Advanced Thermodynamics
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Lecture – 18
Excess Functions and Activity Coefficients

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is excess functions and activity coefficients. Before going into the details of this particular lecture, we will be having a recapitulation of what we have derived in our previous lecture. In the previous lecture, we have a derived relation between excess Gibbs energy and activity coefficient, so that we start with that part and then we go into the more details of obtaining the activity coefficient from this excess Gibbs energy that is what we are going to see.

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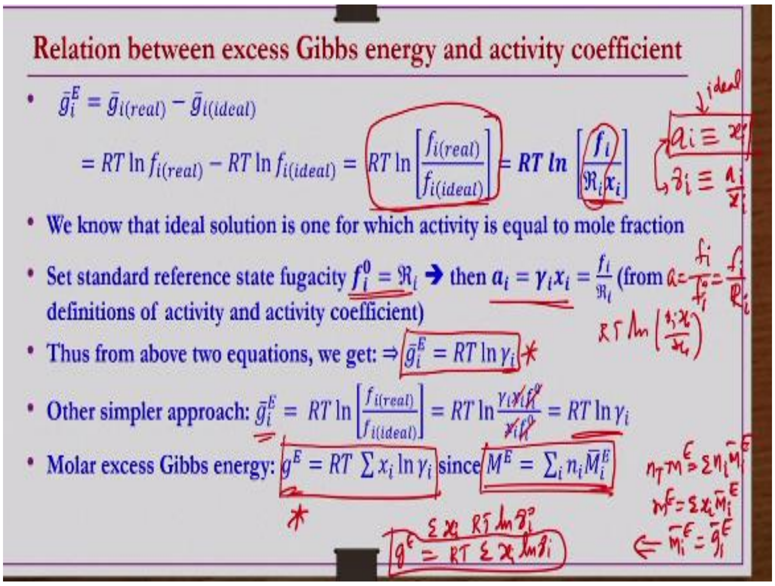

Relation between excess Gibbs energy and activity coefficient

- $\bar{g}_i^E = \bar{g}_{i(real)} - \bar{g}_{i(ideal)}$

  $= RT\ln f_{i(real)} - RT\ln f_{i(ideal)} = RT\ln\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right] = RT\ln\left[\frac{f_i}{\Re_i x_i}\right]$
- We know that ideal solution is one for which activity is equal to mole fraction
- Set standard reference state fugacity $f_i^0 = \Re_i$ → then $a_i = \gamma_i x_i = \frac{f_i}{\Re_i}$ (from definitions of activity and activity coefficient)
- Thus from above two equations, we get: $\Rightarrow \boxed{\bar{g}_i^E = RT\ln\gamma_i}$ *
- Other simpler approach: $\bar{g}_i^E = RT\ln\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right] = RT\ln\frac{\gamma_i \cancel{x_i} \cancel{f_i^0}}{\cancel{x_i} \cancel{f_i^0}} = RT\ln\gamma_i$
- Molar excess Gibbs energy: $\boxed{g^E = RT\sum x_i\ln\gamma_i}$ since $\boxed{M^E = \sum_i n_i\bar{M}_i^E}$

*

ideal

$a_i \equiv x_i$

$\gamma_i \equiv \frac{a_i}{x_i}$

$a_i = \frac{f_i}{f_i^0} = \frac{f_i}{\Re_i}$

$RT\ln\left(\frac{\gamma_i x_i}{x_i}\right)$

$n_T M^E = \sum n_i \bar{M}_i^E$

$M^E = \sum x_i \bar{M}_i^E$

$\Leftarrow \bar{M}_i^E = \bar{g}_i^E$

$\sum x_i RT\ln\gamma_i$

$\boxed{g^E = RT\sum x_i\ln\gamma_i}$

So, we have defined excess thermodynamic property as you know difference between the thermodynamic property under real conditions minus thermodynamic property under ideal conditions or what is the thermodynamic property that is in excess of ideal condition that is what we have defined as excess thermodynamic property and then let us say if you want partial molar Gibbs energy, excess partial molar Gibbs energy then that should be $\bar{g}_i - \bar{g}_{i(ideal)}$ and then we have seen $\bar{g}_{i(real)}$ = RT ln $f_{i(real)}$.

Then $\bar{g}_{i(ideal)}$ = RT ln $f_{i(ideal)}$, so that you substitute here and then simplify, then you have $\bar{g}_i$ = RT ln $\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right]$. So $f_{i(ideal)}$ if you substitute $\Re_i$ x_i, then we get $\bar{g}_i$ = RT ln $\left[\frac{f_i}{\Re_i x_i}\right]$, okay? We know that the ideal solution is one for which activity is equal to the mole fraction, that is this is what we have seen for the case of ideal solutions, okay? For the case of ideal solution, so this is what we have seen and then for the case of non-ideal solution whatever the activity coefficient is there that we have defined it as $\gamma_i = \frac{a_i}{x_i}$.

So, both are interrelated because if you have $\gamma = 1$ that is for the ideal condition, then $a_i = x_i$, okay? Then if you set standard reference state fugacity f_i^0 as $\Re_i$, then what you will be having? You will be having this $\frac{f_i}{f_i^0}$ is nothing but $\frac{f_i}{\Re_i}$ here in this case, okay? And then this, $\frac{f_i}{f_i^0}$ definition is nothing but activity, $\frac{f_i}{f_i^0}$ we have seen as a kind of activity. So, $a_i = \frac{f_i}{f_i^0}$, right? Now, so that we can write f_i^0 if you are writing $\Re_i$, so then $a_i = \frac{f_i}{\Re_i}$ and then $a_i = \gamma_i x_i$ also we have written.

So, what we can write in place for $\frac{f_i}{\Re_i}$ we can write a_i and then a_i in addition it is also equal to $\gamma_i x_i$. So, in this equation in place of $\frac{f_i}{\Re_i}$ if you write $\gamma_i x_i$, then you have RT ln $\frac{\gamma_i x_i}{x_i}$, so then that you have RT ln γ_i. So, that is the relation, this is the derivation that we have derived in the previous lecture and then this relation we are going to use extensively as long as we are discussing non-ideality in the case of liquid solutions. So, now, other simple approach is the $\bar{g}_i$we have seen this RT ln $\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right]$.

So, $f_{i(real)}$ we know that it is nothing but $x_i \gamma_i f_i^0$ and then $f_{i(ideal)}$ is nothing but $x_i f_i^0$ simply So, this x_i, this x_i, f_i^0, f_i^0 you should cancel out, then also you are having $\bar{g}_i$ = RT ln γ_i, right? So, the other way let us say this is if you have this one is as a kind of partial molar excess Gibbs energy, then you can write this g^E, that is excess molar Gibbs energy you can write it as RT $\sum x_i$ln γ_i because we know this for excess functions also this property holds good, right? That is what we have seen in previous lecture.

So, this M^E is nothing but whatever the number of moles n_T m^E, right? $\sum n_i \bar{M}_i^E$. That means, if you write this m^E, then it should be $\sum \frac{n_i}{n_T}$ is x_i $\bar{M}_i^E$, this is what you are going to have and then on this case $\bar{M}_i^E$is nothing but whatever $\bar{g}_i^E$. So, $\bar{g}_i^E$ is nothing but RT ln γ_i. So, that should be $\sum x_i$ RT ln γ_i. So, if you take RT common, you can write RT $\sum x_i$ln γ_i as nothing but

g^E. That means if you have information about g^E, then you can find out the activity coefficient of individual components, you can find out the activity coefficient.

Once you know the activity coefficients of individual components, then you can also know the molar excess Gibbs energy as well. Either way this equation can be used. If left hand side is known, right hand side you can find out. If the right hand side is known, left hand side you can find out without any difficulty. This is what we have seen.

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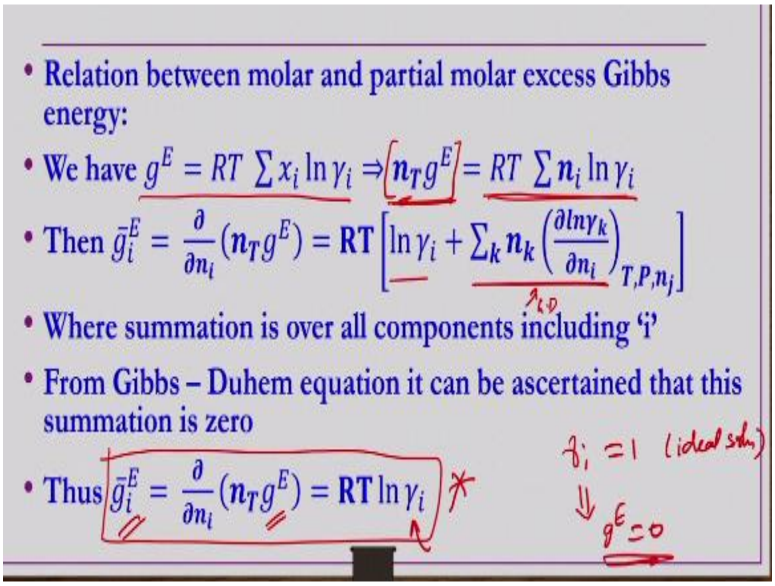

- Relation between molar and partial molar excess Gibbs energy:
- We have $\underline{g^E = RT\sum x_i \ln\gamma_i} \Rightarrow \boxed{n_T g^E} = \underline{RT\sum n_i \ln\gamma_i}$
- Then $\bar{g}_i^E = \frac{\partial}{\partial n_i}(n_T g^E) = \mathrm{RT}\left[\underline{\ln\gamma_i} + \underline{\sum_k n_k\left(\frac{\partial \ln\gamma_k}{\partial n_i}\right)_{T,P,n_j}}\right]$
- Where summation is over all components including 'i'
- From Gibbs – Duhem equation it can be ascertained that this summation is zero
- Thus $\boxed{\bar{g}_i^E = \frac{\partial}{\partial n_i}(n_T g^E) = \mathrm{RT}\ln\gamma_i}$ *

$\gamma_i = 1$ (ideal soln)

$\Downarrow$

$\underline{g^E = 0}$

We have also seen relation between molar and partial molar excess Gibbs energy. So, this g^E = RT $\sum x_i$ ln γ_i we have seen and then as I mentioned this g^E is nothing but molar excess Gibbs energy. If you multiply this one with the n_T, it will give you total excess Gibbs energy and then right hand side whatever the x_i is there that we are writing $\frac{n_i}{n_T}$, so that only if you bring into the left hand side, so then we have n_T g^E = RT $\sum n_i$ln γ_i, this is what we have. Now, if you wanted to know $\bar{g}_i{}^E$what you have to do?

You have to partially differentiate this n_T g^E with respect to x_i, then you will get $\bar{g}_i{}^E$=$\frac{\partial}{\partial n_i}$($n_T$ g^E) and then so this part if you partially differentiate with respect to n_i. So, RT is common and let us say when ln i constant, then $\frac{\partial}{\partial n_i}\sum n_i$ is nothing but 1. So, ln γ_i + here in this case n_i is constant and then do $\frac{\partial \ln\gamma_i}{\partial n_i}$ you are having. So such kind of components you will be having n number of components depending on the number of components.

Let us say if you do summation of all those differential terms, then you have $\sum_k n_k \left(\frac{\partial \ln \gamma_k}{\partial n_i}\right)_{T,P,n_j}$, but this term we know from the Gibbs-Duhem equation, this summation is going to be 0. This summation is going to be 0, then under such condition also, what we have, we can have $\bar{g}_i{}^E$ = RT ln γ_i. So, knowing the importance of how much important is this equation, so we are trying to obtain the different forms of this equation or trying to get the same equation by different approaches.

So, now in this lecture, what we will be using? We will be using some kind of expression for g^E, $\bar{g}^E$ whichever is available and then trying to find out this γ_i and then from there, we try to establish more on this activity coefficients. So, if this γ_i = 1, then we should call it as a kind of ideal solution, right? And then that is possible when this g^E = 0, right? If it is ideal solution then all interactions are uniforms same then obviously there will not be any kind of excess property and then that should be giving that excess property as 0.

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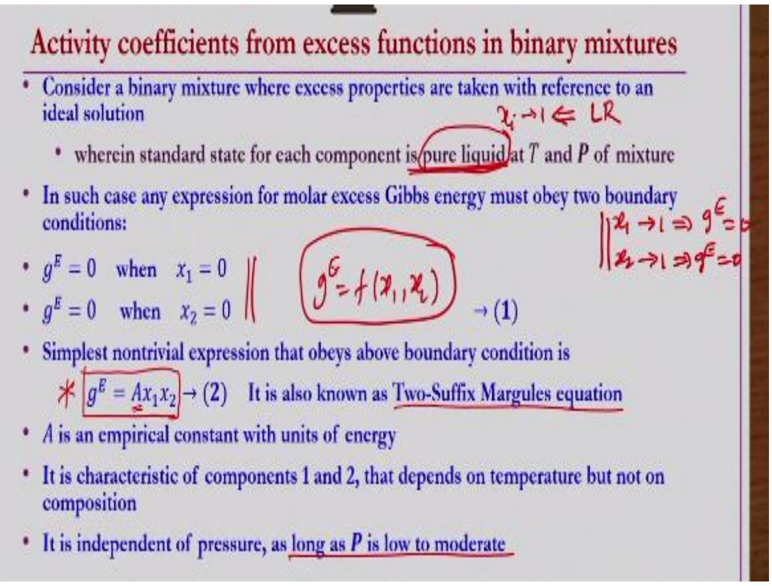

Activity coefficients from excess functions in binary mixtures

- Consider a binary mixture where excess properties are taken with reference to an ideal solution
  - wherein standard state for each component is pure liquid at T and P of mixture

$x_i \to 1 \Leftarrow$ LR

- In such case any expression for molar excess Gibbs energy must obey two boundary conditions:
- $g^E = 0$ when $x_1 = 0$
- $g^E = 0$ when $x_2 = 0$ → (1)

$g^E = f(x_1, x_2)$

$x_1 \to 1 \Rightarrow g^E = 0$

$x_2 \to 1 \Rightarrow g^E = 0$

- Simplest nontrivial expression that obeys above boundary condition is

$*\ \boxed{g^E = Ax_1x_2} \to (2)$ It is also known as Two-Suffix Margules equation

- A is an empirical constant with units of energy
- It is characteristic of components 1 and 2, that depends on temperature but not on composition
- It is independent of pressure, as long as P is low to moderate

So, now we try to obtain activity coefficients from excess functions in binary mixtures. We start with binary mixture for simplicity and then we can extend to the multi-component mixtures. Consider a binary mixture where excess properties are taken with reference to an ideal solution where standard state for each component is pure liquid at constant temperature and pressure of the mixture. So that means, if the reference state is such a way that for each component, the reference state is a pure liquid.

So, that means $x_i \rightarrow 1$ that is the case has been taken as a kind of reference state. So, that means we are doing this calculation with reference to Lewis Randall rule, which says the fugacity and the reference state is nothing but the pure component fugacity. If the component is pure, so then corresponding fugacity is pure component fugacity that should be taken as a kind of fugacity coefficient or fugacity for the reference state. In such case, any expression for molar Gibbs energy must obey 2 boundary conditions.

If this has to be followed, then it must obey 2 boundary conditions. What are the 2 boundary conditions? So that if it is a binary mixture then 2 boundary conditions it should be obeying. So why because in the binary mixture, we have x_1 and then x_2. Let us say $x_1 \rightarrow 1$ then what does it mean by, component 1 is a pure component, is not it? So, that means second component is not there. So that should be giving $g^E = 0$. Other extreme is that $x_2 \rightarrow 1$, that means the mixture is not existing, it is pure second component is existing.

If the component is pure, so then obviously that solution is a kind of ideal solution. So, ideal solution excess properties are 0, so for that condition also g^E should be 0. So, these 2 boundary conditions should be obeyed if you are taking this as a kind of reference state. What is this reference state that you know at the temperature and pressure of the mixture, standard state for each component is pure liquid state, okay? So, that is g^E should be 0 when $x_1 = 0$ and g^E should be 0 when $x_2 = 0$.

These 2 boundary conditions should be satisfied for the case of a binary mixture. So, that means indirectly you should have a kind of g^E as a kind of function of x_1 and x_2 in such a way that this function should obey these 2 boundary conditions, right? So, the simplest one is that this x_1 and x_2 are being multiplied in that function in each term, right? With some powers or something like that. So, then it is possible that these 2 boundary conditions would be satisfied. So but we start with the kind of simplest one.

Simplest one that $g^E = A\, x_1\, x_2$, A is a constant, temperature dependent constant but independent of the composition. So, now if x_1 is 0, then g^E is 0. If x_2 is 0, then also g^E is 0. So, this is the simplest possible expression for g^E, okay? Satisfying these 2 boundary condition and this is for the binary mixture, okay? So, this is also known as the two-suffix Margules equation. So, for this case that is the molar excess Gibbs energy is defined using this equation, so then what are the activity coefficient of those 2 components 1 and 2 in the liquid mixture at the given temperature and pressure as a function of mole fraction.

So, that is what we are going to see now. Now, as I mentioned this is a constant temperature dependent but composition independent constant. Now, this A should have the unit same as g^E, so that the energy unit it must have. It is the characteristics of components 1 and 2 that depends on temperature, but not on the composition. It is independent of pressure as long as the pressure is low to moderate. As long as pressure is low to moderate then also it is independent of the pressure.

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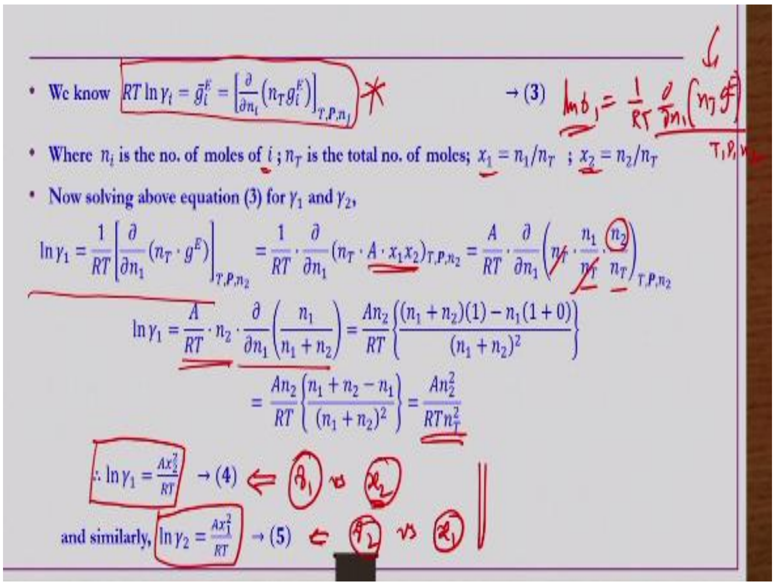

- We know $\boxed{RT\ln\gamma_i = \bar{g}_i^E = \left[\frac{\partial}{\partial n_i}(n_T g_i^E)\right]_{T,P,n_j}}$ ✱ → (3) $\ln\gamma_1 = \frac{1}{RT}\frac{\partial}{\partial n_1}(n_T g^E)_{T,P,n_2}$
- Where n_i is the no. of moles of i ; n_T is the total no. of moles; $x_1 = n_1/n_T$; $x_2 = n_2/n_T$
- Now solving above equation (3) for γ_1 and γ_2,

$$\ln\gamma_1 = \frac{1}{RT}\left[\frac{\partial}{\partial n_1}(n_T\cdot g^E)\right]_{T,P,n_2} = \frac{1}{RT}\cdot\frac{\partial}{\partial n_1}(n_T\cdot A\cdot x_1x_2)_{T,P,n_2} = \frac{A}{RT}\cdot\frac{\partial}{\partial n_1}\left(\cancel{n_T}\cdot\frac{n_1}{\cancel{n_T}}\cdot\frac{n_2}{n_T}\right)_{T,P,n_2}$$

$$\ln\gamma_1 = \frac{A}{RT}\cdot n_2\cdot\frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1+n_2}\right) = \frac{An_2}{RT}\left\{\frac{(n_1+n_2)(1)-n_1(1+0)}{(n_1+n_2)^2}\right\}$$

$$= \frac{An_2}{RT}\left\{\frac{n_1+n_2-n_1}{(n_1+n_2)^2}\right\} = \frac{An_2^2}{RTn_T^2}$$

$$\boxed{\therefore \ln\gamma_1 = \frac{Ax_2^2}{RT}} \rightarrow (4) \Leftarrow \gamma_1 \text{ vs } x_2$$

$$\text{and similarly, } \boxed{\ln\gamma_2 = \frac{Ax_1^2}{RT}} \rightarrow (5) \Leftarrow \gamma_2 \text{ vs } x_1$$

Now, for this case if you wanted to find out γ_1, γ_2, so then $\bar{g}_i^E = RT\ln\gamma_i$, this is what we have already seen, we have derived. So, now that means if you wanted to get $\ln\gamma_1$, you have to do $\ln\gamma_1 = \frac{1}{RT}\left[\frac{\partial}{\partial n_1}(n_T.g^E)\right]_{T,P,n_2}$ you have to do because it is a binary mixture. So, that differentiation you have to do with respect to n_1, whatever the g^E is given that you multiply by n_T and then differentiate with respect to n_1 and then divide by RT.

So, then you will get $\ln\gamma_1$. Here n_i is nothing but the number of moles of component i, n_T is the total number of moles of that particular mixture and then x_1 is nothing but $\frac{n_1}{n_T}$ and x_2 is nothing but $\frac{n_2}{n_T}$. Then now, this equation number 3 we are going to solve for γ_1 and γ_2. So, let us say γ_1 if you do, $\ln\gamma_1 = \frac{1}{RT}\left[\frac{\partial}{\partial n_1}(n_T.g^E)\right]_{T,P,n_2}$. So, now here what we do, g^E is nothing but A x_1 x_2 that is given, for two-suffix Margules equation g^E is A x_1 x_2.

So, A is a constant that you can take out and then $\frac{n_1}{n_T}$ is nothing but x_1, $\frac{n_2}{n_T}$ is nothing but x_2. So, this n_T, n_T is cancelled out and then this n_2 is also independent of n_1. So, that also you can take out as a constant outside of the differentiation, then you have ln $\gamma_1 = \frac{An_2}{RT} \frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1+n_2}\right)$. If you differentiate this one, you will get here now $\frac{n_2}{(n_1+n_2)^2}$ and then n_2 is multiplied here. So, $\frac{n_2^2}{n_T^2}$ is there. So, $\frac{An_2^2}{RTn_T^2}$is there, so that we can write ln $\gamma_1 = \frac{Ax_2^2}{RT}$.

So, now here we can see this γ_1 is written as a function of x_2 not as x_1 why because this γ_1 is there because with this component 1, the component 2 is coming and mixing and then forming some kind of real solution, non-ideality is there because of that second component. So, that is the reason in general this activity coefficients are represented as a kind of other components as function of mole fraction of the other component.

Let us say here for a binary mixture if you are writing on γ_1, it is written as a function of x_2 because γ_1 is there existing because of this second component is coming and joining with the first component, right? So, that is the reason rather the same equation can be written as a kind of A into 1 minus x_1 whole square by RT, but still despite of that one we write this form Ax_2 square divided by RT, right? Same γ_2 also if you do derivation, you will get ln $\gamma_2 = \frac{Ax_1^2}{RT}$.

So, now here γ_2 we are writing as function of x_1 because γ_2 whatever the second component in the second component non-ideality is there because of whatever the first component is coming and then joining with the second component to form the mixture, okay? So, that is the reason γ_2 is written as function of x_1. So, this is the common tradition that may be followed and then you often see such kind of expression rather than γ_2 writing a function of $(1-x_1)^2$ and all those kind of thing, okay?

So, this ln γ_1 and ln γ_2 are for two-suffix Margules equation, okay? So, this is how you can develop the activity coefficient of components that are present in the mixture using the g^E expression, okay? So if that is binary mixture, excess molar Gibbs energy of that mixture is represented by two-suffix Margules equation. Their corresponding non-ideality whatever is there in the solution are represented by γ1, γ2 they have been obtained as a kind of exponential of $\frac{Ax_2^2}{RT}$and exponential of $\frac{Ax_1^2}{RT}$ respectively, right?

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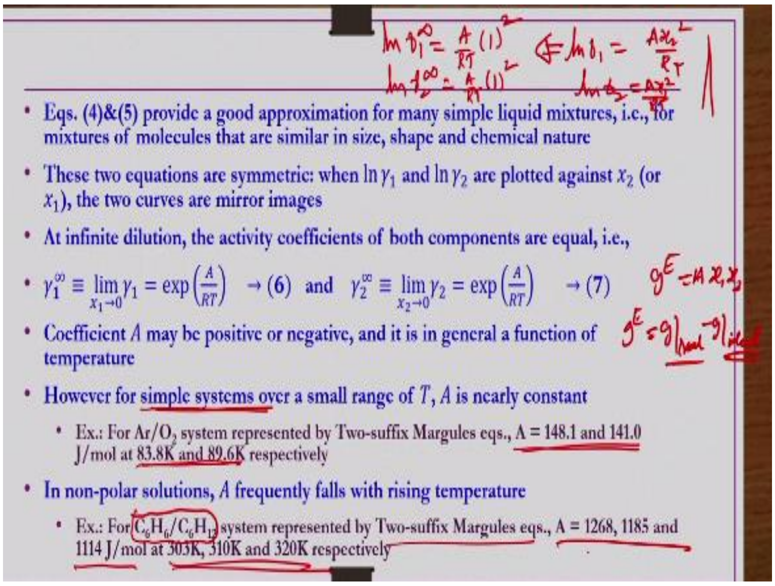

$\ln \gamma_1^\infty = \frac{A}{RT}(1)^2$ ⇐ $\ln \gamma_1 = \frac{Ax_2^2}{RT}$

$\ln \gamma_2^\infty = \frac{A}{RT}(1)^2$ $\ln \gamma_2 = \frac{Ax_1^2}{RT}$

- Eqs. (4)&(5) provide a good approximation for many simple liquid mixtures, i.e., for mixtures of molecules that are similar in size, shape and chemical nature
- These two equations are symmetric: when $\ln \gamma_1$ and $\ln \gamma_2$ are plotted against x_2 (or x_1), the two curves are mirror images
- At infinite dilution, the activity coefficients of both components are equal, i.e.,
- $\gamma_1^\infty \equiv \lim_{x_1 \to 0} \gamma_1 = \exp\left(\frac{A}{RT}\right) \rightarrow (6)$ and $\gamma_2^\infty \equiv \lim_{x_2 \to 0} \gamma_2 = \exp\left(\frac{A}{RT}\right) \rightarrow (7)$
- Coefficient A may be positive or negative, and it is in general a function of temperature
- However for simple systems over a small range of T, A is nearly constant
  - Ex.: For Ar/O_2 system represented by Two-suffix Margules eqs., A = 148.1 and 141.0 J/mol at 83.8K and 89.6K respectively
- In non-polar solutions, A frequently falls with rising temperature
  - Ex.: For C_6H_6/C_6H_{12} system represented by Two-suffix Margules eqs., A = 1268, 1185 and 1114 J/mol at 303K, 310K and 320K respectively

$g^E = A x_1 x_2$

$g^E = g|_{real} - g|_{ideal}$

So, now how much are reliable these equation that also one has to check and in obvious way is to check with the experimental results that are available, okay? It has been found that equations 4 and 5 that is 4 is nothing but ln γ1 = $\frac{Ax_2^2}{RT}$ and then this one is ln γ2 = $\frac{Ax_1^2}{RT}$ is nothing but the equation number 5. These are the equation number 4 and 5. They provide a good approximation for many simple liquid mixtures that is for the mixture of molecules that are similar in size, shape, and chemical nature.

These 2 equations are symmetric, symmetric in this sense when you plot ln γ1 versus x1 and then you also plot ln γ2 versus x2. Then you can see whatever the curve that is being formed they are mirror images of each other. In fact, you can see from these equations also ln γ1 and γ2. So, the x1 is replaced by x2 in the other case, ln γ1 =$\frac{Ax_2^2}{RT}$, so now x2 is replaced by x1 then you get ln γ2.

So, that means they are mirror images of each other and then if you have this ln γ1 versus mole fraction either x1 or x2 mirror images of each other, then we call those activity coefficients are symmetric activity coefficients, we see pictorially also some cases now. So, at infinite dilution, the activity coefficients of both components are equal to, let us say if it is infinite dilution, right? So, that is component γ_1^∞stands for the activity coefficient of the solution where component 1 is present in very small quantity.

Then component 2 is present in large quantity, that component 2 is almost kind of having mole fraction close to 1. So, that means, we can write ln $\gamma_1^\infty = \frac{A}{RT}$ and this is almost close to 1 and then similarly in the second case ln γ_2^∞ because now in the second case, the second component is under the infinite dilution condition that is it is present in very small quantities in the mixture and then component 1 is present in such a large quantity that compared to the component 2, the mole fraction of component 1 is almost close to 1.

So, that is $\frac{Ax_1^2}{RT}$, here in this case x_1 is 1. So, that means, for these two-suffix Margules equations at infinite dilution conditions, the activity coefficients of both components are same that is exponential of $\frac{A}{RT}$. That is γ_1^∞ is exponential of $\frac{A}{RT}$and then γ_2^∞ is exponential of $\frac{A}{RT}$, either way, fine? So, coefficient A may be positive or negative depending on this because g^E we are writing as A x_1 x_2 and then g^E is nothing but g_{real} conditions − g_{ideal} conditions, right?

Depending on the magnitude of g_{real} and g_{ideal}, this g can be positive or negative and accordingly the constant A may be positive or negative and it is general function of temperature obviously. Then however, for simple system over a small range of T, A is nearly constant. For example, if you take Argon Oxygen system, if the temperature range is limited between these mol 83 or 84 to 90 Kelvin roughly then A roughly decreasing from 148 to 141 joule per mole.

So, such small decrease is there for the case of simple system for the case of simple systems like argon and oxygen but if you have some non-polar solutions, under such conditions A frequently falls with increasing temperature. Let us say for example if you take benzene and cyclohexane example, right? So, benzene and cyclohexane again if you represent by two-suffix Margules equation, whatever the excess Gibbs energy the molar excess Gibbs energy of benzene and cyclohexane liquid system.

If you obtain the excess Gibbs energy or molar excess Gibbs energy and then if you mathematically represent it by two-suffix Margules equation having g = A x_1 x_2 form, then that A constant is going to decrease with temperature as the temperature increasing from 303 Kelvin to 320 Kelvin, A is decreasing from 1268 to 1114 joule per mole, right? So, this is how one can make analysis of activity coefficients from g^E information, obtained this activity coefficient from g^E information and then further analysis one can be making further analysis of those components.

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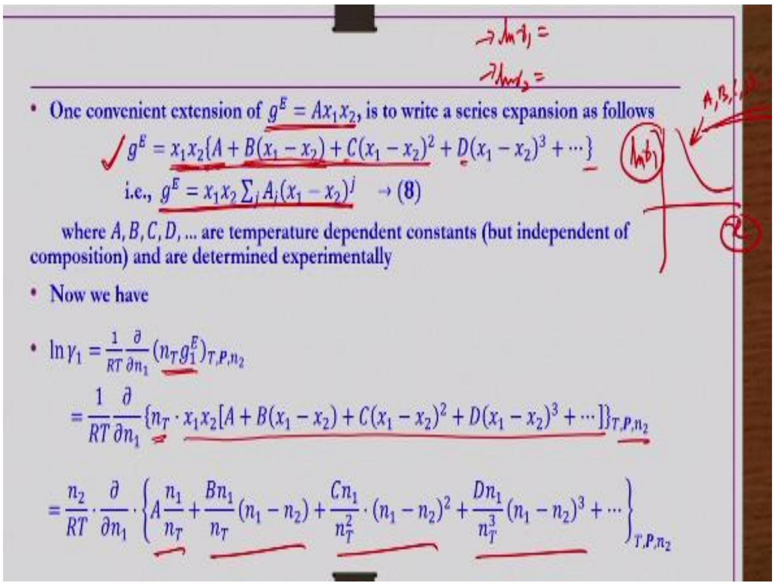

$\rightarrow \ln\gamma_1 =$

$\rightarrow \ln\gamma_2 =$

- One convenient extension of $g^E = Ax_1x_2$, is to write a series expansion as follows

$$g^E = x_1x_2\{A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots\}$$

$$\text{i.e., } g^E = x_1x_2\sum_j A_j(x_1 - x_2)^j \quad \rightarrow (8)$$

where $A, B, C, D, \ldots$ are temperature dependent constants (but independent of composition) and are determined experimentally

- Now we have

- $$\ln\gamma_1 = \frac{1}{RT}\frac{\partial}{\partial n_1}(n_T g_1^E)_{T,P,n_2}$$

$$= \frac{1}{RT}\frac{\partial}{\partial n_1}\{n_T \cdot x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots]\}_{T,P,n_2}$$

$$= \frac{n_2}{RT}\cdot\frac{\partial}{\partial n_1}\cdot\left\{A\frac{n_1}{n_T} + \frac{Bn_1}{n_T}(n_1 - n_2) + \frac{Cn_1}{n_T^2}\cdot(n_1 - n_2)^2 + \frac{Dn_1}{n_T^3}(n_1 - n_2)^3 + \cdots\right\}_{T,P,n_2}$$

So, now, this is the simplest one as we said. So, basically it is not going to be reliable or suitable for all components. So, then we have to make a kind of correction or adding more terms kind of thing and then one of the convenient form is that writing this one in a series expansion form like this. So, that is $g^E = x_1 x_2\{A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots\}$. So, so now here, you can see binary mixture again. So, when $x_1 \rightarrow 1$ that means pure component 1, so x_2 is 0, so then g^E is going to be 0.

When $x_2 = 1$, then x_1 is going to be 0, so then again under such condition also, g^E is going to be 0 irrespective of the values of this A, B, C, D which parameter is constant. So, for this binary mixture this expression as well follows or they obeys both the boundary condition that is when $x_i \rightarrow 1$, g^E is tending to 0, right? And now within these parenthesis whatever there, so if you have only the term A, only first term A, up to that term only if you include, then it is called as it is called as a two-suffix Margules equation, that is simply A x_1 x_2, you are not including additional term.

If you include one more term that is x_1 $x_2\{A + B(x_1 - x_2)\}$up to this one, then the same equation is known as the three-suffix Margules equation. The same equation is known as the three-suffix Margules equation. So, if you add one more term that is $+C(x_1 - x_2)^2$ then this equation is known as the four-suffix Margules equation, right? And then we have seen when it is two-suffix Margules equation, so this ln $\gamma_1 = \frac{Ax_2^2}{RT}$ and then ln $\gamma_2 = \frac{Ax_1^2}{RT}$.

Then mathematically also they are clear and then we can realize this ln γ_1 and ln γ_2 are symmetric coefficients or symmetric activity coefficients, right? But when you added the second term $B(x_1 - x_2)$. Then what happens that the equation becomes three-suffix Margules equation. So this is not going to be valid, they are going to have additional terms or in altogether different functions it may be having, right? So, then because of that one additional term, what happens?

Whatever the activity coefficient that you get for the third and fourth or higher suffix Margules equation, they are not going to be symmetric, okay? So, that we can check anyway, we can crosscheck, we can simplify this equation and then get the γ_1, γ_2 for two-suffix, three-suffix, four-suffix Margules equation and then you can check γ_1, γ_2, by three different forms. So you can get only the two-suffix Margules equation is giving a kind of symmetric activity coefficient but third and fourth Margules equation or four-suffix Margules equation they are not giving a symmetric activity coefficient.

So, if you generalize this one, you can write generalized one like $g^E = x_1 x_2 \sum_j A_j(x_1 - x_2)^j$. So, now what we do? We take this equation and then try to obtain what are the ln γ_1 and then ln γ_2 forms, okay? So, here again A, B, C, D are the temperature dependent constants, but independent of the composition and they have to be determined experimentally obviously. That is let us say A how did you find out that γ_1^∞ is exponential of $\frac{A}{RT}$.

So you can have a kind of solution with the component 1 is in a very small quantity, so that you can say that infinite dilution conditions are there, then you can find out the activity coefficient for that solution experimentally and then curve fit that data using this exploration γ_1^∞ = exponential of $\frac{A}{RT}$and then you can find out what is A for different temperatures, that is simply by curve fitting or let us say under any condition if you plot ln γ_1 versus composition x, so you may be having different curves like this.

So, different curves you can have different temperatures and then you can do the curve fitting and then get those parameters A, B, C, D, etc., through the experimental condition. Now, what we do? We write ln $\gamma_1 = \frac{1}{RT}\left[\frac{\partial}{\partial n_1}(n_T . g_1{}^E)\right]_{T,P,n_2}$ and now here in place of $n_T g$ what we write, this expression we write n_T and g^E is nothing but this expression at constant T, P, n_2. Now here, this x_1, x_2, etc., you replace by $\frac{n_1}{n_T}, \frac{n_2}{n_T}$, etc., and then simplify, then you can have this kind of form.

Now this one, you differentiate all these terms with respect to n_1 and then simplify like in the previous case of two-suffix Margules equation you have done. So, then you get the additional terms here.

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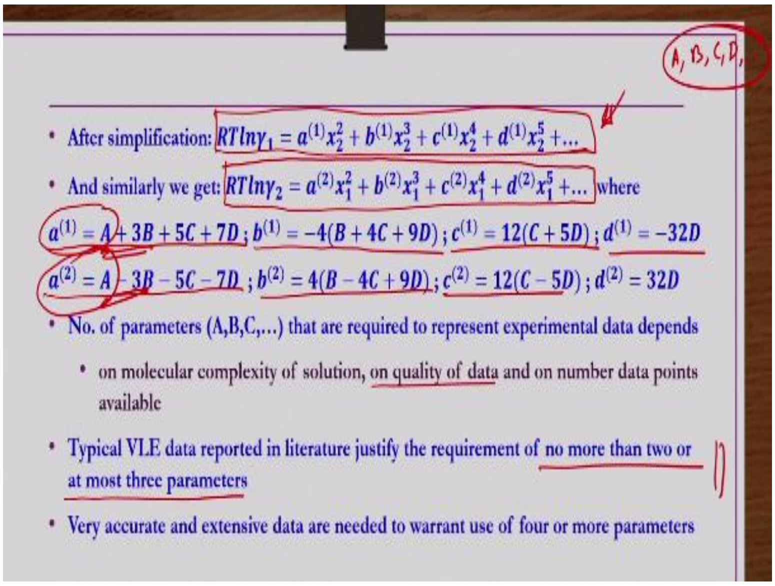

A, B, C, D,

- After simplification: $RT\ln\gamma_1 = a^{(1)}x_2^2 + b^{(1)}x_2^3 + c^{(1)}x_2^4 + d^{(1)}x_2^5 + \ldots$
- And similarly we get: $RT\ln\gamma_2 = a^{(2)}x_1^2 + b^{(2)}x_1^3 + c^{(2)}x_1^4 + d^{(2)}x_1^5 + \ldots$ where

$a^{(1)} = A + 3B + 5C + 7D\,;\ b^{(1)} = -4(B + 4C + 9D)\,;\ c^{(1)} = 12(C + 5D)\,;\ d^{(1)} = -32D$

$a^{(2)} = A - 3B - 5C - 7D\,;\ b^{(2)} = 4(B - 4C + 9D)\,;\ c^{(2)} = 12(C - 5D)\,;\ d^{(2)} = 32D$

- No. of parameters (A,B,C,...) that are required to represent experimental data depends
  - on molecular complexity of solution, on quality of data and on number data points available
- Typical VLE data reported in literature justify the requirement of no more than two or at most three parameters
- Very accurate and extensive data are needed to warrant use of four or more parameters

So, then that if you write RT ln γ_1, you will have some kind of form like this, some constant $a^{(1)}\ x_2^2$ + $b^{(1)}\ x_2^3$ + $c^{(1)}\ x_2^4$ + $d^{(1)}\ x_2^5$ and so on so. Similarly, RT ln γ_2 if you do you have this expression that is RT ln γ_2 = $a^{(2)}\ x_1^2$ + $b^{(2)}\ x_1^3$ + $c^{(2)}\ x_1^4$ + $d^{(2)}\ x_1^5$. So, now here what are these $a^{(1)}$, $b^{(1)}$, $c^{(1)}$, $d^{(1)}$ and $a^{(2)}$, $b^{(2)}$, $c^{(2)}$, $d^{(2)}$. After simplification, you rearrange that expression in this form like that all the terms having x_2 square terms or the factors of all x_2 square terms you group together as $a^{(1)}$.

Similarly factors of x_2 cube terms you group them together as $b^{(1)}$ like that then what are those $a^{(1)}$, $b^{(1)}$; $a^{(1)}$ is nothing but A + 3B + 5C + 7D $c^{(1)}$ and then $b^{(1)}$ = − 4B + 4C + 9D and $c^{(1)}$ = 12 C + 5D, and then $d^{(1)}$ = − 32D, right? Similarly, $a^{(2)}$ also you have these expressions, right?

This is $a^{(2)}$, this is $b^{(2)}$, this is $c^{(2)}$, this is $d^{(2)}$, only that we are writing in this particular form because we know this RT ln γ_i is having some factor like some constant and then x_2^2 let us say.

Because we know this RT ln γ_1 would be having something like some constant x_2^2+ some constant x_2^3 those kind of terms. Those constants are like in terms of this A, B, C, D constants we have obtained like this. So, now if you write only two-suffix Margules equation, that means that B, C, D., etc. are 0, so then only up to this A only there and then you can observe this $b^{(1)}$, $c^{(1)}$, $d^{(1)}$ is not having any A terms. Remember this A, B, C, D, etc., are to be obtained through the experimental data, either from ln γ_1 versus x_2 or either from ln γ_2 versus x_1 data.

That data you plot graphically you plot and then do the curve fitting, then you get this A, B, C, D constants, whereas this $a^{(1)}$, $b^{(1)}$, $c^{(1)}$, $d^{(1)}$, etc., are you know multiplication factors of this x_2 square, x_2^3, x_2^4, x_2^5, etc. So, those multiplication factors are A + 3B + 5C + 7D like that are given here. When you have only up to A term only in the generalized expression of Margules equation, that is two-suffix Margules equation only this part only will be there.

That means, what you get RT ln γ_1 = A $x_2^2$and then RT ln γ_2 = A x_1^2, it is the same as what we have got in the two-suffix Margules equation, previously we have done the simplification. Now, let us say if you include up to the B term, this is two-suffix Margules equation. Now, if you have a three-suffix Margules equation, then that means you are including up to B term. Up to B terms you are including in the generalist the g^E expansion form, whatever the expansion for the g^E that we have written previously, right?

Now, the question is that how many terms should we include in Margules' equation, should we include only A and B or should we include C and D also, up to what terms, what constant, what many number of parameters that you should have in g^E expression, that depends system to system primarily but that again depends on the available experimental literature, it has been found having 2 constants is more than sufficient for the majority of the system, very rarely you need third and fourth parameters in the g^E expression, right, okay?

It is not required, even if you are having then in order to include those third and fourth parameters or constant like in this case C, D, then you need to have a large number of data and then you need to have a very reliable data in order to make a reliable curve fitting for those C and D parameters, okay? So, based on the available experimental literature, any model that you take if you have 2 parameters, 2 constant that is sufficient enough to describe the model or to describe the experimental data with adequate accuracy, right?

So, number of parameters that is A, B, C, D, etc., that are required to represent the experimental data depends on molecular complexity of solution, obviously nature of the solution or the nature of components that are forming the liquid solution and then quality of the data and a number of data points available as well. You need to have sufficiently large number of reliable data points in order to include more number of these parameters or constants A, B, C, D, etc.

But however, typical VLE data reported in literature justify the requirement of no more than 2 or at most 3 parameters, 2 are sufficient enough but at most you can have the 3 parameters that is sufficient to justify the experimental data. This has been found by curve fitting several experimental data using the g^E models were having 2 or 3 parameters. Very accurate and extensive data are needed to warrant use of 4 or more parameters in general, okay?

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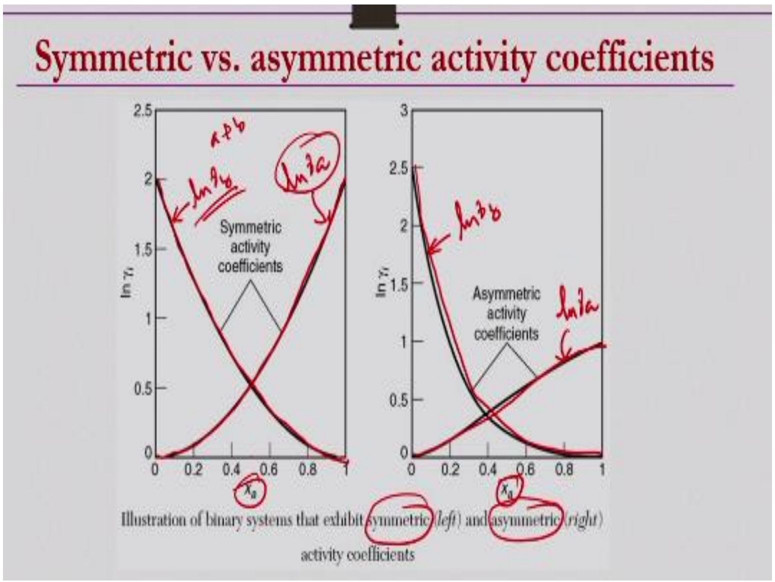

Symmetric vs. asymmetric activity coefficients

Illustration of binary systems that exhibit symmetric (left) and asymmetric (right) activity coefficients

So, as I was mentioning symmetric versus asymmetric activity coefficient, symmetric in the sense ln γ_1 versus x_1 whatever plot is there, so that plot if you compare with ln γ_2 versus x_1 then both of these curves are going to be mirror images and then one example, they may be looking like this one. So, let us say binary mixture of components a and b, this is ln γ_b and then this is ln γ_a for example. So then you can see they are exactly mirror images of each other and then even you can see these points are also matching exactly same for example.

Then you can see this ln γ_b versus x_a curve, whatever this one is there, it is the exactly mirror image of this other curve that is ln γ_a versus x_a curve. So ln γ_b versus x_a curve and then ln γ_a versus again x_a, these curves are mirror images of each other. So, then we can say such kind of activity coefficients are known as the symmetric activity coefficient, but there are kind of situations where this ln γ_b curve and then ln γ_a curve when they are plotted against x_a, then they are entirely different from each other.

They are not mirror images of each other. So, then those activity coefficients are known as the asymmetric activity coefficients. So, for example these plots are shown here, so this ln γ_b you can see here it is very different compared to ln γ_a versus x_a plot. They are not mirror images of each other. So, these things are known as the asymmetric activity coefficients.

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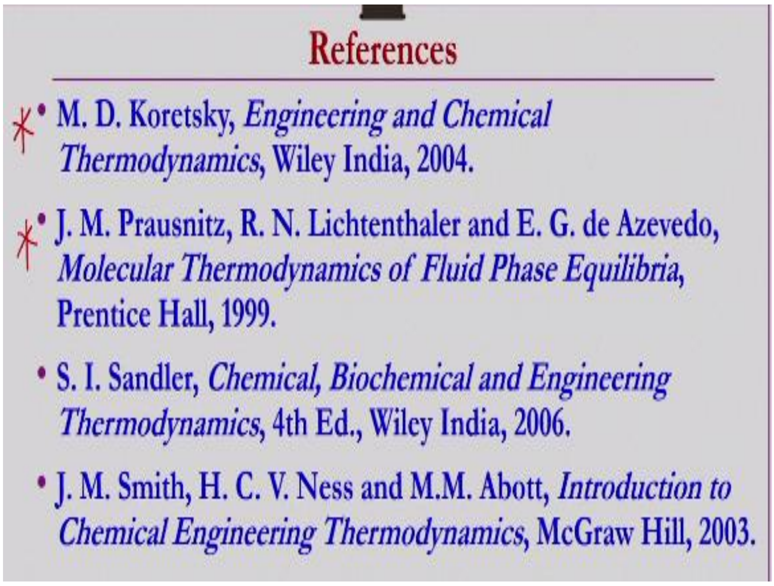

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So, the references for this lecture are given here. Engineering and Chemical Thermodynamics by Koretsky; Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al; and then Chemical Biochemical and Engineering Thermodynamics by Sandler; and Introduction to Chemical Engineering Thermodynamics by Smith et al. Majority of the notes that has been presented in this lecture are taken from this Prausnitz et al and then couple of figures are taken from this reference book Koretsky. Thank you.