Advanced Thermodynamics and Combustion
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Module - IV
Properties of Gas Mixture
Lecture - 16
Gas Mixtures and Multi-Component System

Dear learners, greetings from IIT Guwahati. We are in the MOOCs course, Advanced Thermodynamics and Combustions, module IV- Properties of Gas Mixture.

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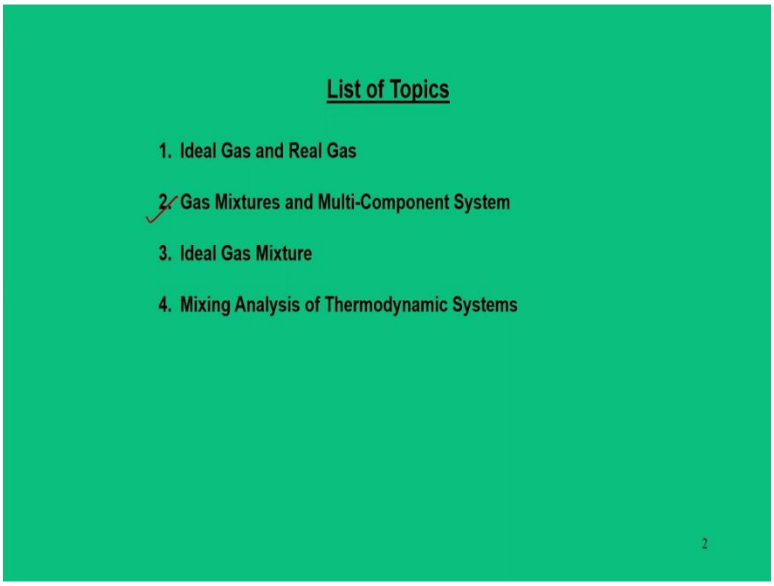

List of Topics

1. Ideal Gas and Real Gas
2. Gas Mixtures and Multi-Component System
3. Ideal Gas Mixture
4. Mixing Analysis of Thermodynamic Systems

In this module, there are 4 lecture topics. In the last lecture, we covered ideal gas and real gas. Today, we are going to discuss about the next topic that is Gas Mixtures and Multi-Component System.

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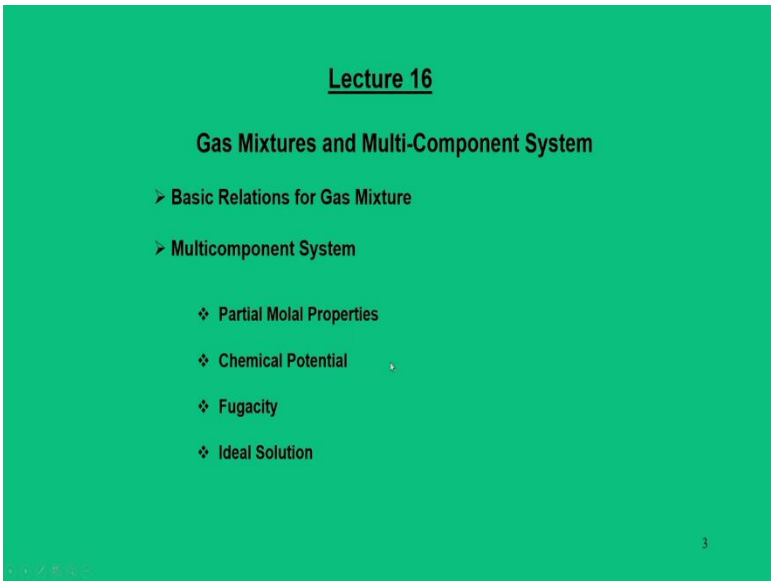

Lecture 16

Gas Mixtures and Multi-Component System

- Basic Relations for Gas Mixture
- Multicomponent System
  - Partial Molal Properties
  - Chemical Potential
  - Fugacity
  - Ideal Solution

And, in this lecture number 16 that is gas mixture and multi-component systems, we will study the following topics. First one is the basic relations for gas mixtures, then we will move on to multi-component systems where we will define important properties like partial molal properties, chemical potential, fugacity and ideal solutions. In fact, all these four parameters are very vital when you are dealing with the multi-component systems and this multi-component systems is a generic name.

It could be a gas mixture, it could be a gas plus liquid mixtures and at the same time there may be many gases and also there may be many liquids. So, basically it means it is the state of a substance either in gas phase or liquid phase. And, at different thermodynamic conditions in terms of pressure, temperatures, also they may have different compositions. So, the topic is very exhaustive and very complicated when you are dealing with multi-component systems.

We will try to simplify certain analysis where a generic or overall picture can be projected. And, we will deal with the substances which are in mainly gas phase and mostly we will be concentrating this is an ideal gas mixture in a multi-component systems. Of course, towards the end of our lectures or modules or this course, we will be dealing with the combustion systems where the combustion products also comes into pictures.

And, we have reactants and as these reactants get oxidized, then we get the combustion products. And in fact, we know that after combustion, reactant vanishes, but what we have left out was the combustion products. So, such a systems also has a great resemblance for the analysis of multi-component systems. So, there are wide variety of examples and we will be dealing with very simple thermodynamic aspects of a multi-component systems.

First thing what you need to do, how to deal with the thermodynamic properties. So, prior to this lecture we have p-v-T data, p-v-T data for pure substances. We have told that these data are available in the tabular form or the property tables and they should be used as and when it is required. And, looking at this data, when you deal with the multi-component systems another parameter that pops in is the compositions.

These compositions are mainly analyzed either on mass basis or molal basis. But, when you deal with the multi-component systems, it is ideal to use a molar concept. Because, the molar concept is uniform, while dealing with the molar systems we can deal with one gas constant that is what we call as universal gas constants when dealing with the equation of states.

So, that is the advantage when you deal with the multi-component systems, it is better to use the molar properties. So, for that these four parameters are of importance like partial molar properties, chemical potential, fugacity and ideal solutions. And in fact, this ideal solution is another model of gas mixtures. Normally, when we have liquid and gas together then we say it is a solutions. But, in some extent there are some relations which are suitable for ideal solutions.

If you can use them for analysis of gas mixtures, it also gives a good estimates. So, that is the reason that this gas mixture and ideal solutions has a some definite linking among them. So, we will study one by one of these properties down the lectures. So, let me start with what do you mean by gas mixtures. So, I have given a brief introduction about the gas mixtures.

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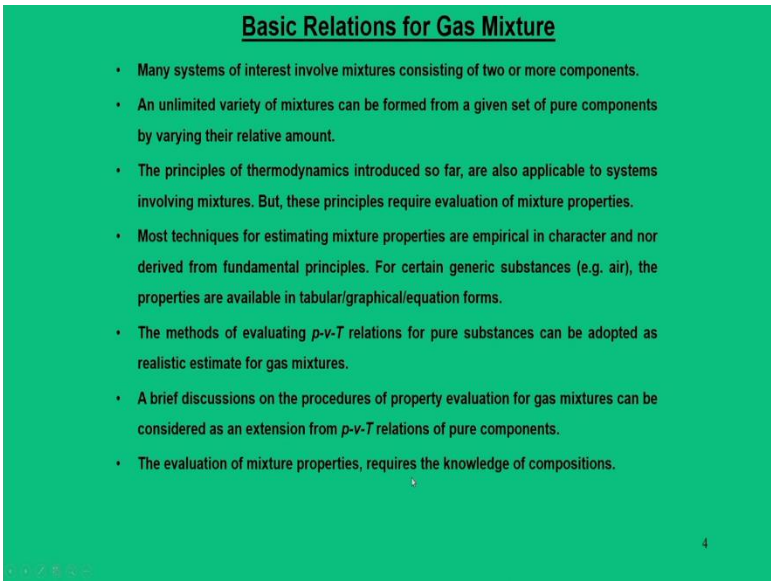

Basic Relations for Gas Mixture

- Many systems of interest involve mixtures consisting of two or more components.
- An unlimited variety of mixtures can be formed from a given set of pure components by varying their relative amount.
- The principles of thermodynamics introduced so far, are also applicable to systems involving mixtures. But, these principles require evaluation of mixture properties.
- Most techniques for estimating mixture properties are empirical in character and nor derived from fundamental principles. For certain generic substances (e.g. air), the properties are available in tabular/graphical/equation forms.
- The methods of evaluating *p-v-T* relations for pure substances can be adopted as realistic estimate for gas mixtures.
- A brief discussions on the procedures of property evaluation for gas mixtures can be considered as an extension from *p-v-T* relations of pure components.
- The evaluation of mixture properties, requires the knowledge of compositions.

Just to summarize that many systems of interest that involve gas mixtures they consist of two or more components. There may be unlimited variety of mixtures that can be formed from a given set of pure components by varying the relative amount. The principle of thermodynamics what we have introduced so far is also applicable to systems involving mixtures.

But, these principles also require the evaluation of mixture properties. There we are talking about the individual properties, thermodynamic properties for an individual pure substance. And, here we will have to find out the how those concepts can be extended for mixture to evaluate the mixture property. Most techniques for estimating mixture properties are empirical in character and they are derived from the fundamental principles.

For certain generic substances and the mixture, properties are also available in tabular form or equation forms or we can say state equations. We are now going to deal with the methods for evaluating p-v-T relations for pure substance which can be also give a realistic estimate for gas mixtures. So, first we will briefly discuss about the property evaluation of gas mixtures which can be considered as an extension of p-v-T relations of the pure components.

So, in summary what we can say each pure component is consist of a gas single phase that is gas and when these gases mix, they form a mixture. And, there also we say that this mixture also assumed to be another pure component. So, this is the main assumptions for the evaluation of mixture properties. But the first thing that we need to know is the knowledge of compositions.

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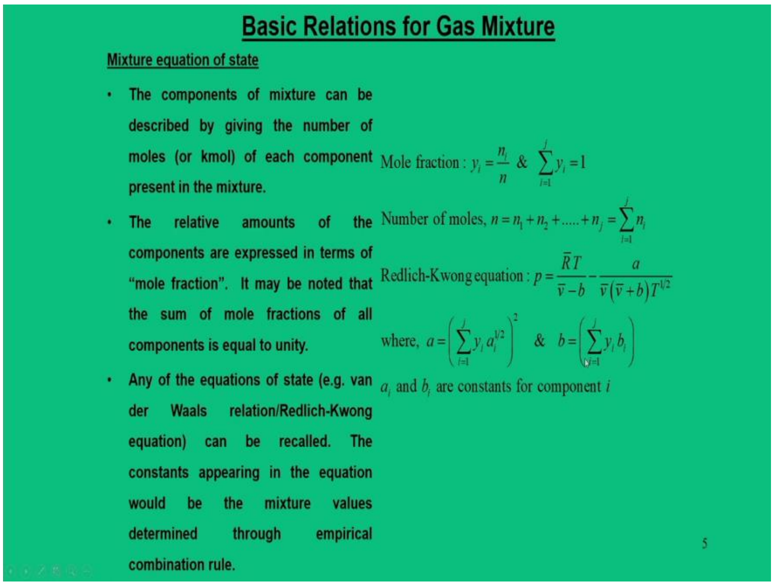

Basic Relations for Gas Mixture

Mixture equation of state

- The components of mixture can be described by giving the number of moles (or kmol) of each component present in the mixture.
- The relative amounts of the components are expressed in terms of "mole fraction". It may be noted that the sum of mole fractions of all components is equal to unity.
- Any of the equations of state (e.g. van der Waals relation/Redlich-Kwong equation) can be recalled. The constants appearing in the equation would be the mixture values determined through empirical combination rule.

Mole fraction : $y_i = \frac{n_i}{n}$ & $\sum_{i=1}^{j} y_i = 1$

Number of moles, $n = n_1 + n_2 + ... + n_j = \sum_{i=1}^{j} n_i$

Redlich-Kwong equation : $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}\left(\bar{v}+b\right)T^{1/2}}$

where, $a = \left(\sum_{i=1}^{j} y_i a_i^{1/2}\right)^2$ & $b = \left(\sum_{i=1}^{j} y_i b_i\right)$

a_i and b_i are constants for component i

As I mentioned, the ideal way of looking at the mixture is through their mole fractions. So, the mole fraction is defined as in a mixture if there are multiple number of components. For any components, the mole fraction $y_i = \frac{n_i}{n}$. And in fact, the summation of this mole fraction in a mixture is always 1, $\sum_{i=1}^{j} y_i = 1$.

And, the summation of total number of moles; that means, if there are j number of constituents in a mixtures, the number of moles can be added to find the total number of moles $n = n_1 + n_2 + ... + n_j = \sum_{i=1}^{j} n_i$. Now, previous lectures we have talked about different state equations that is ideal gas, then we have van der Waal gas equations, we have virial state equations, we have Redlich Kwong equations. And, they gave some kind of estimate of the thermodynamic states.

And, now here what we are trying to say if for a mixture analysis those equations also can be recalled. Like here if you see there is a Redlich Kwong equations which talks about $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{\frac{1}{2}}}$. This equation also can be used for mixtures. But, what changes we need to do? Evaluation of the constants a and b which is appearing in these equations.

These evaluation of these parameters a and b has to be component wise, then they have to be summed up. And, again while looking at the equations; we have to also see that in equations what form they appear. For example, in these particular equations there is a $T^{\frac{1}{2}}$ term.

So, a proper judgment has to be made that how this summation has to take place. One way of looking at for this particular case, the value of a for the mixtures can be found out from the component analysis through summations, where $a = \left(\sum_{i=1}^{j} y_i a_i^{\frac{1}{2}}\right)^2$.

So, basically this gives a good estimate which correlates with respect to these equations. So, this type of mathematical juggler you have to make to make more realistic estimate. But whereas, for b term we do not have to look into because they are having a linear relations, we can simply write $b = \left(\sum_{i=1}^{j} y_i b_i\right)$. So, the idea is we have to make appropriate judgement while evaluating the constants in a state equations through their summation.

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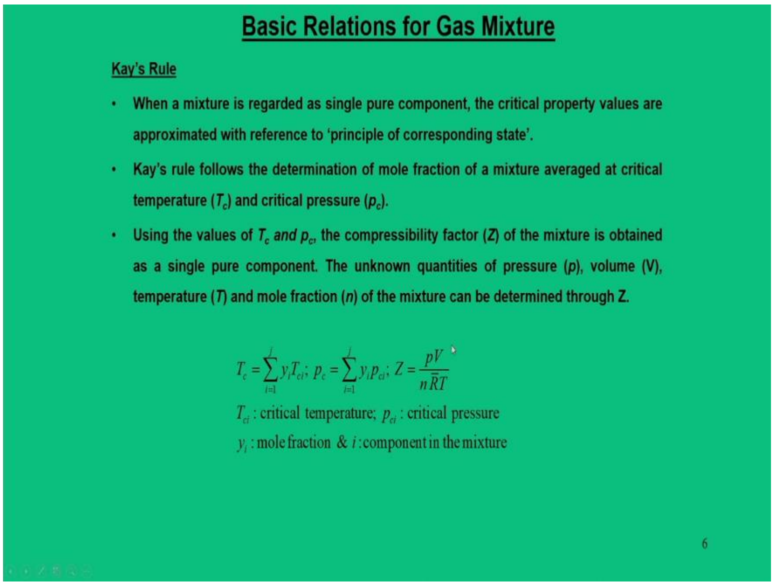

Basic Relations for Gas Mixture

Kay's Rule

- When a mixture is regarded as single pure component, the critical property values are approximated with reference to 'principle of corresponding state'.
- Kay's rule follows the determination of mole fraction of a mixture averaged at critical temperature (T_c) and critical pressure (p_c).
- Using the values of T_c *and* p_c, the compressibility factor (Z) of the mixture is obtained as a single pure component. The unknown quantities of pressure (p), volume (V), temperature (T) and mole fraction (n) of the mixture can be determined through Z.

$$T_c = \sum_{i=1}^{j} y_i T_{ci};\ p_c = \sum_{i=1}^{j} y_i p_{ci};\ Z = \frac{pV}{n\bar{R}T}$$

T_{ci} : critical temperature; p_{ci} : critical pressure

y_i : mole fraction & i : component in the mixture

The next relation that we are going to apply is Kay's rule. Kay's rule talks about the evaluation of the properties based on the principle of corresponding states. In our previous lectures, we discussed about reducing the parameters like pressure, temperature with respect to reduced parameters. And, this reduced parameter was done by taking the values at the critical point for that pure substance; that means, we require critical pressure and critical temperature for a pure substance.

Based on that we can find its reduced parameters, through this reduced parameters and through this compressibility chart all other properties can be estimated. Now, Kay’s rule says that we will also try to apply same fundamental principles based on the principle of corresponding states, but here we look at them as a mixture. For example, if there are multiple number of substances, for each substances we know its mole fractions and we also know its critical temperature and critical pressures.

Then, for the mixture critical temperature and pressure can be found out through this summation. So, $T_c = \sum_{i=1}^{j} y_i T_{ci}\, ; p_c = \sum_{i=1}^{j} y_i p_{ci}$. And, this overall parameters along with the compressibility factor can be used to evaluate the mixture properties.

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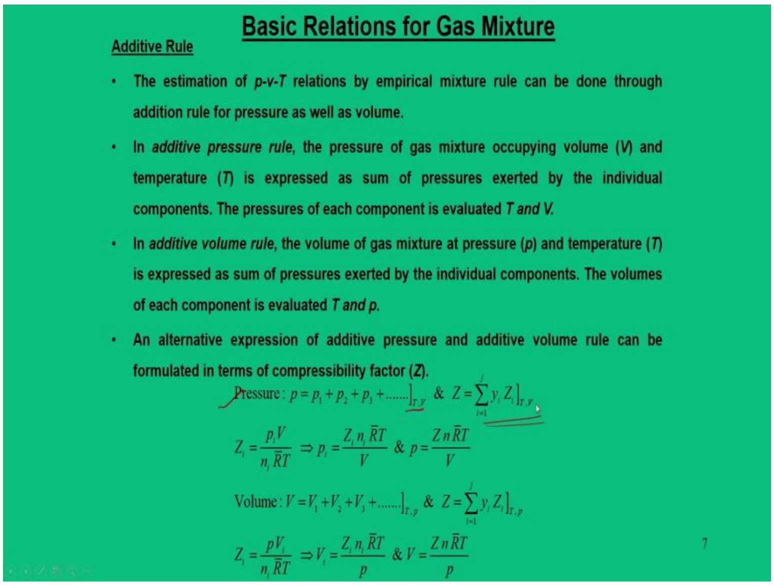

Basic Relations for Gas Mixture

Additive Rule

- The estimation of *p-v-T* relations by empirical mixture rule can be done through addition rule for pressure as well as volume.
- In *additive pressure rule*, the pressure of gas mixture occupying volume (*V*) and temperature (*T*) is expressed as sum of pressures exerted by the individual components. The pressures of each component is evaluated *T and V.*
- In *additive volume rule*, the volume of gas mixture at pressure (*p*) and temperature (*T*) is expressed as sum of pressures exerted by the individual components. The volumes of each component is evaluated *T and p.*
- An alternative expression of additive pressure and additive volume rule can be formulated in terms of compressibility factor (*Z*).

$$\text{Pressure}: p = p_1 + p_2 + p_3 + \ldots\ldots\Big]_{T,V} \;\&\; Z = \sum_{i=1}^{j} y_i Z_i\Big]_{T,V}$$

$$Z_i = \frac{p_i V}{n_i \bar{R} T} \Rightarrow p_i = \frac{Z_i n_i \bar{R} T}{V} \;\&\; p = \frac{Z n \bar{R} T}{V}$$

$$\text{Volume}: V = V_1 + V_2 + V_3 + \ldots\ldots\Big]_{T,p} \;\&\; Z = \sum_{i=1}^{j} y_i Z_i\Big]_{T,p}$$

$$Z_i = \frac{p V_i}{n_i \bar{R} T} \Rightarrow V_i = \frac{Z_i n_i \bar{R} T}{p} \;\&\; V = \frac{Z n \bar{R} T}{p}$$

Then, moving further there is another rule which is called an additive rule and this additive rule applies for pressure and volume of the mixture; that means, we say that mixture is at overall pressure p and temperature T. Now, how that overall pressure and temperature needs to be evaluated. So, for that we have this additive rules. This additive rules apply to evaluate the pressure of gas mixtures when they occupy a total volume V and overall temperature T.

And, when we have this, we can apply this additive pressure rule that is mixture pressure $p = p_1 + p_2 + p_3 + \ldots\ldots]_{T,V}$. And, the summation of these things occupy a common temperature and total volume V. And of course, with through this, can we find out the compressibility factor for this mixtures, by knowing the mole fraction of each component and its individual compressibility factor $Z = \sum_{i=1}^{j} y_i Z_i]_{T,V}$.

And, this has to be evaluated at overall temperature T and V of the mixture. From this we also can find out the compressibility factor for individual component. For that we have to recall its individual pressure; that means, we call this as a partial pressure of that particular component. Then, we have to use its mole fractions. Likewise, we can evaluate individual pressures and then total pressures.

$$Z_i = \frac{p_i V}{n_i \bar{R} T} \Rightarrow p_i = \frac{Z_i n_i \bar{R} T}{V} \& p = \frac{Z n \bar{R} T}{V}$$

Now, same rule also applies for volume. Now, if you say that total volume $V = V_1 + V_2 + V_3 + \ldots\ldots]_{T,p}$. And, we use the same compressibility equations to find the individual compressibility factor, individual volume and total volume. So, basically additive pressure and volume rules can be formulated in terms of compressibility factor.

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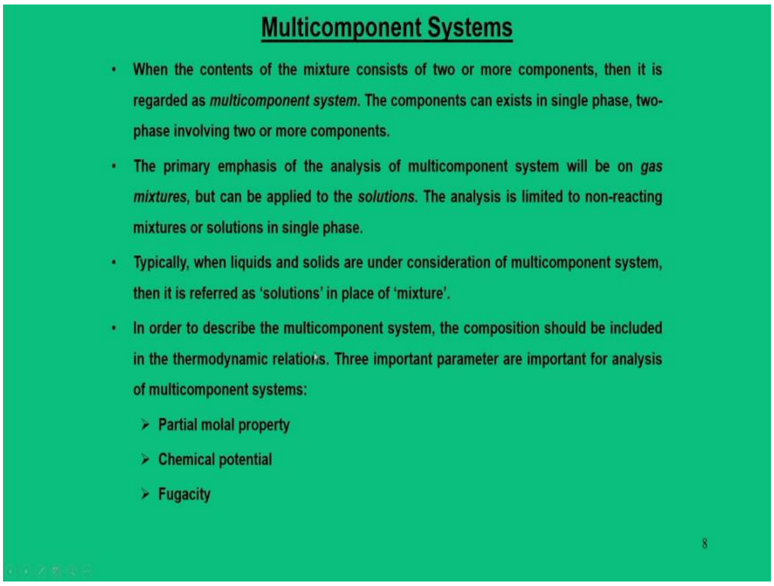

Multicomponent Systems

- When the contents of the mixture consists of two or more components, then it is regarded as *multicomponent system.* The components can exists in single phase, two-phase involving two or more components.
- The primary emphasis of the analysis of multicomponent system will be on *gas mixtures*, but can be applied to the *solutions.* The analysis is limited to non-reacting mixtures or solutions in single phase.
- Typically, when liquids and solids are under consideration of multicomponent system, then it is referred as 'solutions' in place of 'mixture'.
- In order to describe the multicomponent system, the composition should be included in the thermodynamic relations. Three important parameter are important for analysis of multicomponent systems:
  - Partial molal property
  - Chemical potential
  - Fugacity

Now, having said this, we will now move on to multi-component systems. Now, as I said that a multi-component systems is a very generic topics and there may be very complicated mixtures, their phases, their compositions, their relative individual pressures, temperatures. So, all sorts of things. But, to simplify these things we will primarily emphasize analysis of multi-component systems for gas mixtures; that means, we can say deal with the gas mixtures and particular to some solutions.

Typically, when the liquids and solids are under consideration in a multi-component system, we use the word solutions. Otherwise, when you use for gases, it is usually used as mixtures. Now, to deal with this multi-component systems, there are three parameters of importance. One is partial molar properties, chemical potential and fugacity. So, we will deal with them one by one.

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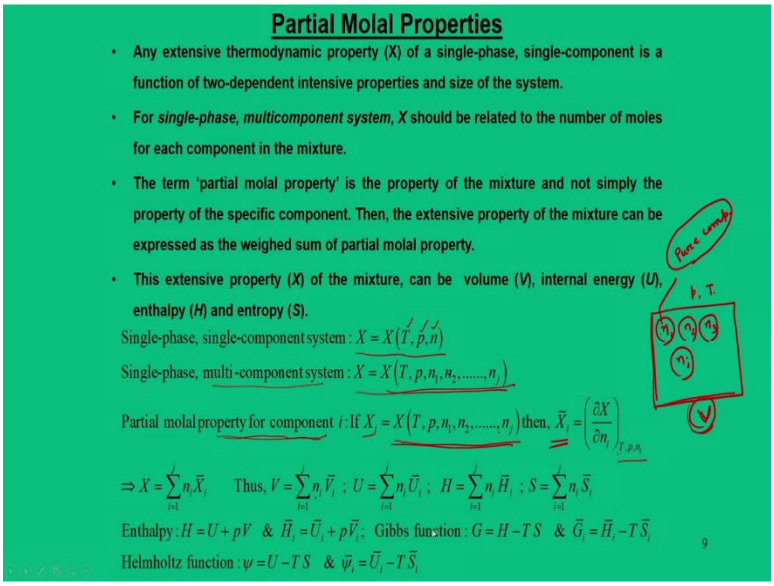

Partial Molal Properties

- Any extensive thermodynamic property (X) of a single-phase, single-component is a function of two-dependent intensive properties and size of the system.
- For *single-phase, multicomponent system, X* should be related to the number of moles for each component in the mixture.
- The term 'partial molal property' is the property of the mixture and not simply the property of the specific component. Then, the extensive property of the mixture can be expressed as the weighed sum of partial molal property.
- This extensive property (*X*) of the mixture, can be volume (*V*), internal energy (*U*), enthalpy (*H*) and entropy (*S*).

Single-phase, single-component system : $X = X(T, p, n)$

Single-phase, multi-component system : $X = X(T, p, n_1, n_2, \ldots\ldots, n_j)$

Partial molal property for component i : If $X_j = X(T, p, n_1, n_2, \ldots\ldots, n_j)$ then, $\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_i}$

$\Rightarrow X = \sum_{i=1}^{j} n_i \bar{X}_i$ Thus, $V = \sum_{i=1}^{j} n_i \bar{V}_i$; $U = \sum_{i=1}^{j} n_i \bar{U}_i$; $H = \sum_{i=1}^{j} n_i \bar{H}_i$; $S = \sum_{i=1}^{j} n_i \bar{S}_i$

Enthalpy : $H = U + pV$ & $\bar{H}_i = \bar{U}_i + p\bar{V}_i$; Gibbs function : $G = H - TS$ & $\bar{G}_i = \bar{H}_i - T\bar{S}_i$

Helmholtz function : $\psi = U - TS$ & $\bar{\psi}_i = \bar{U}_i - T\bar{S}_i$

So, let us talk about the partial molar properties. What does this mean? That means, if you can think of a system consisting of j number of gases with individual components $n_1, n_2, \ldots\ldots, n_j$. And, they have a common pressure p and temperature T that is overall pressure and temperature. But, what we should note is that each component are treated as a pure component.

Now, when they are treated as a pure component, they have their individual properties like internal energy, enthalpy, molar volume. So, when they are treated as a pure component, they are considered with respect to their molar numbers. Now, when this mixture is considered with respect to its overall volume V, then, this mixture has a relative role; that means, this mixture with respect to total volume will have a different number.

So, what means that while dealing with this molar properties, we deal with the properties which needs to be evaluated with respect to its individual parameters of the component. And, when their properties are defined with respect to overall conditions of the mixture, pressure, temperature or volume; then they are treated as a partial molar properties. So, let me put this definition as that the term partial molal property is a property of mixtures.

But, it is not simply property of a specific component and then the extensive properties of the mixture can be expressed as weight sum of the partial molar properties. So, in a general case let us consider an extensive properties X, these extensive properties can be usable for volume, internal energy and enthalpy and entropy. So, for a single phase, single component systems, we write X is equal to X as a function of temperature, pressure and its composition, number of moles; $X = X(T, p, n)$.

Now, when you represent it for a multi-component systems. So, this one that there may be number of components n 1 n 2 n 3 and each will have number of moles we write $X = X\left(T, p, n_1, n_2, \ldots\ldots, n_j\right)$. Then, you have to define the partial molal properties for the component. So, if $X_i = X\left(T, p, n_1, n_2, \ldots\ldots, n_j\right), \bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_i}$.

So, this $\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_i}$, n_i is the number of moles for that component i. And, this differentiation has to take place at mixture temperature, pressure and, but with respect to component n_i. Then, this is called as partial molar properties.

Now, this rule can be applied for the volume V, then we can also write for the internal energy U, we can write it for enthalpy, we can also write it for entropy. So, this is how we define this and in terms of moles we can write with respect to the n_i stands for number of moles, V_i stands for molar volume for the component i. So, here is the total volume of the component is equal to summation of each individual molar volume multiplied its mole fractions. $V = \sum_{i=1}^{j} n_i \bar{V}_i$

So, this is how the partial properties are defined for a component in a mixture. And, this rule also is applicable for all properties like enthalpy, Gibbs function, Helmholtz functions and so on.

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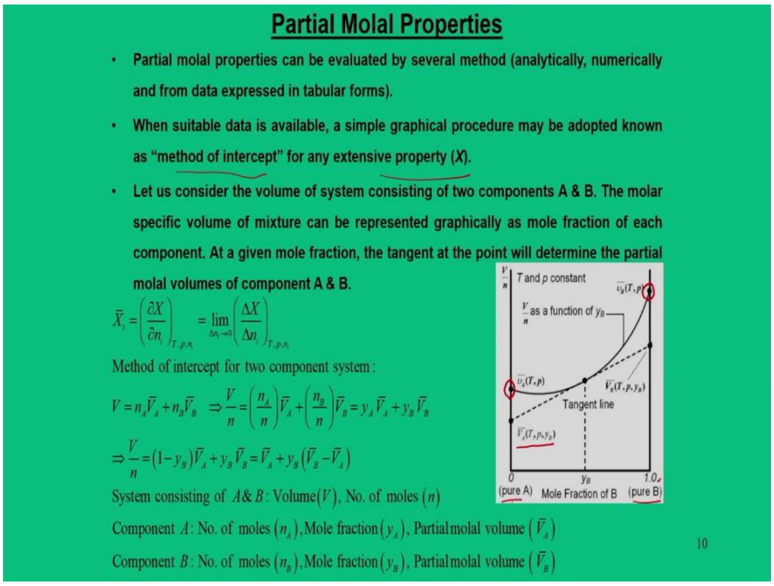

Partial Molal Properties

- Partial molal properties can be evaluated by several method (analytically, numerically and from data expressed in tabular forms).
- When suitable data is available, a simple graphical procedure may be adopted known as "method of intercept" for any extensive property (*X*).
- Let us consider the volume of system consisting of two components A & B. The molar specific volume of mixture can be represented graphically as mole fraction of each component. At a given mole fraction, the tangent at the point will determine the partial molal volumes of component A & B.

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_j} = \lim_{\Delta n_i \to 0}\left(\frac{\Delta X}{\Delta n_i}\right)_{T,p,n_j}$$

Method of intercept for two component system:

$$V = n_A\bar{V}_A + n_B\bar{V}_B \quad \Rightarrow \frac{V}{n} = \left(\frac{n_A}{n}\right)\bar{V}_A + \left(\frac{n_B}{n}\right)\bar{V}_B = y_A\bar{V}_A + y_B\bar{V}_B$$

$$\Rightarrow \frac{V}{n} = (1-y_B)\bar{V}_A + y_B\bar{V}_B = \bar{V}_A + y_B\left(\bar{V}_B - \bar{V}_A\right)$$

System consisting of $A\&B$: Volume(V), No. of moles (n)

Component A: No. of moles (n_A), Mole fraction (y_A), Partial molal volume $(\bar{V}_A)$

Component B: No. of moles (n_B), Mole fraction (y_B), Partial molal volume $(\bar{V}_B)$

Now, of course, the molar properties are can be find out for a individual components. There are many techniques that are available, several methods we can do it analytically, numerically and in the form of tabular forms of data. But, if suitable datas are available, one simplest way of representing is in the graphical form which is called as method of intercept for any extensive property X.

So, what do you do is that you take this simple coordinate systems x-y; that means, two y axis or two ordinate axis, one abscissa axis. And, abscissa we put is as a mole fraction and one ordinate we put it for molar volume for component A and other side of this ordinate, we have molar volume for component B.

And, each mole fractions we can locate these points and draw a curve. So, the curve that stands for is that if I take any particular line on this axis, left side of this ordinate and we will arrive it is a pure component. And, in this line there is no component of ϕ and on the right side of this line, we have pure component B. So, basically this point stands for molar volume V_A at T, p for the component A and this point stands for molar specific volume for B at T and p.

And so, basically if you want to find out any value on this point, you can draw a tangent. And wherever they intersect, we can find out the molar volume; that means, total molar volume for the component A, T, p and y_B. So, this way we can frame the method of intercept equations for two component systems as total volume V will be $n_A\bar{V}_A + n_B\bar{V}_B$.

So, by simplifying these equations and; that means, when you divide by number of moles then we write $\frac{V}{n} = (1 - y_B)\bar{V}_A + y_B\bar{V}_B = \bar{V}_A + y_B(\bar{V}_B - \bar{V}_A)$. So, this is the simplest way we can find out for the molar volume in a partial molar properties in a mixture.

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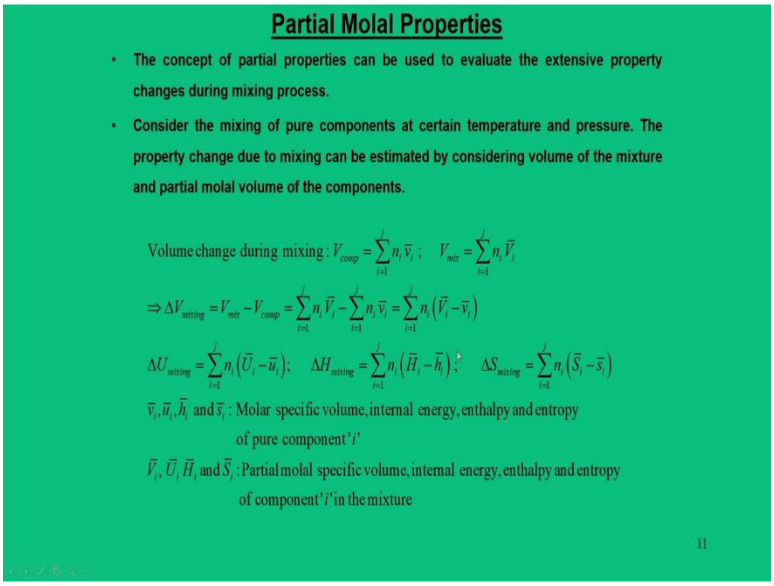

Partial Molal Properties

- The concept of partial properties can be used to evaluate the extensive property changes during mixing process.
- Consider the mixing of pure components at certain temperature and pressure. The property change due to mixing can be estimated by considering volume of the mixture and partial molal volume of the components.

$$\text{Volume change during mixing}: V_{comp} = \sum_{i=1}^{j} n_i \bar{v}_i \,; \quad V_{mix} = \sum_{i=1}^{j} n_i \bar{V}_i$$

$$\Rightarrow \Delta V_{mixing} = V_{mix} - V_{comp} = \sum_{i=1}^{j} n_i \bar{V}_i - \sum_{i=1}^{j} n_i \bar{v}_i = \sum_{i=1}^{j} n_i \left(\bar{V}_i - \bar{v}_i\right)$$

$$\Delta U_{mixing} = \sum_{i=1}^{j} n_i \left(\bar{U}_i - \bar{u}_i\right); \quad \Delta H_{mixing} = \sum_{i=1}^{j} n_i \left(\bar{H}_i - \bar{h}_i\right); \quad \Delta S_{mixing} = \sum_{i=1}^{j} n_i \left(\bar{S}_i - \bar{s}_i\right)$$

$\bar{v}_i, \bar{u}_i, \bar{h}_i$ and $\bar{s}_i$: Molar specific volume, internal energy, enthalpy and entropy of pure component 'i'

$\bar{V}_i, \bar{U}_i, \bar{H}_i$ and $\bar{S}_i$: Partial molal specific volume, internal energy, enthalpy and entropy of component 'i' in the mixture

Then, in many instances we also require the change of the volume during the mixing. So; that means, the component i will have individual molar value, specific volume, molar specific internal energy, molar specific enthalpy. But, after mixing it will have a different number. So, then that means, there is a change in the volume of the property after mixing. So, that mixing properties we can find out $\Delta V_{mixing} = V_{mix} - V_{comp}$.

So, had these properties be treated as a total volume, then the mixture volume has to take the form $\sum_{i=1}^{j} n_i\bar{V}_i$. If they are treated as a component wise, then it will $\sum_{i=1}^{j} n_i\bar{v}_i$. So, difference will give you the volume change during mixing. So, similar expression can also be find out for internal energy, enthalpy and entropy after mixing.

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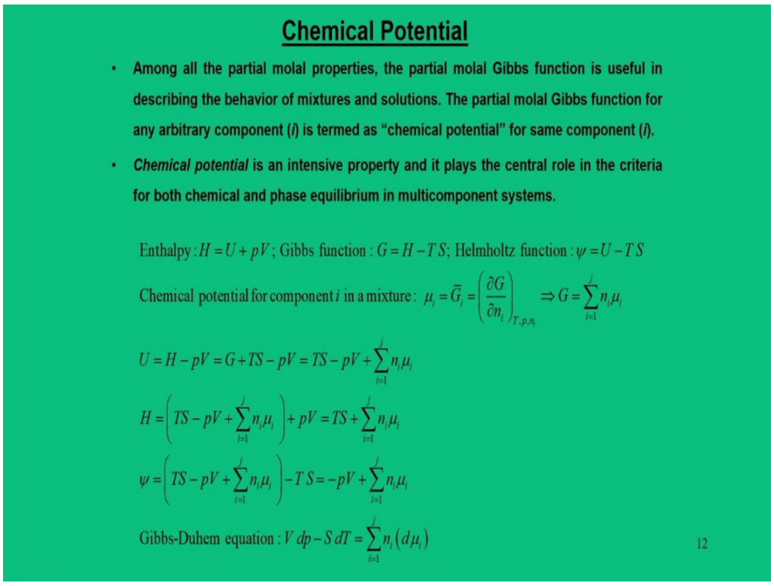

Chemical Potential

- Among all the partial molal properties, the partial molal Gibbs function is useful in describing the behavior of mixtures and solutions. The partial molal Gibbs function for any arbitrary component (*i*) is termed as "chemical potential" for same component (*i*).
- *Chemical potential* is an intensive property and it plays the central role in the criteria for both chemical and phase equilibrium in multicomponent systems.

Enthalpy : $H = U + pV$; Gibbs function : $G = H - TS$; Helmholtz function : $\psi = U - TS$

Chemical potential for component i in a mixture : $\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i} \Rightarrow G = \sum_{i=1}^{j} n_i \mu_i$

$$U = H - pV = G + TS - pV = TS - pV + \sum_{i=1}^{j} n_i \mu_i$$

$$H = \left(TS - pV + \sum_{i=1}^{j} n_i \mu_i\right) + pV = TS + \sum_{i=1}^{j} n_i \mu_i$$

$$\psi = \left(TS - pV + \sum_{i=1}^{j} n_i \mu_i\right) - TS = -pV + \sum_{i=1}^{j} n_i \mu_i$$

Gibbs-Duhem equation : $V\,dp - S\,dT = \sum_{i=1}^{j} n_i (d\mu_i)$

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So, this is how the partial molar properties are defined. Now, we will move on to another important properties for mixture and that is called as a chemical potential. So, among all partial molar properties, the partial molar Gibbs function is useful in describing the behavior of mixture and solutions. This partial molal Gibbs function for an arbitrary component i is termed as the chemical potential for the same component.

And, this chemical potential is an intensive properties and it plays a very central role for chemical and phase equilibrium for a multi-component system. So, what does this mean is that. So, we all know that we have the term enthalpy, we have term the Gibbs function, we have Helmholtz functions. But, what the chemical potential means it is the Gibbs functions that is take the lead role.

So, for an chemical potential component i in a mixture is defined as mu i is equal to molar value of Gibbs function for the component y, that is $\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i} \Rightarrow G = \sum_{i=1}^{j} n_i \mu_i$.

Now, based on these chemical properties, we are now going to alter the enthalpy, Gibbs function and Helmholtz functions in this form, where the term chemical potential is introduced that is μ_i is introduced in the all the equations. So, based on that we have another important equations for the mixture which is called as Gibbs-Duhem equations.

Like earlier time you have Maxwell equations and while dealing with the mixtures we arrive at another equations, what we call as Gibbs-Duhem equations which is $Vdp - SdT = \sum_{i=1}^{j} n_i(d\mu_i)$. Now, let us find what is the role of this chemical properties when dealing with the analysis of the mixture.

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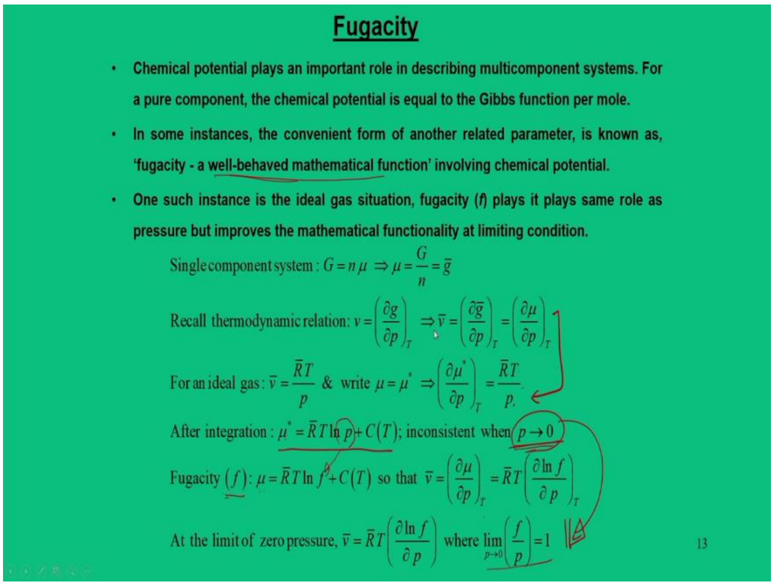

Fugacity

- Chemical potential plays an important role in describing multicomponent systems. For a pure component, the chemical potential is equal to the Gibbs function per mole.
- In some instances, the convenient form of another related parameter, is known as, 'fugacity - a well-behaved mathematical function' involving chemical potential.
- One such instance is the ideal gas situation, fugacity (*f*) plays it plays same role as pressure but improves the mathematical functionality at limiting condition.

Single component system : $G = n\mu \Rightarrow \mu = \frac{G}{n} = \bar{g}$

Recall thermodynamic relation: $v = \left(\frac{\partial g}{\partial p}\right)_T \Rightarrow \bar{v} = \left(\frac{\partial \bar{g}}{\partial p}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_T$

For an ideal gas: $\bar{v} = \frac{\bar{R}T}{p}$ & write $\mu = \mu^* \Rightarrow \left(\frac{\partial \mu^*}{\partial p}\right)_T = \frac{\bar{R}T}{p}$.

After integration : $\mu^* = \bar{R}T \ln p + C(T)$; inconsistent when $p \to 0$

Fugacity (f): $\mu = \bar{R}T \ln f + C(T)$ so that $\bar{v} = \left(\frac{\partial \mu}{\partial p}\right)_T = \bar{R}T\left(\frac{\partial \ln f}{\partial p}\right)_T$

At the limit of zero pressure, $\bar{v} = \bar{R}T\left(\frac{\partial \ln f}{\partial p}\right)$ where $\lim_{p \to 0}\left(\frac{f}{p}\right) = 1$

The next important property which has a similar viewpoint with respect to chemical potential is the fugacity. Now, we may ask what is the role of fugacity and we also say that fugacity has a similar role with respect to chemical potential.

Now, let us say what is the demerits or why another term we are using fugacity in place of chemical potential? It has been shown that fugacity is a well behaved mathematical functions. In fact, chemical potential μ_i is also a mathematical function and fugacity is also a mathematical function, but it is a well behaved. Well behaved means that it gives a realistic approach something like that. Now how that happens?

So, let us analyze the consequence of a chemical potential and if we represent in it in terms of fugacity what advantage we will get. For a single component systems, when you talk about Gibbs function $G = n\mu \Rightarrow \mu = \frac{G}{n} = \bar{g}$. Now, in one of the thermodynamic relations we recall in our previous module, specific volume $v = \left(\frac{\partial g}{\partial p}\right)_T$.

Now, by putting this in terms of chemical potential, we can write this equation as $\bar{v} = \left(\frac{\partial \bar{g}}{\partial p}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_T$. Now, if we apply this concept for an ideal gas; that means, you define a chemical potential for an ideal gas. So, for an ideal gas we can write the molar specific volume $\bar{v} = \frac{\bar{R}T}{p}$ and for that we write $\mu = \mu^* \Rightarrow \left(\frac{\partial \mu^*}{\partial p}\right)_T = \frac{\bar{R}T}{p}$.

Then after integrating this, you arrive at these equations like $\mu^* = \bar{R}T \ln p + C(T)$. But, here the important consequence that we see that when p tends to 0, μ^* is not defined. So, it poses a mathematical problem, how to deal with this fact that when you find out the chemical potential for a mixture for which the pressure tends to 0, what is going to happen? We do not have any answer.

For that we define another function what we call a fugacity, that is what we call this as a well behaved mathematical functions. So, how it behaves well? So, instead of writing μ^*, we define the fugacity instead of why define this chemical potential μ and instead of writing p here, that is replaced with a parameter f. So, chemical potential is expressed in terms of fugacity, $\mu = \bar{R}T \ln f + C(T)$.

So, that from this equation we get v$\bar{v} = \left(\frac{\partial \mu}{\partial p}\right)_T = \bar{R}T \left(\frac{\partial \ln f}{\partial p}\right)_T$. And, what we see is that at the limit of 0 pressure, this $\bar{v} = \bar{R}T \left(\frac{\partial \ln f}{\partial p}\right)$, that point at the limit of 0 where $\lim_{p \to 0} \left(\frac{f}{p}\right) = 1$.

So, this condition; that means, was when pressure tends to 0, mathematically it is treated in a different form in a limiting situations where $\lim_{p \to 0} \left(\frac{f}{p}\right) = 1$. Other way is I can say that fugacity plays the same role as that of pressures, but it improves the mathematical functionality at the limiting conditions.

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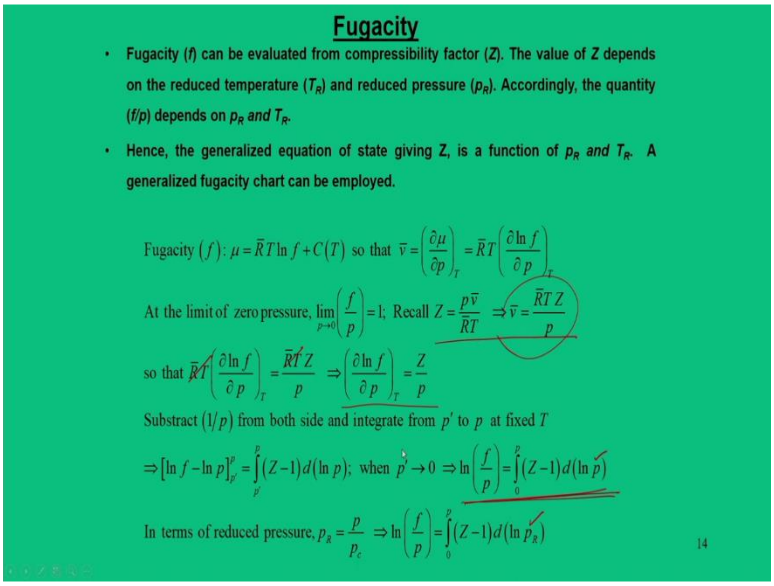

Fugacity

- **Fugacity (*f*) can be evaluated from compressibility factor (*Z*). The value of *Z* depends on the reduced temperature (T_R) and reduced pressure (p_R). Accordingly, the quantity (*f/p*) depends on p_R and T_R.**
- **Hence, the generalized equation of state giving Z, is a function of p_R and T_R. A generalized fugacity chart can be employed.**

Fugacity (f): $\mu = \bar{R}T \ln f + C(T)$ so that $\bar{v} = \left(\frac{\partial \mu}{\partial p}\right)_T = \bar{R}T\left(\frac{\partial \ln f}{\partial p}\right)_T$

At the limit of zero pressure, $\lim_{p \to 0}\left(\frac{f}{p}\right) = 1$; Recall $Z = \frac{p\bar{v}}{\bar{R}T} \Rightarrow \bar{v} = \frac{\bar{R}T\,Z}{p}$

so that $\cancel{\bar{R}T}\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{\cancel{\bar{R}T}\,Z}{p} \Rightarrow \left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{Z}{p}$

Substract $(1/p)$ from both side and integrate from p' to p at fixed T

$\Rightarrow \left[\ln f - \ln p\right]_{p'}^{p} = \int_{p'}^{p}(Z-1)\,d(\ln p)$; when $p' \to 0 \Rightarrow \ln\left(\frac{f}{p}\right) = \int_0^p (Z-1)\,d(\ln p)$

In terms of reduced pressure, $p_R = \frac{p}{p_c} \Rightarrow \ln\left(\frac{f}{p}\right) = \int_0^p (Z-1)\,d(\ln p_R)$

So, once you know the fugacity instead of chemical potential, if you represent in terms of fugacity, it has some other advantages. This fugacity also can be found out with correlations from the compressibility factor at reduced pressure p_R, reduced temperature T_R for the mixture. And, based on this reduced conditions, we can also find out the generalized equation of state that gives Z that means, compressibility factor as a function of p_R and T_R. How you are going to get it?

So, let us start with the expression for fugacity f and that we start with the basic definition $\mu = \bar{R}T \ln f + C(T)$. So, at the limiting case $\lim_{p \to 0}\left(\frac{f}{p}\right) = 1$, then we recall this expression $Z = \frac{p\bar{v}}{\bar{R}T} \Rightarrow \bar{v} = \frac{\bar{R}TZ}{p}$. You now replace this $\bar{v}$ in terms of Z. So, we write $\bar{R}T\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{\bar{R}TZ}{p} \Rightarrow \left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{Z}{p}$ and Z is your compressibility factor and p is your pressure. Now, when you subtract $\frac{1}{p}$ from the both sides, then it will give you integrations in a workable form what we call as $\ln\left(\frac{f}{p}\right) = \int_0^p (Z-1)\, d(\ln p)$. This particular parameter and instead of p, we can use it in terms of p_R that is reduced pressure. So, this will tell us that how you are going to evaluate the fugacity.

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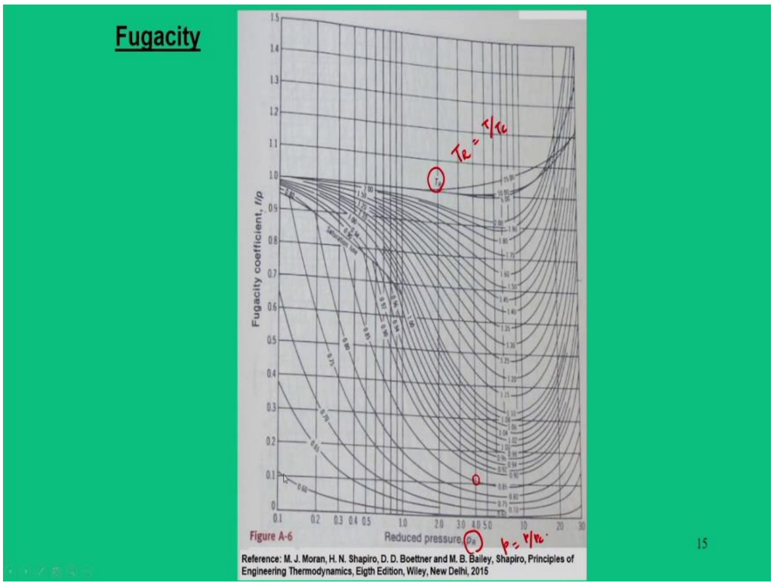

Fugacity

Figure A-6

Reference: M. J. Moran, H. N. Shapiro, D. D. Boettner and M. B. Bailey, Shapiro, Principles of Engineering Thermodynamics, Eigth Edition, Wiley, New Delhi, 2015

Now, let us see how you are going to get is that if you go through any thermodynamic books, you will find one particular chart which talks about fugacity coefficient. So, basically $\frac{f}{p}$ is nothing, but your fugacity coefficients. Although that means, f approaches p, but f is not equal to p. So, that is the reason we call this $\frac{f}{p}$ as a fugacity coefficient. And, this fugacity coefficient in a mixture is represented in terms of the reduced parameters.

So, $p_R = \frac{p}{p_c}$ and $T_R = \frac{T}{T_c}$; p_c and T_c are the critical pressure and temperature for that substance. Either, you get can get it for an individual component pure substance, but here the fugacity coefficient when we are talking about, we are talking about the mixture. So, basically we have to find out the mixtures critical pressure and temperatures and from there we have to find out the fugacity coefficients.

So, when these are represented; so, you can see this is the temperature line at different T_R, we will have different reduced pressure values. So, basically for a given data you have to find T_R and p_R. So, let us say you have p_R 4 and T_R may be 0.85, look at this, point gives you this number; fugacity coefficient $\frac{f}{p} = 0.1$. So, this is how this chart has to be referred.

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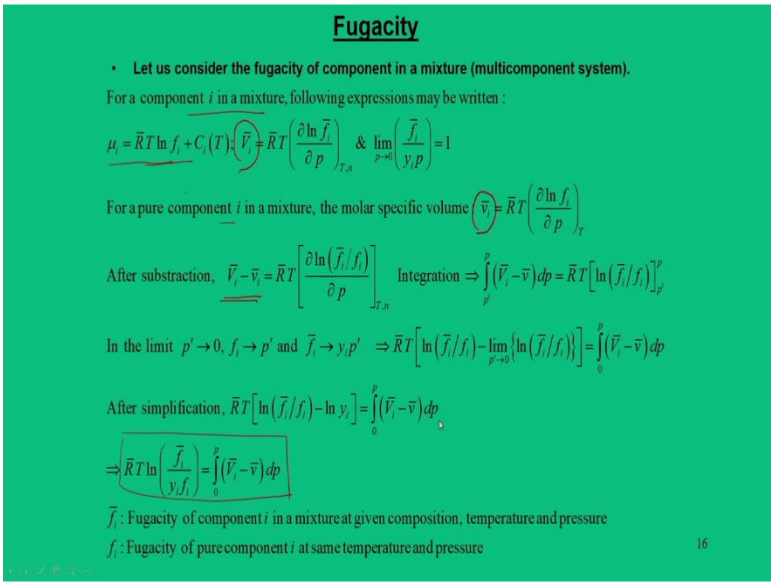

Fugacity

- **Let us consider the fugacity of component in a mixture (multicomponent system).**

For a component i in a mixture, following expressions may be written :

$$\mu_i = \bar{R}T \ln f_i + C_i(T);\ \bar{V}_i = \bar{R}T\left(\frac{\partial \ln \bar{f}_i}{\partial p}\right)_{T,n} \ \&\ \lim_{p\to 0}\left(\frac{\bar{f}_i}{y_i p}\right) = 1$$

For a pure component i in a mixture, the molar specific volume $\bar{v}_i = \bar{R}T\left(\frac{\partial \ln f_i}{\partial p}\right)_T$

After substraction, $\bar{V}_i - \bar{v}_i = \bar{R}T\left[\frac{\partial \ln\left(\bar{f}_i/f_i\right)}{\partial p}\right]_{T,n}$ Integration $\Rightarrow \int_{p'}^{p}\left(\bar{V}_i - \bar{v}\right)dp = \bar{R}T\left[\ln\left(\bar{f}_i/f_i\right)\right]_{p'}^{p}$

In the limit $p' \to 0,\ f_i \to p'$ and $\bar{f}_i \to y_i p'$ $\Rightarrow \bar{R}T\left[\ln\left(\bar{f}_i/f_i\right) - \lim_{p'\to 0}\left\{\ln\left(\bar{f}_i/f_i\right)\right\}\right] = \int_0^p\left(\bar{V}_i - \bar{v}\right)dp$

After simplification, $\bar{R}T\left[\ln\left(\bar{f}_i/f_i\right) - \ln y_i\right] = \int_0^p\left(\bar{V}_i - \bar{v}\right)dp$

$$\Rightarrow \boxed{\bar{R}T \ln\left(\frac{\bar{f}_i}{y_i f_i}\right) = \int_0^p\left(\bar{V}_i - \bar{v}\right)dp}$$

$\bar{f}_i$: Fugacity of component i in a mixture at given composition, temperature and pressure

f_i : Fugacity of pure component i at same temperature and pressure

Now, we are talking about the fugacity coefficients for a multi-component systems, when you deal with the multi-component systems basically we have to find the fugacity coefficient for this individual component i, also the fugacity of the overall mixture. So, based on that we have two numbers, like if the component i is treated in the mixture as a mixture that is μ_i.

And, this same component i is treated as pure components, it will have a molar specific volume $\bar{v}_i$ and when it is mixture, it will be have a mixture volume $\bar{V}_i$. So, difference between these two; that means, $\bar{V}_i - \bar{v}_i$ will be represented in terms of the fugacity. So, $\bar{V}_i - \bar{v}_i = \bar{R}T\left[\frac{\partial \ln\left(\frac{\bar{f}_i}{f_i}\right)}{\partial p}\right]_{T,n}$.

And, after performing the integrations we will arrive at the workable form; that means, which relates the mixture fugacity and fugacity for the component i, means we say the fugacity for the component i in the mixture and, the fugacity for the component i, if you treated as a pure component. But, all these things are taken at the given composition and temperature and pressure.

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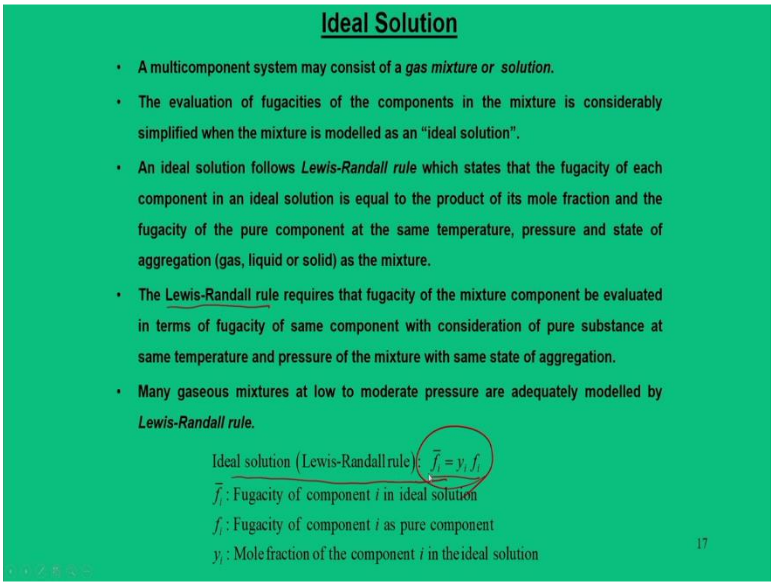

Ideal Solution

- A multicomponent system may consist of a *gas mixture or solution.*
- The evaluation of fugacities of the components in the mixture is considerably simplified when the mixture is modelled as an "ideal solution".
- An ideal solution follows *Lewis-Randall rule* which states that the fugacity of each component in an ideal solution is equal to the product of its mole fraction and the fugacity of the pure component at the same temperature, pressure and state of aggregation (gas, liquid or solid) as the mixture.
- The Lewis-Randall rule requires that fugacity of the mixture component be evaluated in terms of fugacity of same component with consideration of pure substance at same temperature and pressure of the mixture with same state of aggregation.
- Many gaseous mixtures at low to moderate pressure are adequately modelled by *Lewis-Randall rule.*

Ideal solution (Lewis-Randall rule): $\bar{f}_i = y_i f_i$

$\bar{f}_i$: Fugacity of component i in ideal solution

f_i : Fugacity of component i as pure component

y_i : Mole fraction of the component i in the ideal solution

So, the last part of our lecture today is the ideal solutions. So, till this point of time we have talked about the different parameters that are useful or they need to be calculated for evaluation of the thermodynamic parameters of the mixture. But, what we are going to discuss now is an ideal solutions.

The advantage of the ideal solution is that it gives a simplified version. What this ideal solution is that it follows a rule what we call as Lewis-Randall rule. That means, an ideal solution follows a rule what we call as Lewis-Randall rule which says that the fugacity for the component i in an ideal solution $\bar{f_i} = y_i f_i$; that means, fugacity of the component i as a pure component, and it is multiplied by its mole fraction.

So, this particular lesson is applicable for ideal solutions. But, in our previous slide we said that we found the $\bar{V_i} - \bar{v}_i$, that is expressed in terms of fugacity. Now, when you apply this Lewis-Randall rule for that equation, what is going to happen?

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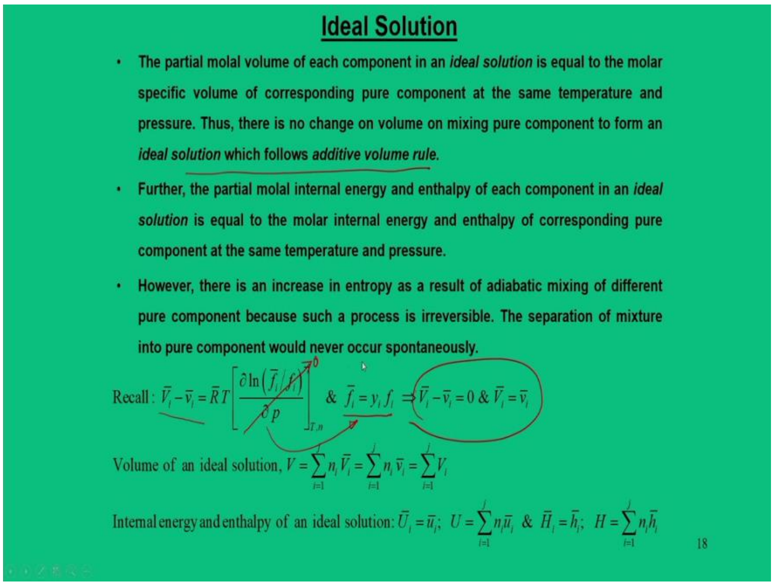

Ideal Solution

- The partial molal volume of each component in an *ideal solution* is equal to the molar specific volume of corresponding pure component at the same temperature and pressure. Thus, there is no change on volume on mixing pure component to form an *ideal solution* which follows *additive volume rule.*
- Further, the partial molal internal energy and enthalpy of each component in an *ideal solution* is equal to the molar internal energy and enthalpy of corresponding pure component at the same temperature and pressure.
- However, there is an increase in entropy as a result of adiabatic mixing of different pure component because such a process is irreversible. The separation of mixture into pure component would never occur spontaneously.

Recall: $\bar{V}_i - \bar{v}_i = \bar{R}T\left[\cancelto{0}{\frac{\partial \ln\left(\bar{f}_i / f_i\right)}{\partial p}}\right]_{T,n}$ & $\bar{f}_i = y_i f_i \Rightarrow \boxed{\bar{V}_i - \bar{v}_i = 0 \;\&\; \bar{V}_i = \bar{v}_i}$

Volume of an ideal solution, $V = \sum_{i=1}^{j} n_i \bar{V}_i = \sum_{i=1}^{j} n_i \bar{v}_i = \sum_{i=1}^{j} V_i$

Internal energy and enthalpy of an ideal solution: $\bar{U}_i = \bar{u}_i;\; U = \sum_{i=1}^{j} n_i \bar{u}_i$ & $\bar{H}_i = \bar{h}_i;\; H = \sum_{i=1}^{j} n_i \bar{h}_i$

So, what is the advantage of assuming mixture to be treated as ideal solution is that when you use this concept of ideal solution or Lewis-Randall rule by taking $\bar{f}_i = y_i f_i$. Then, we recall this particular expressions $\bar{V}_i - \bar{v}_i = \bar{R}T\left[\frac{\partial \ln\left(\frac{\bar{f}_i}{f_i}\right)}{\partial p}\right]_{T,n}$.

So, this particular term vanishes because we have used this Lewis-Randall rule. When you vanishes, it gives a simplest simple type of expressions that is $\bar{V}_i - \bar{v}_i = 0 \& \bar{V}_i = \bar{v}_i$. It assumes that volume of an ideal solution V is nothing, but the summation of the total volume V_i of each component. $V = \sum_{i=1}^{j} n_i \bar{V}_i = \sum_{i=1}^{j} n_i \bar{v}_i = \sum_{i=1}^{j} V_i$

This is nothing but your additive volume rule and similar way; the ideal solution follows this additive volume rule. So, this gives the simplified version of our calculations, while dealing with the fugacity if they are modeled as an ideal solutions. So, of course, through this modeling what we can find out is that partial molar internal energy, enthalpy of each component of an ideal solution can be calculated.

And, it is seen that if you use this concept of ideal solution, the partial molar properties of internal energy, enthalpy of each component of an ideal solution is equal to molal internal energy and enthalpy of the corresponding pure component at the same temperature and pressure.

But, this rule does not apply for entropy because, entropy increase during a mixing. So, basically we can apply this for internal energy and enthalpy, but we cannot apply for entropy because entropy is associated with an irreversible phenomena. And, separation of mixture into pure component would never occur simultaneously.

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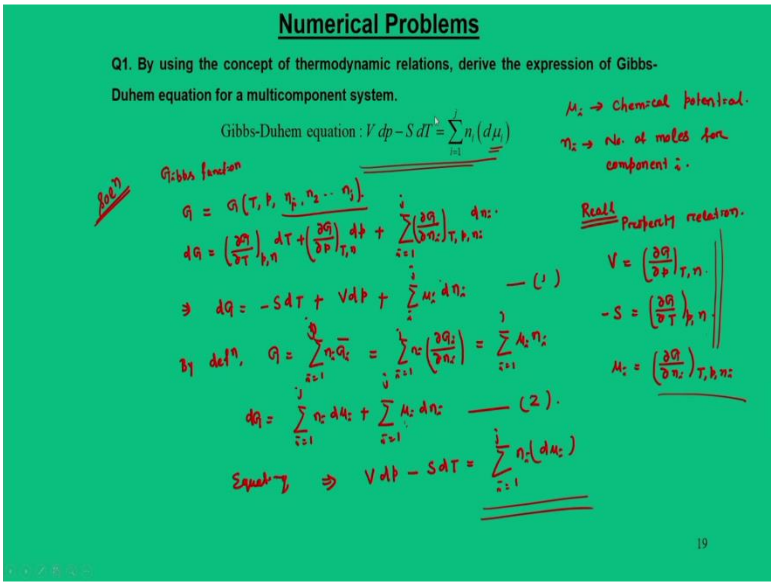

Numerical Problems

Q1. By using the concept of thermodynamic relations, derive the expression of Gibbs-Duhem equation for a multicomponent system.

Gibbs-Duhem equation : $V\,dp - S\,dT = \sum_{i=1}^{j} n_i\left(d\mu_i\right)$

$\mu_i \rightarrow$ Chemical potential.

$n_i \rightarrow$ No. of moles for component i.

Soln

Gibbs function

$$G = G(T, p, n_i, n_2 \cdots n_j)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{j}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i} dn_i$$

$$\Rightarrow dG = -S\,dT + V\,dp + \sum_{i}^{j} \mu_i\,dn_i \quad \text{— (1)}$$

$$\text{By def}^n,\quad G = \sum_{i=1}^{j} n_i \bar{G}_i = \sum_{i=1}^{j} n_i\left(\frac{\partial G_i}{\partial n_i}\right) = \sum_{i=1}^{j} \mu_i n_i$$

$$dG = \sum_{i=1}^{j} n_i\,d\mu_i + \sum_{i=1}^{j} \mu_i\,dn_i \quad \text{— (2).}$$

$$\text{Equating} \Rightarrow V\,dp - S\,dT = \sum_{i=1}^{j} n_i(d\mu_i)$$

Recall Property relation.

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n}.$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,n}$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i}$$

So, this is how we have dealt so far, that ideal solution modeling will help us in simplifying the analysis of gas mixtures. So, now, we will try to solve some simple numerical problems and here there is no numerical problems rather it is a derivation.

So, basically in one of our slides, we introduced Gibbs-Duhem equations which is $Vdp - SdT = \sum_{i=1}^{j} n_i(d\mu_i)$, where μ_i is your chemical potential and n_i stands for number of moles for component i. So, how to solve these equations? To solve this equations or to prove this equations, what do we have to recall? These three important things.

First one is Gibbs functions. $G = G(T, p, n_1, n_2, \ldots\ldots, n_j)$. So, based on this we can find $dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum_{i=1}^{j}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i} dn_i$.

So, we can recall the property relations. Few property relations are like we have $V = \left(\frac{\partial G}{\partial p}\right)_{T,n}$. This we derived in the previous module, $-S = \left(\frac{\partial G}{\partial T}\right)_{p,n}$. And of course, $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i}$. So, these three things when you introduce here; so, this expression takes the form $dG = -SdT + Vdp + \sum_{i=1}^{j} \mu_i \, dn_i$. Then, by definition of Gibbs function, we can write $G = \sum_{i=1}^{j} n_i \bar{G}_i = \sum_{i=1}^{j} n_i \left(\frac{\partial G}{\partial n_i}\right) = \sum_{i=1}^{j} \mu_i \, n_i$. So, we have this equation and we will have another equation by differentiating $dG = \sum_{i=1}^{j} \mu_i \, dn_i + \sum_{i=1}^{j} n_i \, d\mu_i$.

So, we have equation 1 and equation 2. When equating, we can prove that $Vdp - SdT = \sum_{i=1}^{j} n_i (d\mu_i)$because, these two terms will get cancelled. So, this is the derivation that we get Gibbs-Duhem equations based on the concept of thermodynamic property relations.

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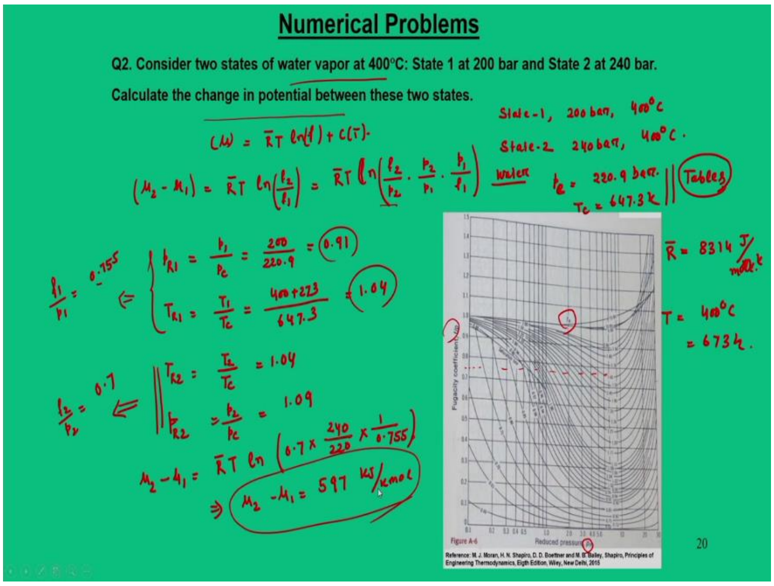

Numerical Problems

Q2. Consider two states of water vapor at 400°C: State 1 at 200 bar and State 2 at 240 bar. Calculate the change in potential between these two states.

State-1, 200 bar, 400°C

State-2 240 bar, 400°C.

$(\mu) = \bar{R}T \ln(f) + C(T)$.

$(\mu_2 - \mu_1) = \bar{R}T \ln\left(\frac{f_2}{f_1}\right) = \bar{R}T \ln\left(\frac{f_2}{p_2} \cdot \frac{p_2}{p_1} \cdot \frac{p_1}{f_1}\right)$

water $p_c = 220.9$ bar. $T_c = 647.3$ K || Tables

$\bar{R} = 8314$ J/mole.K

$T = 400°C = 673$ K.

$\frac{f_1}{p_1} = 0.755 \Leftarrow \begin{cases} p_{R1} = \frac{p_1}{p_c} = \frac{200}{220.9} = 0.91 \\ T_{R1} = \frac{T_1}{T_c} = \frac{400+273}{647.3} = 1.04 \end{cases}$

$\frac{f_2}{p_2} = 0.7 \Leftarrow \left\| \begin{array}{l} T_{R2} = \frac{T_2}{T_c} = 1.04 \\ p_{R2} = \frac{p_2}{p_c} = 1.09 \end{array} \right.$

$\mu_2 - \mu_1 = \bar{R}T \ln\left(0.7 \times \frac{240}{220} \times \frac{1}{0.755}\right)$

$\Rightarrow \boxed{\mu_2 - \mu_1 = 597 \text{ kJ/kmol}}$

Reference: M. J. Moran, H. N. Shapiro, D. D. Boettner and M. B. Bailey, Shapiro, Principles of Engineering Thermodynamics, Eigth Edition, Wiley, New Delhi, 2015

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This next problem we are going to calculate the change in the chemical potential. So, chemical potential we have represented in terms of μ. So, change in the potential means you have you are going to find out change from state 2 minus state 1. We need to calculate what is $\mu_2 - \mu_1$.

So, by definition we write $\mu = \bar{R}T \ln f + C(T)$. So $\mu_2 - \mu_1 = \bar{R}T \ln\frac{f_2}{f_1} = \bar{R}T \ln\left(\frac{f_2}{p_2} . \frac{p_2}{p_1} . \frac{p_1}{f_1}\right)$, 1 and 2 stands for states. So, we have state 1, water at $400°C$, 200 bar, state 2- 240 bar and $400°C$.

And, for water the critical values are p_c, critical pressure is 220.9 bar, critical temperature is 647.3 K. This data you can find out from the tables in any thermodynamics books. But, what we require is reduced parameters and here if you can see that we have the fugacity coefficient f by p is represented in terms of p_R and T_R.

$$p_{R1}=\frac{p_1}{p_c}=\frac{200}{220.9}=0.91;\ T_{R1}=\frac{T_1}{T_c}=\frac{400+273}{647.3}=1.04;\frac{f_1}{p_1}=0.755$$

$$p_{R2}=\frac{p_2}{p_c}=1.09;\ T_{R2}=\frac{T_2}{T_c}=1.04;\frac{f_2}{p_2}=0.7$$

$$\mu_2-\mu_1=\bar{R}T\ln\ln\left(\frac{f_2}{p_2}.\frac{p_2}{p_1}.\frac{p_1}{f_1}\right)$$

$$=8314\times 673\times\ln\left(0.7\times\frac{240}{220}\times\frac{1}{0.755}\right)=596\ kJ/kMol$$

So, chemical potential for potential change between these two states is 597 kilojoule per kilomole. So, with this I conclude this lecture for today.

Thank you for your attention.