Upstream LNG Technology
Prof. Pavitra Sandilya
Department of Cryogenic Engineering Centre
Indian Institute of Technology, Kharagpur

Lecture – 08
Vapor Liquid Equilibrium

Welcome. Now we shall learn about vapor liquid equilibrium which is necessary to find out the any kind of separation which is happening in the system and whatever we have learned earlier about the dew point, bubble point, etcetera, there we found that we need the value of the equilibrium constant, this value may be found out from the principles of vapor liquid equilibrium.

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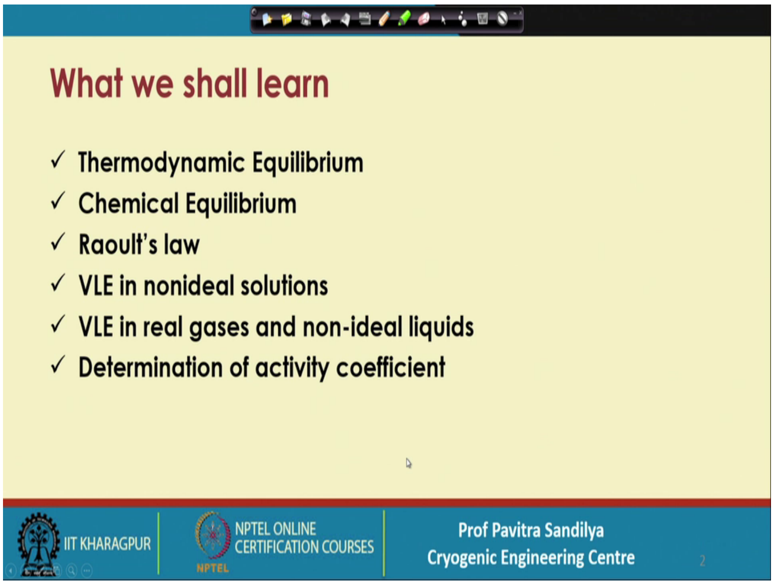

What we shall learn

- ✓ Thermodynamic Equilibrium
- ✓ Chemical Equilibrium
- ✓ Raoult's law
- ✓ VLE in nonideal solutions
- ✓ VLE in real gases and non-ideal liquids
- ✓ Determination of activity coefficient

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In this particular lecture series, what we shall learn? We shall learn about what is thermodynamic equilibrium, what is chemical equilibrium and Raoult's law, then vapor liquid equilibrium in non ideal solutions, then vapor liquid equilibrium in the real gases and non ideal liquids determination of activity coefficients.

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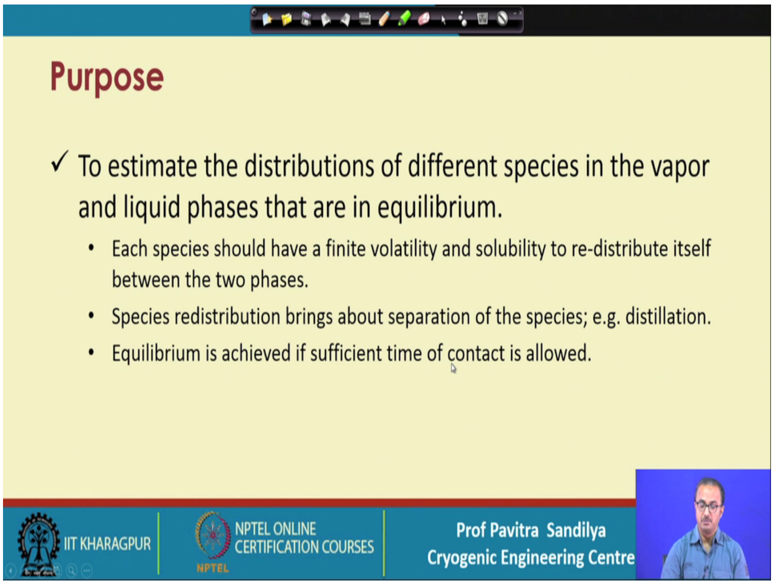

Purpose

✓ To estimate the distributions of different species in the vapor and liquid phases that are in equilibrium.

- Each species should have a finite volatility and solubility to re-distribute itself between the two phases.
- Species redistribution brings about separation of the species; e.g. distillation.
- Equilibrium is achieved if sufficient time of contact is allowed.

So, why do we need this vapor liquid equilibrium calculations? This is because whenever there is any kind of separation involving a vapor and liquid phase, then to know how the various species are distributing themselves between the two phases; we need to carry out such vapor liquid equilibrium calculations.

Now, in this some of the conditions to be satisfied are that each species should have a finite volatility and finite solubility to redistribute itself between the various phases by volatility, we mean that a tendency of a given species to go from the liquid phase to the vapor phase and solubility is the meaning of that how a particular species gets dissolved in a liquid. So, we want that whenever we are carrying out, the vapor liquid equilibrium calculations each of the species should be enough volatile and should have enough solubility in the liquid.

Then there are many processes where we need such kind of calculations. One of them is distillation which is a very common separation process in the chemical and allied industries 2 for establishing equilibrium in a system, there should be sufficient contact time between the various phases.

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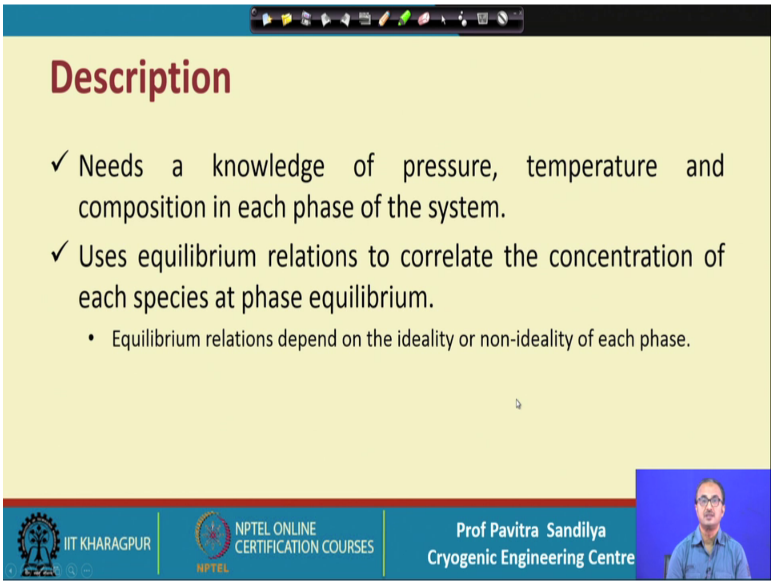

Description

- ✓ Needs a knowledge of pressure, temperature and composition in each phase of the system.
- ✓ Uses equilibrium relations to correlate the concentration of each species at phase equilibrium.
  - Equilibrium relations depend on the ideality or non-ideality of each phase.

Now, to describe the equilibrium, we need to know the pressure temperature and the composition in each of the phases in the system.

And to analyze it, we need to know the various types of equilibrium relations which will correlate the concentration of each species which are at equilibrium in the various phases present, please note that equilibrium may involve more than two phases, two phases are immersed, but it may involve three phases also. So, we may have two liquid phase, one vapor phase or liquid solid and vapor ok. So, these equilibrium relations depend on the ideality or non ideality of each phase about which we shall just see in a short while.

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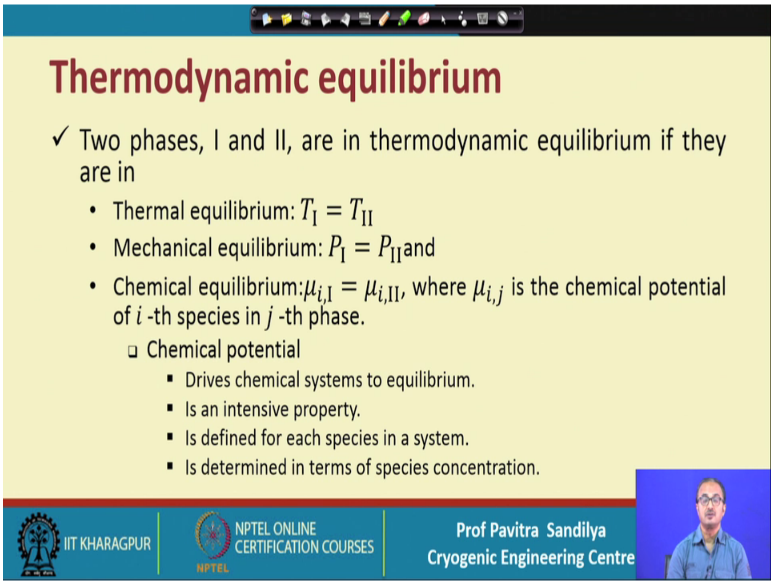

Thermodynamic equilibrium

✓ Two phases, I and II, are in thermodynamic equilibrium if they are in

- Thermal equilibrium: $T_{\mathrm{I}} = T_{\mathrm{II}}$
- Mechanical equilibrium: $P_{\mathrm{I}} = P_{\mathrm{II}}$and
- Chemical equilibrium:$\mu_{i,\mathrm{I}} = \mu_{i,\mathrm{II}}$, where $\mu_{i,j}$ is the chemical potential of i -th species in j -th phase.
  - ❑ Chemical potential
    - ▪ Drives chemical systems to equilibrium.
    - ▪ Is an intensive property.
    - ▪ Is defined for each species in a system.
    - ▪ Is determined in terms of species concentration.

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Now, let us first understand what we mean by thermodynamic equilibrium, we say that suppose there are two phases 1 and 2 and they are saved to be at thermodynamic equilibrium if they satisfy the following conditions. First is thermal equilibrium; that means, the temperature of phase one must be equal to temperature of phase two. Second, we have mechanical equilibrium; that means, the pressure in phase one must be equal to pressure in phase two and thirdly, we have chemical equilibrium in which there is one parameter which is called the chemical potential of ith species in jth phase ok. So, here you see that mu i 1 means the chemical potential of ith species in phase number one must be equal to the chemical potential of the same ith species in phase two.

So, you can see that in case of thermo thermal equilibrium, we have only one relation in mechanical equilibrium, we have only one relation, but for the chemical equilibrium, we have see number of relationships; that means, as many components as many chemical equilibrium relationships. So, these give rise to C plus 1 plus 1 that is C plus 2 number of relations at the thermodynamic equilibrium.

Now, this chemical potential is what is it the significance is it drives chemical systems to equilibrium and it is an intensive property like temperature, pressure, etcetera and is defined for each species in a given system; that means, a given species will have different values of the chemical potential in different phases and it can be determined; it can it cannot be determined by any experimental things, but it is represented in terms of the species concentrations.

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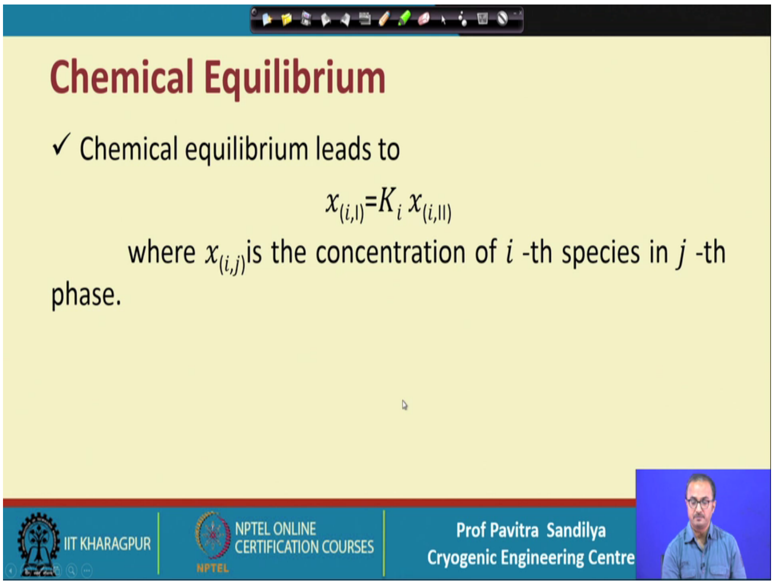

Chemical Equilibrium

- ✓ Chemical equilibrium leads to

$$x_{(i,\mathrm{I})} = K_i\, x_{(i,\mathrm{II})}$$

where $x_{(i,j)}$ is the concentration of i -th species in j -th phase.

Now, chemical equilibrium leads to this particular type of in equation in which what is i am showing that how the concentration of species i in phase one is related to the its concentration in phase two and here the relationship is within by is related by this particular parameter K i.

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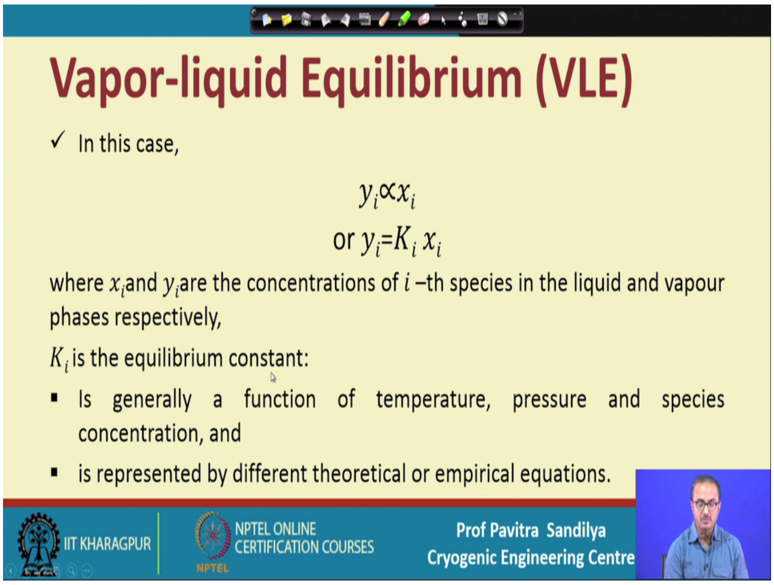

Vapor-liquid Equilibrium (VLE)

- ✓ In this case,

$$y_i \propto x_i$$

$$\text{or } y_i = K_i\, x_i$$

where x_i and y_i are the concentrations of i –th species in the liquid and vapour phases respectively,

K_i is the equilibrium constant:

- Is generally a function of temperature, pressure and species concentration, and
- is represented by different theoretical or empirical equations.

This K i is the equilibrium constant which is generally a function of the temperature pressure and species concentration and there are various ways to find out this value of K i; they may be theoretical or they may be empirical equations.

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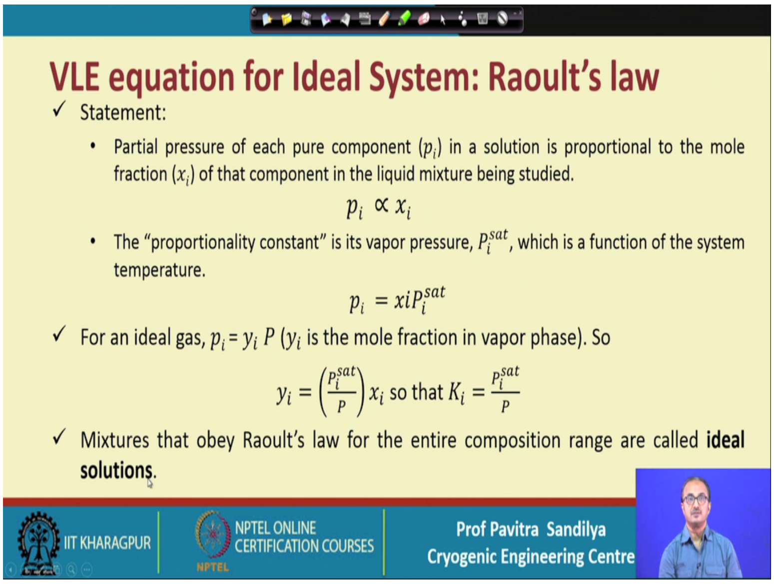

VLE equation for Ideal System: Raoult's law

- ✓ Statement:
  - Partial pressure of each pure component (p_i) in a solution is proportional to the mole fraction (x_i) of that component in the liquid mixture being studied.

$$p_i \propto x_i$$

  - The "proportionality constant" is its vapor pressure, P_i^{sat}, which is a function of the system temperature.

$$p_i = xiP_i^{sat}$$

- ✓ For an ideal gas, $p_i = y_i\ P$ (y_i is the mole fraction in vapor phase). So

$$y_i = \left(\frac{P_i^{sat}}{P}\right) x_i \text{ so that } K_i = \frac{P_i^{sat}}{P}$$

- ✓ Mixtures that obey Raoult's law for the entire composition range are called **ideal solutions**.

Now, first we come to the ideal system for ideal systems we have particular law which is called Raoult's law. Now let us see the statement of this particular vapor liquid equations equilibrium system for ideal cases. Now it says that the partial pressure of each pure species that is given by small p with a subscript i partial pressure in a solution is proportional to the mole fraction of the component in the liquid mixture being studied.

So, as we know the partial pressure is the pressure exerted by a species in a vapor mixture, if it had been occupying the same volume at the same temperature as the mixture. So, that partial pressure is proportional to the mole fraction of the same species in the liquid solution and it is given mathematically like this. So, this proportionality constant we put in terms of the P i sat that is the partial pressure is equal to this should be x with this subscript i. So, this xi into P i sat.

So, this with this we find out that we have this is the statement of the Raoult's law for ideal gas this partial pressure is given from the Dalton's equation and this is y i into P where y i is the mole fraction of ith species in the vapor phase and P is the total pressure and with this substitution, we get that y i is equal to P i sat by P into x i and this P i sat by

P is given as K i. So, this in case of the ideal system the equilibrium constant is nothing, but the ratio of the vapor pressure of the ith species to the total pressure of the system.

Now, any mixture that obeys the Raoult's law are the called the ideal solutions.

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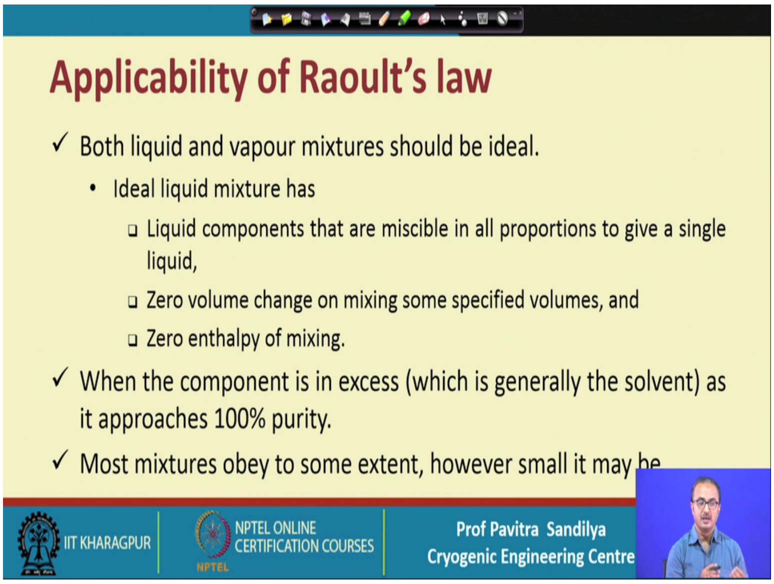

Applicability of Raoult's law

- ✓ Both liquid and vapour mixtures should be ideal.
  - Ideal liquid mixture has
    - ❑ Liquid components that are miscible in all proportions to give a single liquid,
    - ❑ Zero volume change on mixing some specified volumes, and
    - ❑ Zero enthalpy of mixing.
- ✓ When the component is in excess (which is generally the solvent) as it approaches 100% purity.
- ✓ Most mixtures obey to some extent, however small it may be

Now, Raoult's law has its own limitations. Limitations are that both the vapor and the liquid phases must be ideal and when I say ideal liquid; what I mean that I liquid components that are miscible should be miscible in all proportions that is an ideal liquid mixture. Next when we are mixing the various liquids, then the total volume must be the summation of the individual volumes of each liquid species, if it is not, then it is a non ideal liquid solution.

And lastly whenever the mixing is taking place there should not be any evolution or absorption of heat energy, if there is no evolution or absorption energy, then this is an ideal solution. If there is any kind of energy transfer, then it is a non ideal. For example, whenever we are mixing an acid with water, we find that the system becomes heated up. So, in that case, it is not in an ideal liquid solution, generally when a particular component is present in excess, we can always apply the Raoult's law; that means, even if we have some impurity and, but the impurity amount is very very small, we can still go with Raoult's law.

And in especially, in case of natural gas and petroleum, we find several times that there are many impurities present, but if we find the main ingredient main component is in excess then we can use Raoult's law and most mixtures obey to some extent ; however, small it may be this particular Raoult's law.

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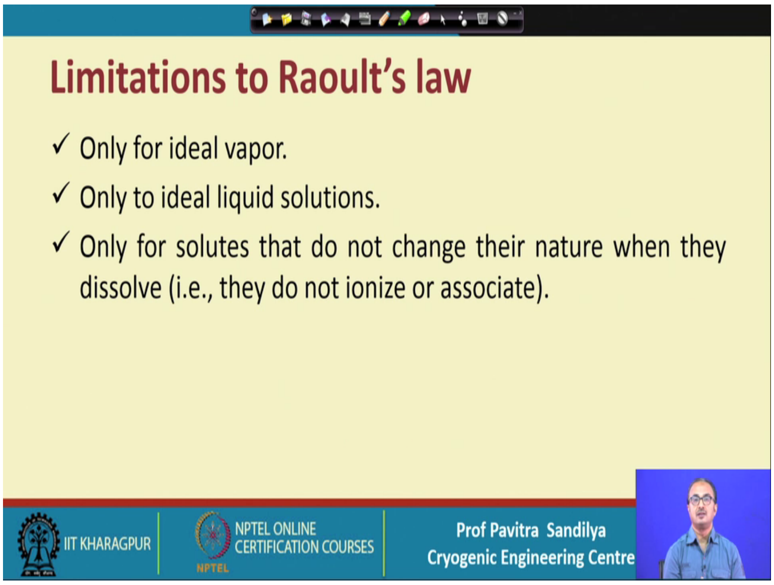

Limitations to Raoult's law

- ✓ Only for ideal vapor.
- ✓ Only to ideal liquid solutions.
- ✓ Only for solutes that do not change their nature when they dissolve (i.e., they do not ionize or associate).

So, Raoult's law is a very handy equation which can be used for estimation of vapor liquid equilibrium. So, these are the following situations that ideal vapor ideal liquid and there should not be any change in the nature of the liquid; that means, there should not be any kind of reaction that will change the species.

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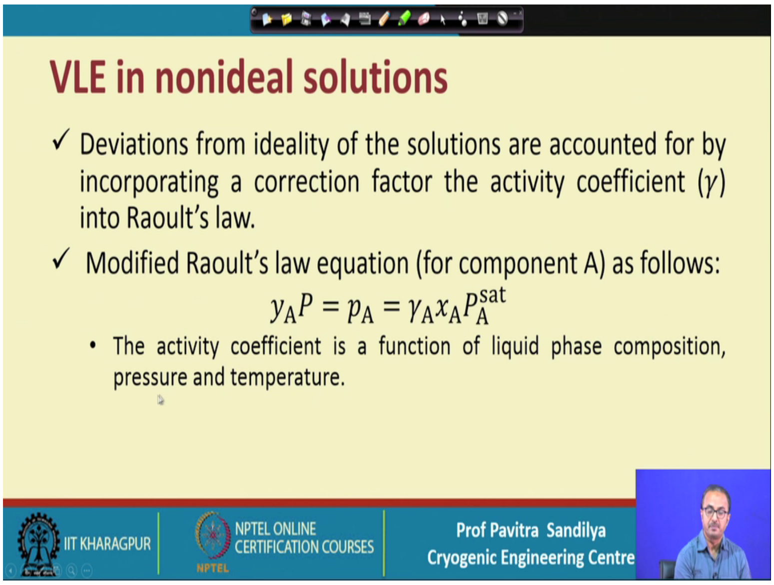

VLE in nonideal solutions

- ✓ Deviations from ideality of the solutions are accounted for by incorporating a correction factor the activity coefficient (γ) into Raoult's law.
- ✓ Modified Raoult's law equation (for component A) as follows:

$$y_A P = p_A = \gamma_A x_A P_A^{sat}$$

  - The activity coefficient is a function of liquid phase composition, pressure and temperature.

Now, real systems may deviate from the Raoult's law, in that case, let us see, how we go about doing the vapor liquid equilibrium calculations and if the liquid is non ideal, then we choose a term what we call activity coefficient, all these things are fundamental thermodynamic principles which about which we are not to be talk about and these are they are described very nicely in many good a thermodynamic books and I will give some reference also at the end of this lecture only thing that we understand that if the liquid is non ideal, what we do?.

We use this particular gamma value that is the activity coefficient here, we say that species a is non ideal in a liquid phase. So, we have the partial pressure of a in the vapor phase is equal to the x A into P A sat, this is still the Raoult's law into with which we modify it by putting this activity coefficient.

And the activity coefficient is generally a function of the liquid phase composition pressure and temperature.

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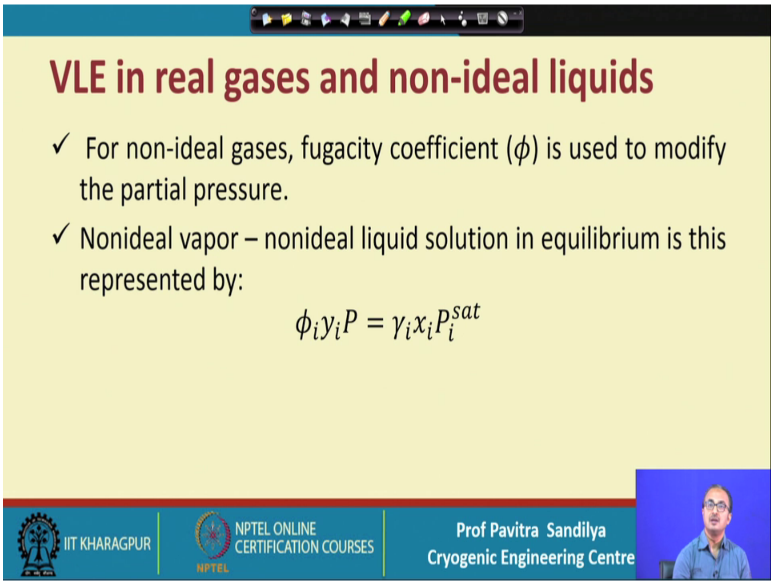

VLE in real gases and non-ideal liquids

- ✓ For non-ideal gases, fugacity coefficient (ϕ) is used to modify the partial pressure.
- ✓ Nonideal vapor – nonideal liquid solution in equilibrium is this represented by:

$$\phi_i y_i P = \gamma_i x_i P_i^{sat}$$

Now, if the gas is non ideal, in that case, we use another parameter that is called the fugacity coefficient. So, if we include the fugacity coefficient. Now, we can write the vapor liquid equilibrium by modifying the Raoult's law in this manner that all the partial pressure side, we are modifying the partial pressure with by multiplying, it with the fugacity coefficient and we are modifying this right hand side x i P i sat with the inclusion of activity coefficient and they all belong to the i th species.

So, in this case is partial pressure in this side, we have the total pressure of the system and the P i sat is a function of the temperature that is how the temperature is coming into picture indirectly through the vapor pressure.

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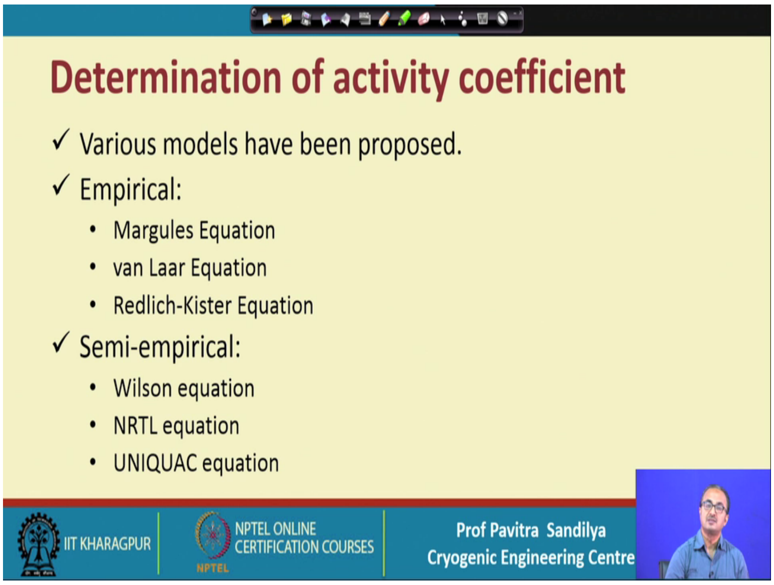

Determination of activity coefficient

- ✓ Various models have been proposed.
- ✓ Empirical:
  - Margules Equation
  - van Laar Equation
  - Redlich-Kister Equation
- ✓ Semi-empirical:
  - Wilson equation
  - NRTL equation
  - UNIQUAC equation

For determination of the activity coefficient there are many models some of them are empirical models like Margules equation, van Laar equation, Redlich Kister equation and some are semi empirical; for example, Wilson equation, NRTL equation, UNIQUAC equation, these are just some representative equation, there are many more equations given in any standard thermodynamic book and these equations apply to some specific systems.

So, it is just suffice here to tell that we should be aware of the various types of equation and depending on the case to case basis, we should be able to apply the right kind of equations. So, we will not be going into detail of this equation that will take a separate lecture to know this, but in future course we will try to take up some example problems to demonstrate how we can use one or the other type of these equations for the VLV calculation.

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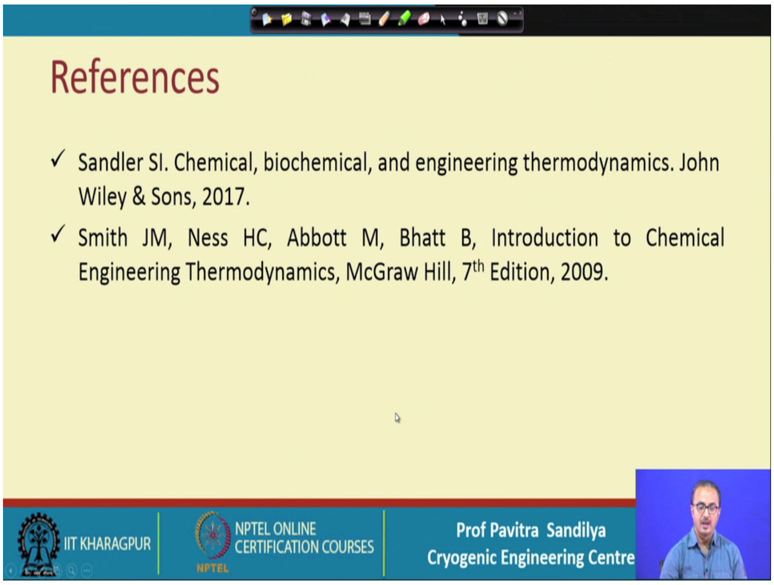

References

- ✓ Sandler SI. Chemical, biochemical, and engineering thermodynamics. John Wiley & Sons, 2017.
- ✓ Smith JM, Ness HC, Abbott M, Bhatt B, Introduction to Chemical Engineering Thermodynamics, McGraw Hill, 7th Edition, 2009.

And these are some of the references the Sandler’s and Smith and Sandler’s which you may refer to know in detail about the concepts which have been covered in this particular lecture.

Thank you.