C - P - r since it is nonreactive So, r = 0 then it will be coming as 2 + C = 1 - phase is 3 then - 0 then is simply 0 that means, here a mixture of liquid solid and vapour what will give you the degrees of freedom is 0 that means, here you have to specify a particular you know that specific variables there and it cannot be changed. So here you know that degrees Freedom will be equal to 0.

So, they are will see that it is coming as that only you know that there will be no you know pressure and temperature or other variables to be you know specified there. So, similarly here you will see that other cases like a vapor up liquid mixture of acetone and we tell it I will be acetone then you just calculate here.

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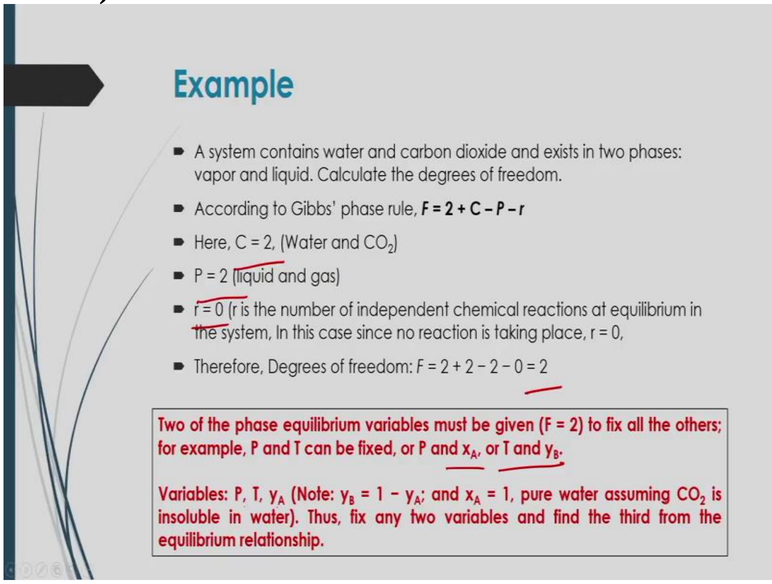

Example

- A system contains water and carbon dioxide and exists in two phases: vapor and liquid. Calculate the degrees of freedom.
- According to Gibbs' phase rule, **$F = 2 + C - P - r$**
- Here, $C = 2$, (Water and CO_2)
- $P = 2$ (liquid and gas)
- $r = 0$ (r is the number of independent chemical reactions at equilibrium in the system, In this case since no reaction is taking place, $r = 0$,
- Therefore, Degrees of freedom: $F = 2 + 2 - 2 - 0 = 2$

Two of the phase equilibrium variables must be given ($F = 2$) to fix all the others; for example, P and T can be fixed, or P and x_A, or T and y_B.

Variables: P, T, y_A (Note: $y_B = 1 - y_A$; and $x_A = 1$, pure water assuming CO_2 is insoluble in water). Thus, fix any two variables and find the third from the equilibrium relationship.

Other example like this here is system contains water and carbon dioxide and exist in 2 phases vapor and liquid calculate the decrease degrees of freedom there. So, according to this Gibbs phase rule component is 2 phase is 2 reaction r = 0 here since there is no reaction, so, degrees of freedom will be equal to 2 here. So, 2 of the phase equilibrium variables must be given to fix all the others for example, pressure and temperature can be fixed or you can say pressure or A or temperature and yB like more fraction of that component.

Variables PT yA note yB will be = 1 - yA x will be = 1 pure water assuming here carbon dioxide is insoluble in water does fix any 2 variables and find the third from the equilibrium relationship.

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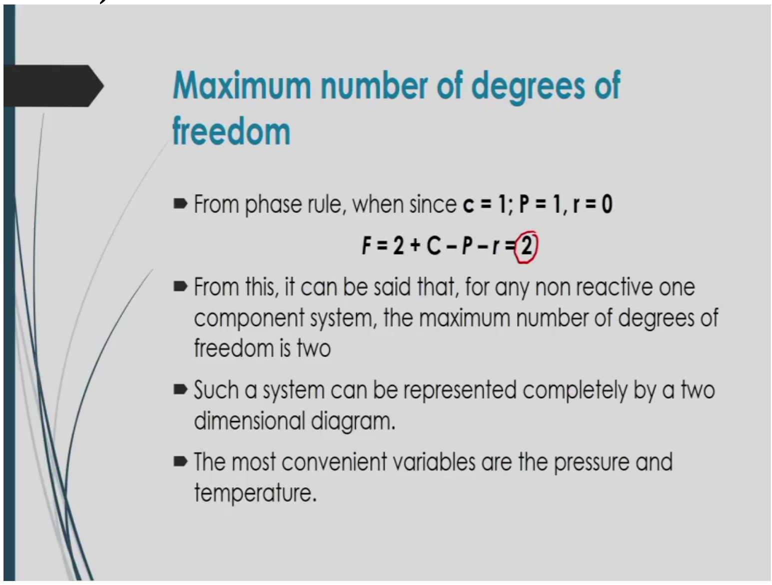

Maximum number of degrees of freedom

- From phase rule, when since **c = 1; P = 1, r = 0**

$$F = 2 + C - P - r = \boxed{2}$$

- From this, it can be said that, for any non reactive one component system, the maximum number of degrees of freedom is two
- Such a system can be represented completely by a two dimensional diagram.
- The most convenient variables are the pressure and temperature.

Now, maximum number of degrees of freedom is equal to what you see that from the phase rule, 1 component will be 1 phase will be close to only one and there will be no reaction if it is there, then according to that phase rule, degrees of freedom will be coming 2 So, anywhere you have to you know minimum 1 phase to be there and component if it is minimum 1 then degrees of freedom will be minimum of 2.

So, from these it can be saved that for any nonreactive 1 component system, the maximum number of degrees of freedom will be 2 and such a system can be presented completely by 2 dimensional diagram and the moles convenient variables are the pressure and temperature there.

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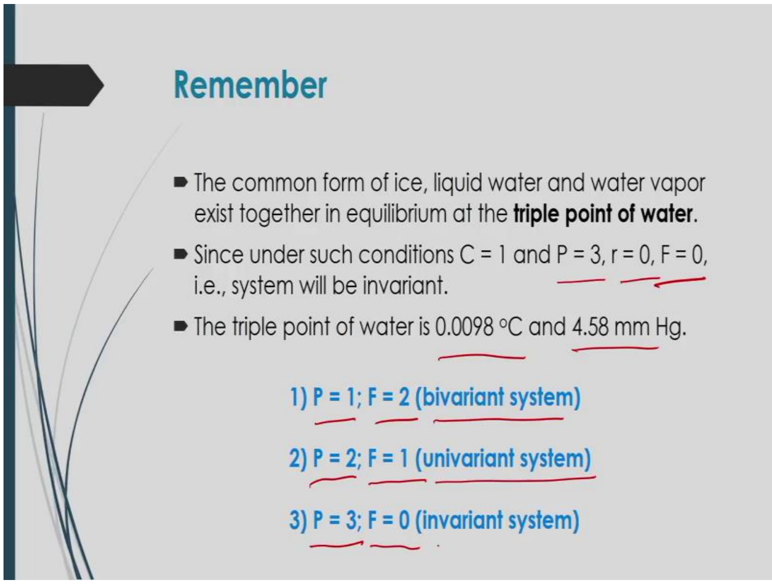

Remember

- The common form of ice, liquid water and water vapor exist together in equilibrium at the **triple point of water**.
- Since under such conditions C = 1 and P = 3, r = 0, F = 0, i.e., system will be invariant.
- The triple point of water is 0.0098 °C and 4.58 mm Hg.

1) P = 1; F = 2 (bivariant system)
2) P = 2; F = 1 (univariant system)
3) P = 3; F = 0 (invariant system)

Now, in this case remember that the common form of ice liquid water and water vapor it just together in an equilibrium at the triple point of water. Since under such conditions C which = 1 P = 3 r = 0, then degrees of freedom will be equal to 0 that means system will be invariant, the triple point of water will be is equal to 0.098 degrees Celsius and 4.58 millimeters of mercury. And if P = 1 and F = 2, then you can say that it is by inherent system. If phase 2 and degrees of freedom is 1 it would be called as univariant system for as is phase = 3 and F = 0 then it would be called invariant system. So, this to be remembered.

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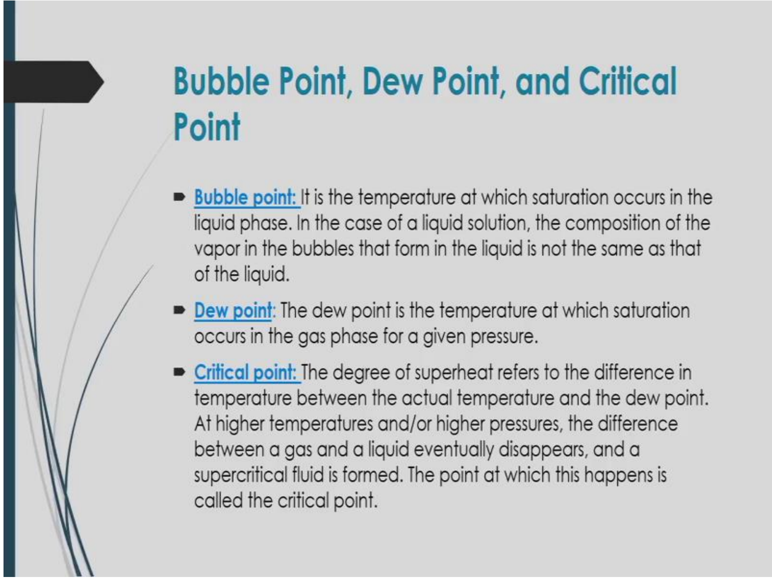

Bubble Point, Dew Point, and Critical Point

- Bubble point: It is the temperature at which saturation occurs in the liquid phase. In the case of a liquid solution, the composition of the vapor in the bubbles that form in the liquid is not the same as that of the liquid.
- Dew point: The dew point is the temperature at which saturation occurs in the gas phase for a given pressure.
- Critical point: The degree of superheat refers to the difference in temperature between the actual temperature and the dew point. At higher temperatures and/or higher pressures, the difference between a gas and a liquid eventually disappears, and a supercritical fluid is formed. The point at which this happens is called the critical point.

Next, let us considered that bubble point viewpoint and critical point as far as that phase diagram. Now, this bubble point is basically it is a temperature at which that saturation occurs in the liquid phase. In the case of liquid solution, you will see that composition of the vapor in the bubbles that form in the liquid is not same as that of the liquid and you point it will be the temperature at which saturation occurs in the gas phase for a given pressure.

And Critical point it is basically the degrees of superheat condition that will refers to the difference in the temperature between the actual temperature and the dew point and you will see that higher temperature and or higher pressures, the difference between a gas and a liquid eventually to disappears, and a super critical fluid is formed and appoint at who is this super critical condition of the fluid happened, it will be called as critical point.

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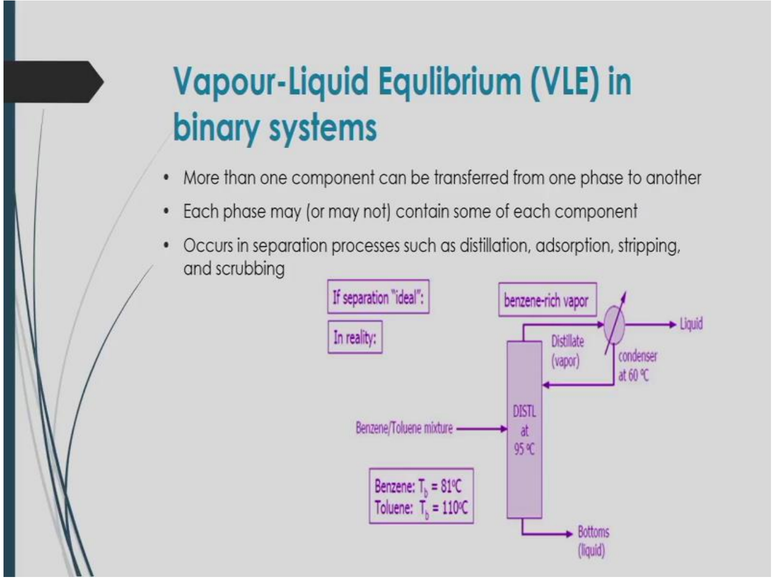

Vapour-Liquid Equlibrium (VLE) in binary systems

- More than one component can be transferred from one phase to another
- Each phase may (or may not) contain some of each component
- Occurs in separation processes such as distillation, adsorption, stripping, and scrubbing

So, this things to be remembered now, we are talking about that vapor liquid equilibrium in a binary system if it is coming then r this you know that vapor liquid equilibrium will be required basically in distillation column moles of the you know chemical engineering process they are if 2 phases are involved with the vapor and liquid there you will see that you have to consider this vapor liquid equilibrium system.

More than 1 component can be transferred from 1 phase to another they are and is phase may or may not contain some you know that obvious you know component and occurs in separation processes. Success distillation absorption stripping and scrubbing processes. So, this case these are important.

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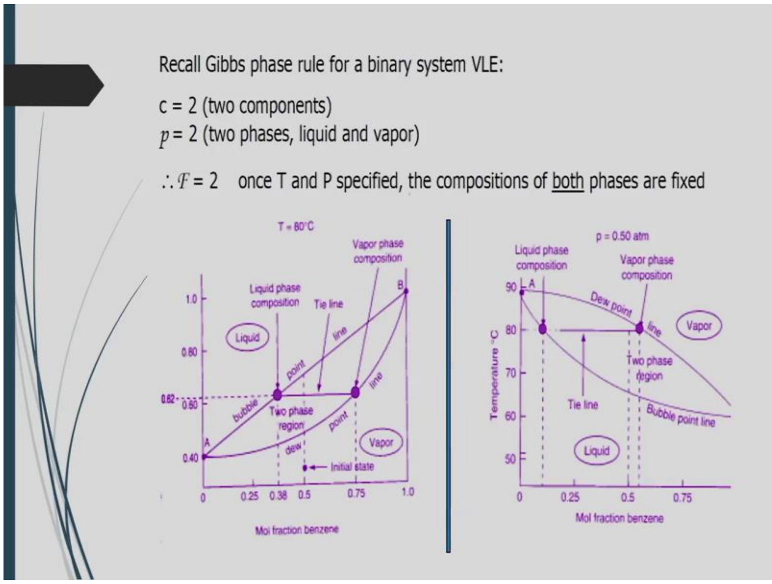

Recall Gibbs phase rule for a binary system VLE:

c = 2 (two components)
p = 2 (two phases, liquid and vapor)

$\therefore \mathcal{F} = 2$ once T and P specified, the compositions of both phases are fixed

And based on that Gibbs phase rule for binary system of this vapor liquid equilibrium, since there is component is 2 and phase is 2 and in that case degrees of freedom will be too. So, once temperature and pressure will be specified the composition of both the phases will be fixed there. So, according to that, this you know based on that, you know you will see that you can you know represent that how pressure will be changing.

According to the mole fraction and temperature will be changing according to the you know more fraction and how that bubble point or viewpoint and at its saturation condition can be represented that can you know, we, you know, from this you know this page diagram here.

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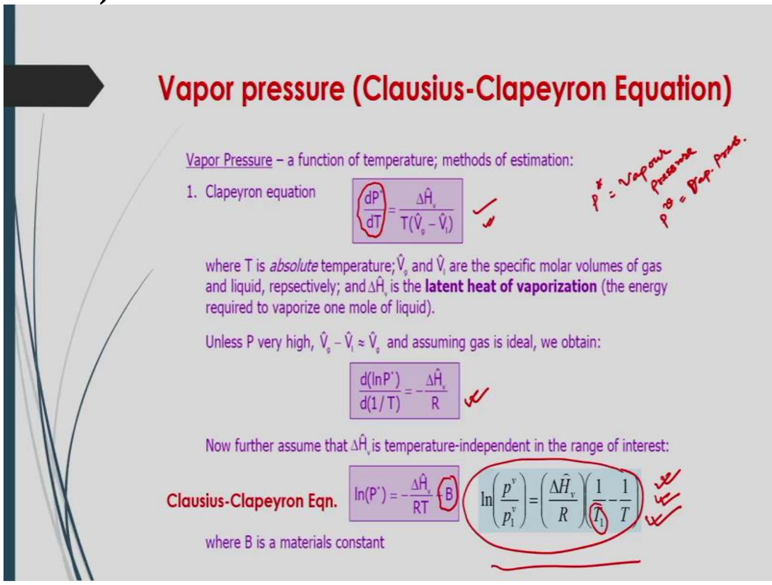

Vapor pressure (Clausius-Clapeyron Equation)

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

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

p^* = vapour pressure
p^0 = vap. pres.

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:

$$\frac{d(\ln P^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R}$$

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

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

where B is a materials constant

Based on more fraction, now, at this equilibrium condition, you will see that vapor pressure is important there, because whenever you know liquid will be converting into vapour evaporate you know liquid state there will be you know that some pressure will be exerting that you know vapor phase, then it will be regarded as that you know that vapour pressure now, how that vapor pressure will be you know, calculated. So, vapor pressure is basically the function of temperature and there will be sorting a method to estimate in this case, I am not going to derive that equation.

Just simply I am giving that what is then you know, equation that we are following to calculate that vapour pressure. It is called Clausius-Clapeyron equation by which you can calculate that vapour pressure. So, as for you know, Clausius-Clapeyron equation the vapour pressure will be you know that represented by this here dP star by dT are P star is nothing but you know that vapor pressure and sometimes these vapor pressure will be represented by PV also you know vapor pressure and it is actually a function of temperature.

So, this can be regarded by this equation and what is absolute temperature and here Vg at and you know that Vl at other specific molar volumes of gas and liquid that is in equilibrium condition and delta H at that you know that is the latent heat of vaporization that is energy required to vaporize 1 mole of liquid unless the pressure is very high this you know that difference in you know that specific molar volume of you know gas and liquid will be you know equal to you know that only molar volume of gas.

They are and in that case, assuming gas is ideal, then according to that we can write if this equation. Now, further assume that you know that enthalpy change will discuss the letter and also the enthalpy and separate lecture there and in this case, this enthalpy change is actually temporary independent in the range of you know certain interest. So, based on two is this you know this Clausius-Clapeyron equation is modified by you know another equation based on this you know equation and it is called Clausius-Clapeyron equation.

And this can be anodic represented by this equation here, where in this case 1 V terms is coming it is called you know materials constant. Now, it depends on that temperature and pressure accordingly. So, at a particular temperature and pressure if you know that, you know vapour pressure at a particular temperature you know that vapour pressure then if you substitute it and then if you know, simplify it you can get this equation at 2 different temperatures.

Now, in that case, you need to know that 1 temperature to find it out other temperature and corresponding its vapour pressure there. So, this equation will be used to calculate to the vapour pressure as for this Clausius-Clapeyron equation.

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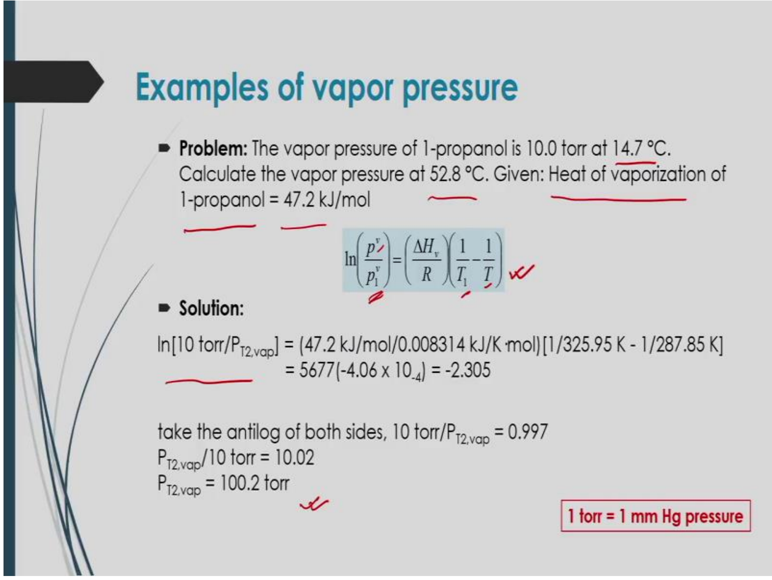

Examples of vapor pressure

- **Problem:** The vapor pressure of 1-propanol is 10.0 torr at 14.7 °C. Calculate the vapor pressure at 52.8 °C. Given: Heat of vaporization of 1-propanol = 47.2 kJ/mol

$$\ln\left(\frac{p^v}{p_1^v}\right) = \left(\frac{\Delta H_v}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

- **Solution:**

$\ln[10 \text{ torr}/P_{T2,vap}] = (47.2 \text{ kJ/mol}/0.008314 \text{ kJ/K·mol})[1/325.95 \text{ K} - 1/287.85 \text{ K}]$

$= 5677(-4.06 \times 10_{-4}) = -2.305$

take the antilog of both sides, $10 \text{ torr}/P_{T2,vap} = 0.997$

$P_{T2,vap}/10 \text{ torr} = 10.02$

$P_{T2,vap} = 100.2 \text{ torr}$

1 torr = 1 mm Hg pressure

Now, let us do an example based on this Clausius-Clapeyron equation to calculate the vapour pressure in this case, the, you know, if we say that vapour pressure on 1 propanol is attained 10 torr at 14.7 degrees Celsius. Now, calculate the paper pressure at 40 or 52.8 degrees Celsius in this case given that heat of vaporization of 1 proportional is given 47.2 kilojoules per mole. So, if we use these Clausius-Clapeyron equation here.

We can find out what should be the, you know vapour pressure of that 1 propanol at disdain toward atmospheric pressure at 14.7 degrees Celsius. So, in this case a first of all you calculate this value, you know these vapour pressure at this you know 14.7 degrees Celsius. So, accordingly if you substitute here one you know temperature like P 1 you know that P 1 you know that or if you know that P or Pv they are then accordingly what should be that will be and you know that T 1 there P 1 V and T 1 there.

So, after substitution of these values you can calculate that you know paper pressure at that temperature you know, here 52.8 degrees Celsius = 100.2 torr here 1 torr is actually equals to 1 millimeter mercury pressure.

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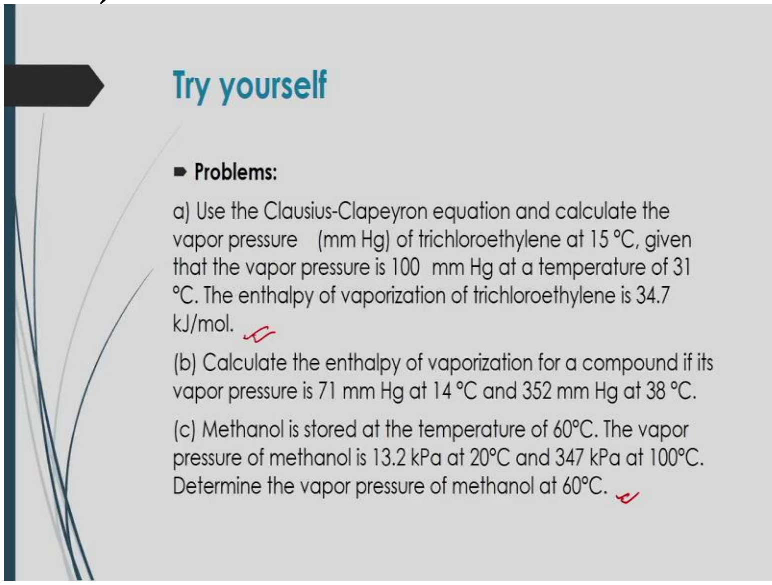

Try yourself

- **Problems:**

a) Use the Clausius-Clapeyron equation and calculate the vapor pressure (mm Hg) of trichloroethylene at 15 °C, given that the vapor pressure is 100 mm Hg at a temperature of 31 °C. The enthalpy of vaporization of trichloroethylene is 34.7 kJ/mol.

(b) Calculate the enthalpy of vaporization for a compound if its vapor pressure is 71 mm Hg at 14 °C and 352 mm Hg at 38 °C.

(c) Methanol is stored at the temperature of 60°C. The vapor pressure of methanol is 13.2 kPa at 20°C and 347 kPa at 100°C. Determine the vapor pressure of methanol at 60°C.

So, remember each now similarly, you can try other you know exercise problems like it is given here, see problems are given here for your you know, practice and accordingly you just you have to hear use that Clausius-Clapeyron equation to find out that you know vapour pressure there.

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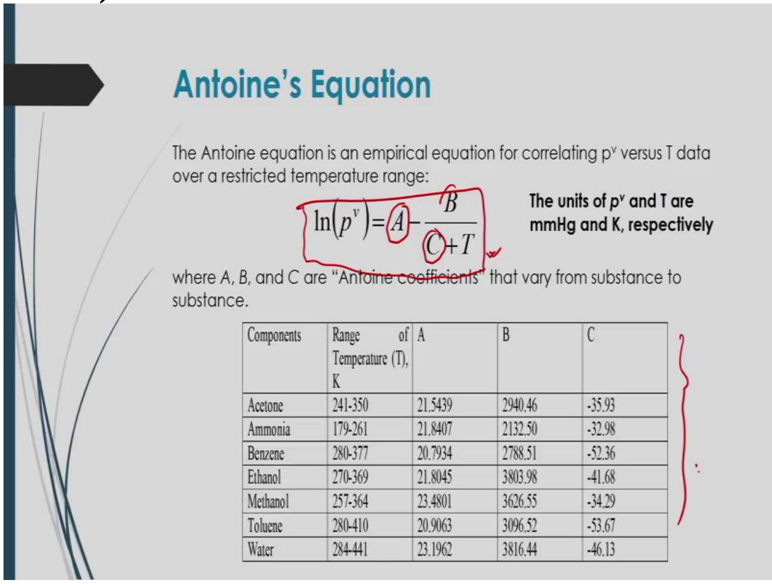

Antoine's Equation

The Antoine equation is an empirical equation for correlating p^v versus T data over a restricted temperature range:

$$\boxed{\ln\left(p^v\right) = A - \frac{B}{C+T}}$$

The units of p^v and T are mmHg and K, respectively

where A, B, and C are "Antoine coefficients" that vary from substance to substance.

Components	Range of Temperature (T), K	A	B	C
Acetone	241-350	21.5439	2940.46	-35.93
Ammonia	179-261	21.8407	2132.50	-32.98
Benzene	280-377	20.7934	2788.51	-52.36
Ethanol	270-369	21.8045	3803.98	-41.68
Methanol	257-364	23.4801	3626.55	-34.29
Toluene	280-410	20.9063	3096.52	-53.67
Water	284-441	23.1962	3816.44	-46.13

Now, another equation is very important to find out that vapour pressure this called Antoine's equation. This is an empirical equation for correlating that vapor pressure with the temperature data over a restricted temperature range. So, in this case, this equation of this Antoine is represented by this equation here lnpv that will be = A - B by C + T here, in this case the units of vapour pressure and temperature are millimeter mercury and kelvin respectively.

So, when a bar you are going to use this Antoine's equation to find out the vapour pressure, you have to convert all the pressure units in terms of you know millimeter mercury and temperature in Kelvin, then only you will get. So, otherwise you have to convert other parameters also to get this paper pressure in other units in this case see constants A, B and C are there, these are called material you know constants or sometimes it is called Antoine is constants or Antoine coefficients.

And these coefficients actually vary from substance to substance for different substance this you know coefficients will be different. e has some of the examples given 4 different components here for like se 2 pneumonia, B methanol ethanol even what are what should be that you know coefficient ABC at different temperature range there. So, you can use these you know coefficients to calculate the vapor pressure at each different temperatures are based on the Antoine's equation.

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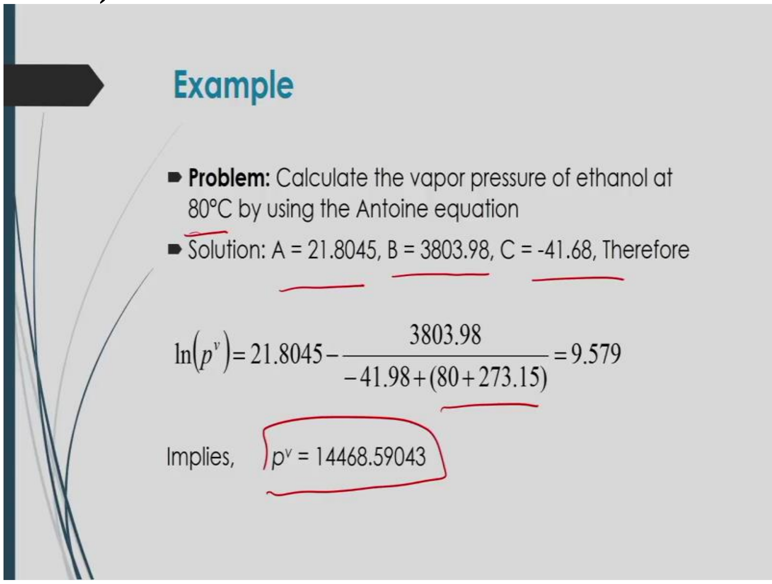

Example

- **Problem:** Calculate the vapor pressure of ethanol at 80°C by using the Antoine equation
- Solution: A = 21.8045, B = 3803.98, C = -41.68, Therefore

$$\ln(p^v) = 21.8045 - \frac{3803.98}{-41.98+(80+273.15)} = 9.579$$

Implies, $\boxed{p^v = 14468.59043}$

Now, let us do an example for this. Now, you have given to calculate the vapor pressure of ethanol at 80 degree Celsius by using the Antoine's equation. So, in this case the vapor pressure of ethanol you have to find out whereas, the coefficients are given for that, you know, ethanol are here A = 21.8045 and here B is given C is given here. So, if you substitute that ABC value in that Antoine’s equation.

And temperature is you know 80 degrees Celsius you have to convert it to absolute temperature in Kelvin, so, it would be 80 + 273.15. So, accordingly, after calculation you will get this vapour pressure will be you know that will be coming 14,468 you know that millimeter mercury like this.

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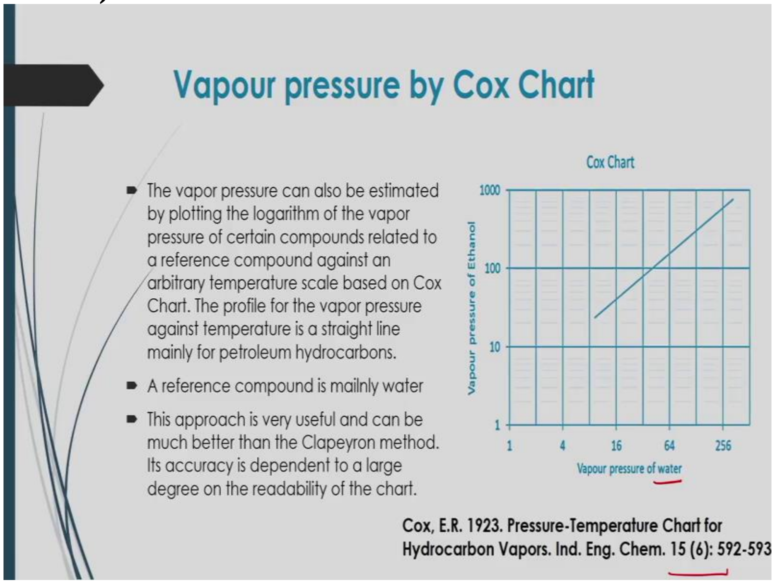

Vapour pressure by Cox Chart

- The vapor pressure can also be estimated by plotting the logarithm of the vapor pressure of certain compounds related to a reference compound against an arbitrary temperature scale based on Cox Chart. The profile for the vapor pressure against temperature is a straight line mainly for petroleum hydrocarbons.
- A reference compound is mailnly water
- This approach is very useful and can be much better than the Clapeyron method. Its accuracy is dependent to a large degree on the readability of the chart.

Cox, E.R. 1923. Pressure-Temperature Chart for Hydrocarbon Vapors. Ind. Eng. Chem. 15 (6): 592-593

Now, you can calculate the vapour pressure by other method, which is called Cox chart in this case the vapour pressure you know can be estimated by plotting the logarithm of the vapor pressure of certain compounds that is related to a reference compound against is an arbitrary temporary scale based on this Cox chart you are given in this slides on chart is given the higher vapor pressure off the tunnel is you know how it is changing based on that reference, you know, materials or reference you know substance of vapour pressure there.

So, this propel for the vapor pressure against a temperature is a straight line mainly for you know petroleum hydrocarbons and in this case a reference compound will be mainly water and this approach is very useful and can be much better than the clapeyron method and its accuracy is you know that dependent to a large degrees on the readability of the chart. So, this past has given by Cox in 1923 they are and it has been published in industrial engineering and chemistry they are all in 15 in 1923.

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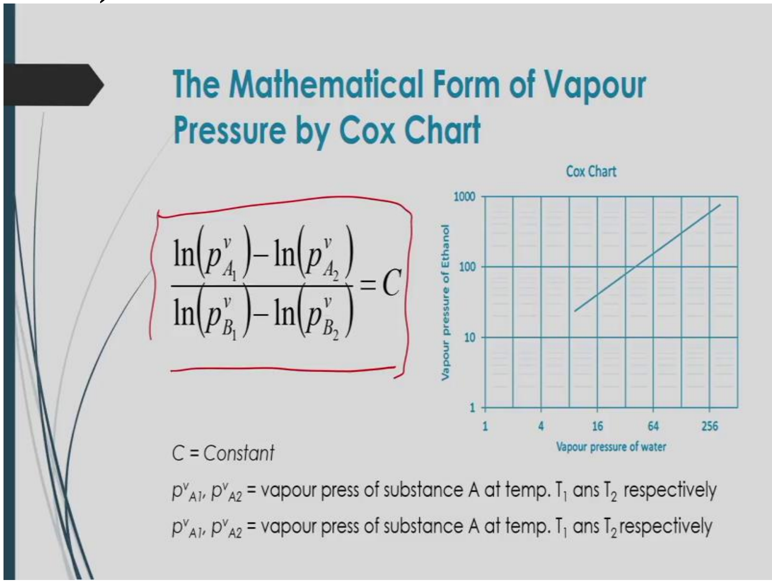

The Mathematical Form of Vapour Pressure by Cox Chart

$$\boxed{\frac{\ln\left(p^{v}_{A_1}\right)-\ln\left(p^{v}_{A_2}\right)}{\ln\left(p^{v}_{B_1}\right)-\ln\left(p^{v}_{B_2}\right)}=C}$$

C = Constant

p^{v}_{A1}, p^{v}_{A2} = vapour press of substance A at temp. T_1 ans T_2 respectively

p^{v}_{A1}, p^{v}_{A2} = vapour press of substance A at temp. T_1 ans T_2 respectively

So, according to that you can you know represent these are you know vapour pressure by that Cox chart mathematically and this mathematical form of this equation is the ACR here C important that C constant here in this equation and PvA1 here PvA2 these are the you know that vapour pressure of substance A at temperature T 1 and T 2 respectively. And this PA you know 1 V and PVA2 these are vapour pressure of substance A and you know that at temperature T 1 and T 2 respectively.

Now, if you know the vapour pressure of this either set of this temperature, then you can easily calculate the other set of this, you know, vapour pressure of the components they are different, you know temperature you know, just by calculating the efficiency here.

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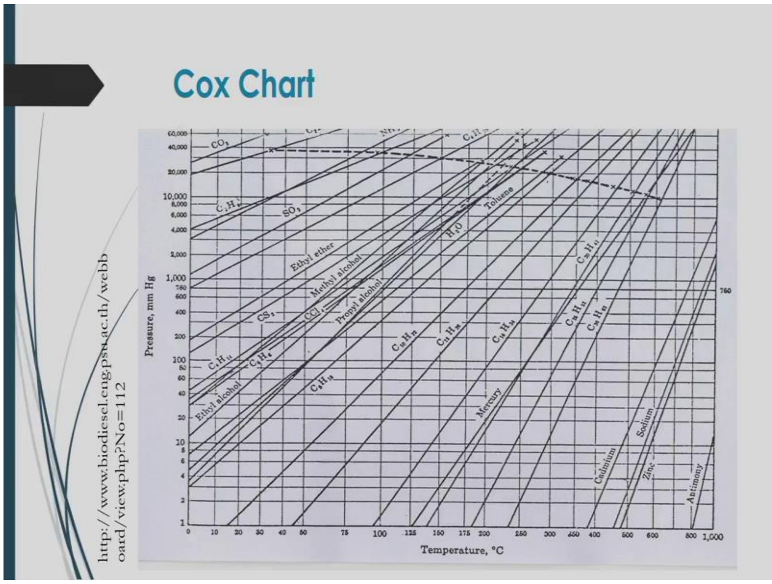

Cox Chart

http://www.biodiesel.eng.psu.ac.th/webboard/view.php?No=112

These are also are given these vapor pressure at different temperatures based on this Cox chart how these you know that vapor pressure will be changing, you know, according to the temperature for the different you know hydrocarbons there.

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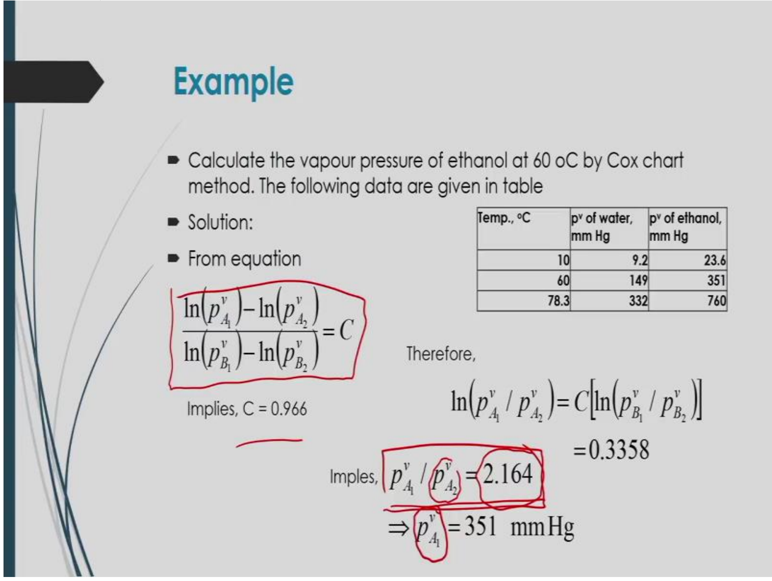

Example

- Calculate the vapour pressure of ethanol at 60 oC by Cox chart method. The following data are given in table
- Solution:
- From equation

Temp., °C	p^v of water, mm Hg	p^v of ethanol, mm Hg
10	9.2	23.6
60	149	351
78.3	332	760

$$\boxed{\frac{\ln(p^v_{A_1})-\ln(p^v_{A_2})}{\ln(p^v_{B_1})-\ln(p^v_{B_2})}=C}$$

Implies, C = 0.966

Therefore,

$$\ln(p^v_{A_1}/p^v_{A_2})=C[\ln(p^v_{B_1}/p^v_{B_2})]$$

$$=0.3358$$

Imples, $\boxed{p^v_{A_1}/p^v_{A_2}=2.164}$

$$\Rightarrow p^v_{A_1}=351 \quad \text{mmHg}$$

Now, let us do an example here. Now, it is told that calculated the vapor pressure of the tunnel at 60 degrees Celsius by Cox chart method, the following data are given in table here. So, in the table it is given that at a different temperature, the vapor pressure of water and vapour pressure of water ethanol. Now, from equation here you know as per Cox chart mathematical form, we can say that, if we substitute this value of Pv for the components A1 and A2 you know that at 2 at a particular temperature even for vapor pressure of component B at that particular temperature you will see that you will get that you know that no component C there.

So, you just substitute here then you will see that the values of C = 0.966 and therefore, then you can find it out after a substitution of value of C and then for other temperature what should be that you know vapor pressure there you can easily calculate. So, this ratio of vapor pressure of this component A1 A2 will be equal to 2.164. So, at that other temperature if you know that vapour pressure you know that of component A1.

Then you can easily calculate what the vapor pressure of component A1 based on this you know that value of this ratio of this vapour pressure of component A1 and A2. So, we have discussed, you know that different issue of this vapour liquid equilibrium condition how to calculate the vapor pressure at that equilibrium condition and how pressure and temperature can be changed to get that different equilibrium condition of this you know.

State and also how to calculate the vapour pressure by different you know, methods that has been discussed in this lecture. And also some examples are given you just, you know, practice are based on that examples and also you can collect other examples from other different books and you can solve that problem based on this, you know, theory of calculating the vapour pressure. So, I would suggest you to read part that the stakes book here.

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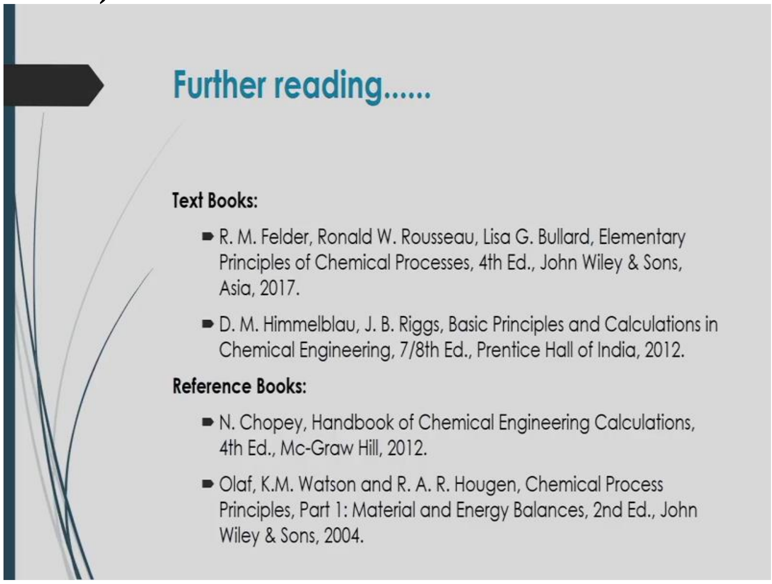

Further reading......

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017.
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

And follow some examples problem based on this theory and how you can you know assess this vapour pressure based on the calculation of this you know, vapour pressure equation and also how you can assess that equilibrium condition at different temperature and pressure. Next lecture, we will try to discuss more about that equilibrium. Conditions there I will try to discuss some laws of equilibrium condition, how to you know, you know calculate that posture pressure.

And vapour pressure at its equilibrium condition and how to be changing with respect to temperature and how mole faction will be changed of the system and also how to calculate the humidity and saturation condition based on this equilibrium system condition will be discussing so, thank you for this.