Chemical and Biological Thermodynamics: Principles to Applications
Prof. Nand Kishore
Department of Chemistry and Biochemistry
Indian Institute of Technology, Bombay

Lecture - 23
Tutorial on thermodynamics of mixing and deviations from ideality

Today we will discuss some tutorial problems based upon the equations that we developed on thermodynamics of mixing, and we will also further discuss on the deviations from ideality. This we will do in the form of some numerical problems let us take the first question.

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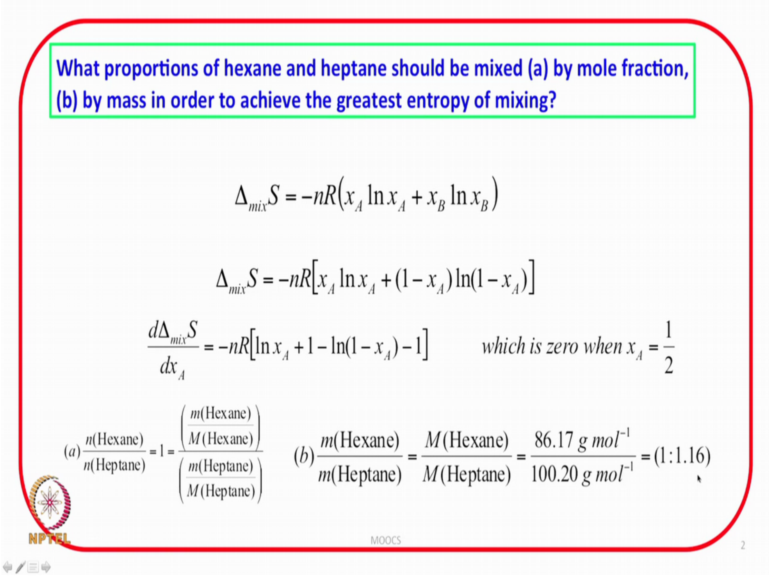

What proportions of hexane and heptane should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

$$\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix}S = -nR[x_A \ln x_A + (1-x_A)\ln(1-x_A)]$$

$$\frac{d\Delta_{mix}S}{dx_A} = -nR[\ln x_A + 1 - \ln(1-x_A) - 1] \qquad \text{which is zero when } x_A = \frac{1}{2}$$

$$(a)\ \frac{n(\text{Hexane})}{n(\text{Heptane})} = 1 = \frac{\left(\frac{m(\text{Hexane})}{M(\text{Hexane})}\right)}{\left(\frac{m(\text{Heptane})}{M(\text{Heptane})}\right)} \qquad (b)\ \frac{m(\text{Hexane})}{m(\text{Heptane})} = \frac{M(\text{Hexane})}{M(\text{Heptane})} = \frac{86.17\ g\ mol^{-1}}{100.20\ g\ mol^{-1}} = (1:1.16)$$

The question is what proportions of hexane and heptane should be mixed by mole fraction or by mass in order to achieve greatest entropy of mixing. Let us realize that when we are talking about ideal mixing the free energy of mixing has to be negative and the enthalpy of mixing is zero, because in gases there is no intermolecular interactions and in liquid the nature of intermolecular interactions in solute solute, solute solvent and solvent solvent are the same. Therefore, the enthalpy of mixing is an expected to be 0. Does the mixing is driven by entropic considerations that is the entropy of mixing is positive.

So, the question is that what proportions of hexane and heptane should be mixed that we achieve greatest entropy of mixing.

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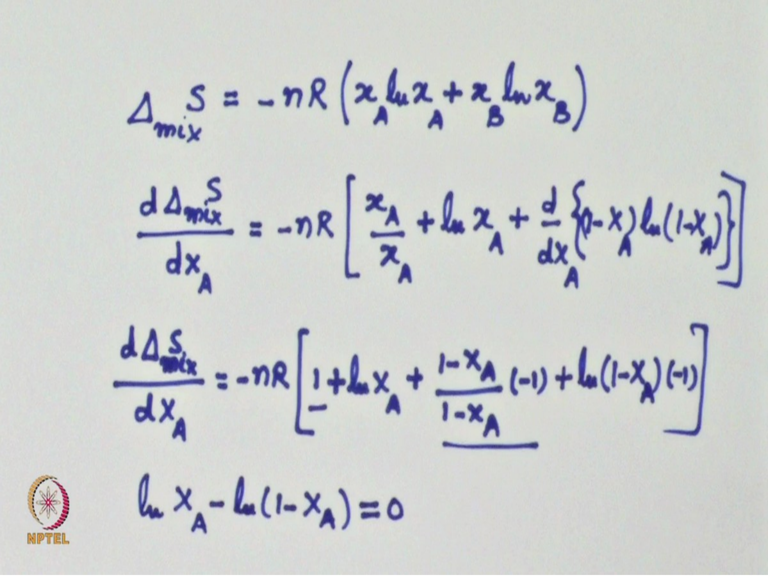

$$\Delta_{mix} S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

$$\frac{d\Delta_{mix} S}{dx_A} = -nR\left[\frac{x_A}{x_A} + \ln x_A + \frac{d}{dx_A}\left\{(1-x_A)\ln(1-x_A)\right\}\right]$$

$$\frac{d\Delta_{mix} S}{dx_A} = -nR\left[\underline{1} + \ln x_A + \underline{\frac{1-x_A}{1-x_A}(-1)} + \ln(1-x_A)(-1)\right]$$

$$\ln x_A - \ln(1-x_A) = 0$$

Let us see how to solve this question. Since we are talking about hexane and heptane let me represent one by a and the other by b; the entropy of mixing entropy is equal to minus n R x A log x A plus x B log x B; where A is for hexane and B is for heptane. What we want to know is that when will we achieve the greatest entropy of mixing that is the maximum entropy of mixing. How do you find a maxima is for any function or any expression, you take the first derivative and set it equal to 0, that is what we will do we will take the first derivative of entropy of mixing let us say we take with respect to x A and we will set it equal to 0; what will be equal to this? Minus n R we take a derivative of this this will be x A by x A plus log x A.

This is differentiation of x A into log x A plus we need to differentiate x B; and x B is equal to 1minus x A. So, what we need to do is d d x A of 1 minus x A into log 1 minus x A let me close this. So, d delta mix s with respect to x A derivative, minus n R what I have is 1 plus log x A and when I take the derivative of this this is plus 1minus x A over 1 minus x A into minus 1 plus log x A in to minus 1this is what I am going to get and in this, this and this will cancel out and what we have is now within this expression log x A minus log into 1.

Minus x A this we set it equal to 0 that is we are setting this derivative equal to 0 n R cannot be 0 therefore, whatever is there within the bracket has to be set equal to 0.

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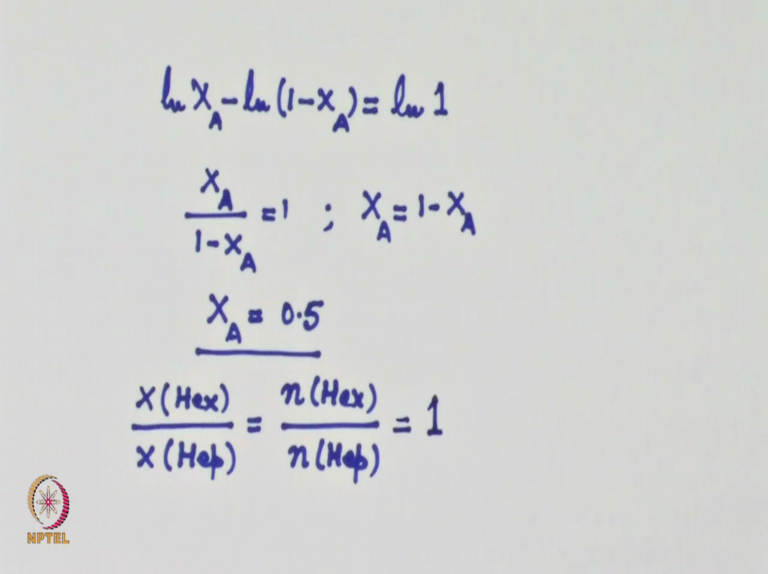

$$\ln x_A - \ln(1-x_A) = \ln 1$$

$$\frac{x_A}{1-x_A} = 1 \quad ; \quad x_A = 1 - x_A$$

$$\underline{x_A = 0.5}$$

$$\frac{x(\text{Hex})}{x(\text{Hep})} = \frac{n(\text{Hex})}{n(\text{Hep})} = 1$$

We have log x A minus log 1 minus x A is equal to 0 which is what we just discussed is log x A minus log 1 minus x A is equal to 0, let me put this equal to log 1, 0 is equal to log 1. Log a minus log b is log a by b; that means, this equation tells me x A over 1 minus x A is equal to 1 which is x a is equal to 1 minus x A or your x A is equal to 0.5.

We have been able to find out the mole fraction of one of the component when the entropy of mixing will be maximum and you see; how did we find the maxima by taking the first derivative and setting it equal to 0. Now let us take a look at the slide the entropy of mixing as I discussed is given by delta s mixing minus n R x A log x A and that is what I did instead of x B I wrote 1 minus x A as I just discussed to take the first derivative, which is equal to 0 when x A is equal to 1 by 2.

And that is what we will do we will substitute x A equal to 1 by 2 into this equation and get an answer. So, what is the answer we can get delta s mixing that will be maximum, but the question is by mole fraction what proportions of x in hexane and heptane should be mixed. So, when we talk about mole fraction; that means, if I write x. So, the question is that what proportion of hexane and heptane should be mixed by mole fraction. So, I want to know the ratio of the mole fractions of hexane and heptane. Mole fraction is number of moles of hexane divided by the total number of moles and for similarly mole fraction of heptane will be equal to number of moles of heptane divided by the total number of moles.

So, total and total I am not writing because these will cancel out therefore, n hexane number of moles of hexane divided by number of mole of heptane since we found out that each mole fraction is equal to 0.5; that means, this is equal to 1. So, the proportion by mole fraction of hexane and heptane will be one is to one to get the highest or the greatest value of entropy of mixing. Now we want to find out in terms of mass: if you look at the slide number of moles is equal to mass divided by molecular weight. So, number of moles of hexane will be equal to mass of hexane divided by molecular weight of hexane, for number of moles of heptane will be mass of heptane divided by number of moles of heptanes.

Now this has to be equal to 1; once you rearrange it then the ratio was mass of hexane to heptane can be calculated from the ratio of molecular weights of hexane and heptanes, after substitution of the values of molecular weight we find out that by mass the proportion should be one is to 1.16. So, to solve this kind of question what we need to know is first the expression for the entropy of mixing, and then we need to know what should be the value of mole fraction under the given conditions.

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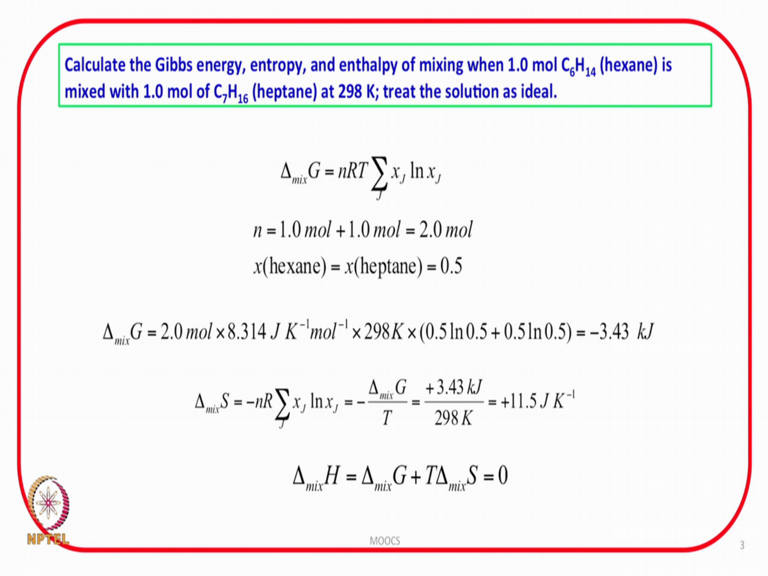

Calculate the Gibbs energy, entropy, and enthalpy of mixing when 1.0 mol C_6H_{14} (hexane) is mixed with 1.0 mol of C_7H_{16} (heptane) at 298 K; treat the solution as ideal.

$$\Delta_{mix}G = nRT\sum_J x_J \ln x_J$$

$$n = 1.0\,mol + 1.0\,mol = 2.0\,mol$$

$$x(\text{hexane}) = x(\text{heptane}) = 0.5$$

$$\Delta_{mix}G = 2.0\,mol \times 8.314\,J\,K^{-1}mol^{-1} \times 298K \times (0.5\ln 0.5 + 0.5\ln 0.5) = -3.43\ kJ$$

$$\Delta_{mix}S = -nR\sum_J x_J \ln x_J = -\frac{\Delta_{mix}G}{T} = \frac{+3.43\,kJ}{298\,K} = +11.5\,J\,K^{-1}$$

$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = 0$$

MOOCS

Let us take up another question a similar question.

The question is; calculate the Gibbs energy entropy and enthalpy of mixing when one mole of hexane is mixed with one mole of heptane at 298 Kelvin: treat the solution as ideal.

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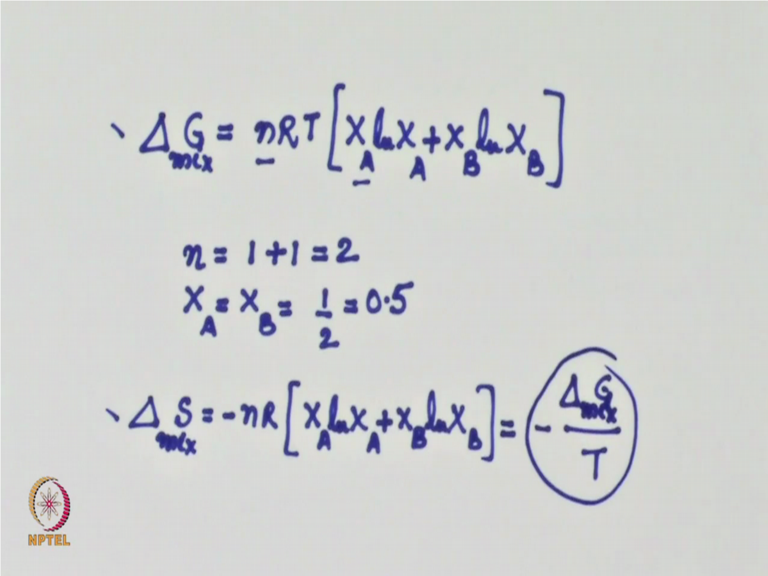

$$\Delta G_{mix} = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$$

$$n = 1 + 1 = 2$$

$$x_A = x_B = \frac{1}{2} = 0.5$$

$$\Delta S_{mix} = -nR\left[x_A \ln x_A + x_B \ln x_B\right] = \boxed{-\frac{\Delta G_{mix}}{T}}$$

This is a very easy question we need to calculate free energy of mixing which will be equal to n R T, you have x A log x A plus x B log x B. What we need is the value of n we need the value of x A n in this case is going to be equal to 2 because there is one mole of hexane plus one mole of heptane the value is two therefore, x A and x B are going to be equal because number of mole is equal is 1 by 2; mole fraction is number of moles of each divided by the total number of moles this is equal to 0.5, and once we substitute this values equal to 0.5 we can get delta G mixing.

Let us take a look at the slide when you substitute n R T n is 2 r is 8.314 joule per Kelvin per mole T is 298 Kelvin and x as we just discussed is 0.5 in each case. So, after substitution we get a value of minus 3.43 kilo joule. Entropy of mixing is easy we have just discussed in the previous example entropy of mixing is minus n R x A log x A plus x B log x B; and if you compare this and this then simply I can write this as minus delta G mixing divided by t.

If you compare this two equations this is simply you divide this expression by T with a negative sign; and since we have already calculated delta G mixing we need we know T we can easily calculate delta s mixing as you can see in the slide the delta s mixing is minus delta G mixing by T and this value is 3.43 divided by T is equal to 11.5 joules per Kelvin. The next question was enthalpy of mixing and since we have been given these conditions that treat the solution as ideal.

Ideal solution means the enthalpy of mixing has to be 0 and you can actually show it by substituting the values for delta G mixing that we calculated as minus 3.43 kilo joule and delta S mixing as 11.5 joules per Kelvin, once you substitute this values you will find out that this turn out to be equal to 0. And let us analyze the results a little more carefully, the free energy of mixing is coming out to be negative that is what is expected the enthalpy of mixing is 0 and entropy of mixing is 11.5 joules per Kelvin this is plus. So, this numerical problem also demonstrates that the spontaneous mixing is driven by the entropic consideration entropic factors it is the entropy of mixing which drives this reaction or which drive this process of mixing.

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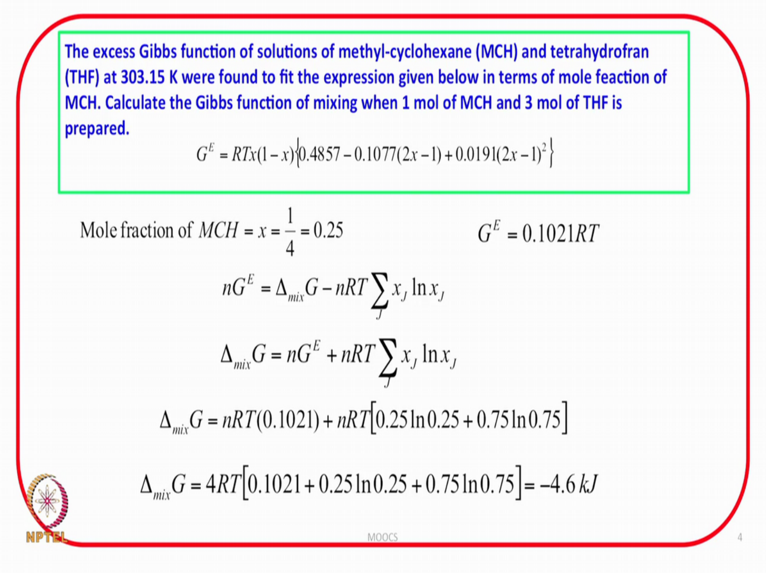

The excess Gibbs function of solutions of methyl-cyclohexane (MCH) and tetrahydrofran (THF) at 303.15 K were found to fit the expression given below in terms of mole feaction of MCH. Calculate the Gibbs function of mixing when 1 mol of MCH and 3 mol of THF is prepared.

$$G^E = RTx(1-x)\{0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2\}$$

$$\text{Mole fraction of } MCH = x = \frac{1}{4} = 0.25 \qquad G^E = 0.1021RT$$

$$nG^E = \Delta_{mix}G - nRT\sum_J x_J \ln x_J$$

$$\Delta_{mix}G = nG^E + nRT\sum_J x_J \ln x_J$$

$$\Delta_{mix}G = nRT(0.1021) + nRT[0.25\ln 0.25 + 0.75\ln 0.75]$$

$$\Delta_{mix}G = 4RT[0.1021 + 0.25\ln 0.25 + 0.75\ln 0.75] = -4.6\,kJ$$

Now let us take another example which allows deviations from ideality, so far what we have discussed is mixing in the case of ideal solution. Now we will talk about deviations from ideality the real solution, if you recall in the previous lecture we have introduced excess function. Excess function depends upon how much the solution deviates from ideal behavior. And let us take a look at this question, according to this question the excess Gibbs function of solutions of methyl cyclohexane represented as MCH, and tetrahydrofuran at 303.15 Kelvin were found to fit the expression given below in terms of mole fraction of MCH.

Calculate the Gibbs function of mixing when one mole of MCH and three mole of THF is prepared. The expression is given here in terms of mole fraction of MCH, this is how the excess Gibbs function depends upon the mole fraction of MCH this is an experimental observation. So, how to solve this question if we look at the expression? The first thing that we need to know is the value of mole fraction of MCH, what we have number of moles of MCH is equal to 1 and number of moles of THF is equal to 3.

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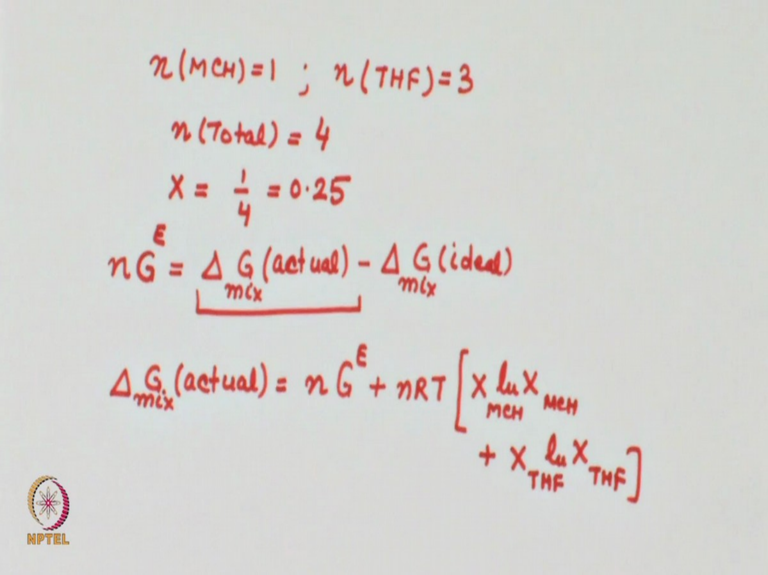

$n(MCH) = 1 \; ; \; n(THF) = 3$

$n(Total) = 4$

$X = \frac{1}{4} = 0.25$

$$nG^E = \underbrace{\Delta_{mix} G(actual)} - \Delta_{mix} G(ideal)$$

$$\Delta_{mix} G(actual) = nG^E + nRT\left[X_{MCH} \ln X_{MCH} + X_{THF} \ln X_{THF}\right]$$

So, total number of moles is equal to 4 therefore, x in this expression is going to be 1 by 4 because x is in the expression the mole fraction of MCH this is equal to 0.25.

So, we have obtained this x equal to 0.25 and now you substitute x into this expression the resulting expression will condense to G E is equal to 0.1021 R T, let us written r T for the time. So, at a given mole fraction this expression takes up this form; we have been asked to calculate Gibbs function of mixing Gibbs function of mixing that is the experimental value. How do we get from? We get it from the definition of excess Gibbs function usually this is given per mole if it is a molar quantity I will multiply by n to get the actual value of the excess Gibbs function, this will be equal to delta G mixing this is actual; actual means which we obtain experimentally minus delta G mixing ideal; we have been asked to calculate this.

So, what I have delta G mixing actual is equal to n times excess Gibbs function plus n R T inside I have X MCH log X MCH plus X THF log X THF. Let us go to slide now this is what I was discussing that we can use this general equation for excess function and needs to be introduced to account for the total number of moles is equal to the actual experimentally determined delta G mixing minus that for the ideal one and after substitution we have arrived at this equation and we know that G E is equal to 0.1021 R T we have to as I said put n because r is joules per Kelvin per mole.

Therefore, we put 4 n, n is equal to 1 plus 3 as we just discussed n is equal to 4; and then mole fraction of MCH is 0.25 is obviously, mole fraction of THF is 0.75. So, once you solve this you get the value equal to minus 4.6 kilojoules this is the experimentally observed free energy of mixing Gibbs and as Gibbs free energy of mixing and obviously, this value will be different is different than the one which is predicted by ideal solution. And as I earlier discuss the excess functions are very important because excess functions indicate the extent of deviation from ideality. Now let us discuss more about allowances for deviations from ideality from the usually derived equations.

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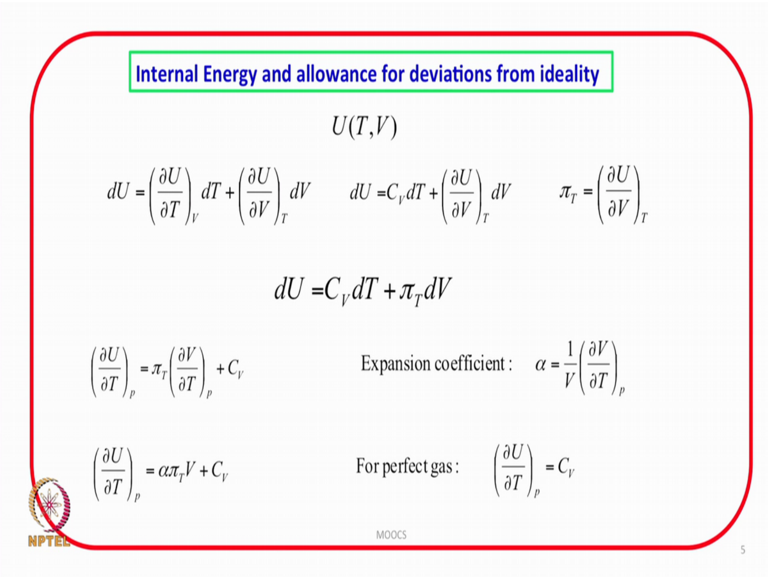

Internal Energy and allowance for deviations from ideality

$$U(T,V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$dU = C_V dT + \pi_T dV$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

Expansion coefficient : $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$$

For perfect gas : $\left(\frac{\partial U}{\partial T}\right)_p = C_V$

First let us take internal energy: internal energy can be a function of temperature, it can be a function of volume, it can be a function of pressure I can express internal energy.

As a function of any two variables to begin with or I can take all the three variables, but here if you look at the slide I am beginning with internal energy depending upon T and V function of T and V. I do not need to express all the 3 p V and T because p v and T are interrelated to each other. So, if I write p T v automatically can be calculated. So, I will begin by taking internal energy as a function of temperature and volume.

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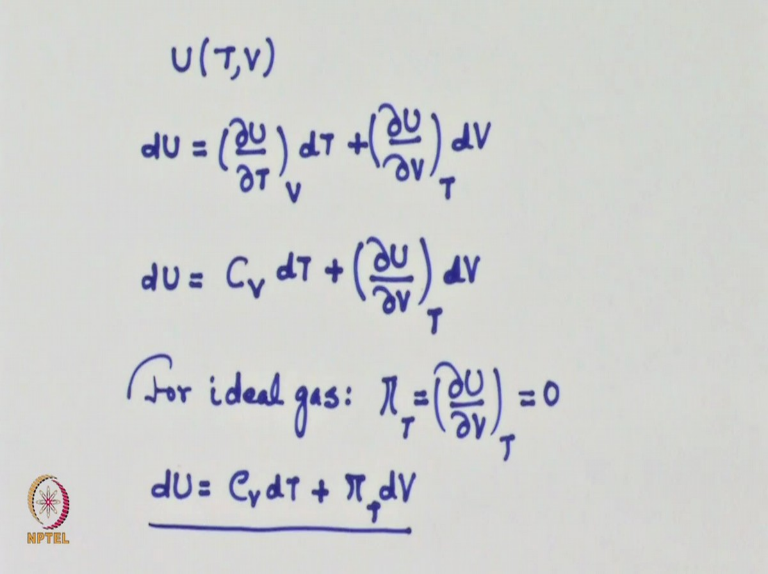

$U(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

For ideal gas: $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\underline{dU = C_V\, dT + \pi_T\, dV}$$

So, if I start with internal energy as a function of temperature and volume you will see that I will end up with some very useful relation. Let there be some change so, d u will be equal to partial derivative of u with respect to t at constant volume d T plus partial derivative of u with respect to v at constant temperature d V right. Now let us start recognizing the different parameters d u is equal to d u or dou u or dou T of constant volume is C v we have discussed many times d T plus variation ask internal energy with volume at constant temperature d V this equation is very important please note here if the volume is constant.

Then d u is equal to C v d T; you remember earlier I have been saying that d u is equal to c v d T you can use only if volume is constant and that is proved by this equation the d u is equal to C v d T only if volume is held constant otherwise we have to account for this variation of internal energy with volume and you know that for ideal gas or perfect gas I will introduce this definition pi T which is equal to variation of internal energy with volume at constant temperature. You know that if the temperature is held constant the internal energy of a perfect gas does not change because there are no intermolecular interactions. So, for perfect gas this is equal to 0.

Now I will rearrange this or I will substitute for this here pi T. So, d u is equal to C v d T plus pi T d V, and if there are deviations from my reality then this derivative will not be equal to 0. So, deviations from ideality will be captured into this and d u will be automatically adjusted here. So, according to this equation d u is equal to C v d T when volume is held constant and d u is equal to C v d T can always be used when pi T is equal to 0 that means, when perfect for a perfect gas we can always use d u is equal to C v d T. And that is what is shown on this slide that d u is equal to C v d T plus dou u dou v at constant T into d v and if you identify this as pi T this is the equation that we just derived. If I divide both the left hand side and right hand side by d T at constant pressure, I divide both the sides by d T at constant pressure what do I get? I get dou u dou T at constant pressure is equal to pi T into dou v dou T at constant pressure plus C v. I am just dividing this throughout by d T at constant pressure.

Please note here that, this expression gives the variation of internal energy with temperature at constant pressure, variation of internal energy with temperature at constant pressure C v is variation of internal energy at constant volume and here we have an expression for variation of internal energy with temperature at constant pressure; and for an ideal gas we will put pi T equal to 0 because we just discussed pi T is equal to 0 for ideal gas, if you substitute pi T equal to 0 then what we get is the following expression when you substrate pi T is equal to 0 then C v is equal to dou u by dou T at constant pressure.

Whether you use this equation or this equation when pi T is equal to 0 c v is equal to dou u dou T at constant pressure. And here I am introducing the definition of expansion coefficient alpha, which is 1 by V d V d T at constant pressure that is how much the volume changes when at constant pressure the substance is heated per unit volume, and when you substitute for dou v dou T at constant pressure into this expression you will get this expression; because dou v dou T at constant pressure is alpha times v when you substitute over here you get this expression.

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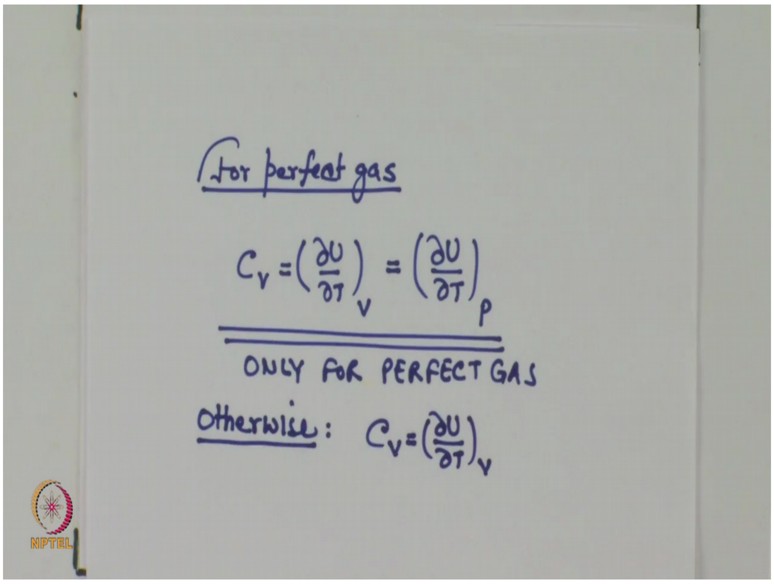

For perfect gas

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P$$

ONLY FOR PERFECT GAS

Otherwise: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

So, what we have come up with that for an ideal gas; C v is equal to variation of internal energy with temperature at constant volume, and this is also equal to variation of internal energy with temperature at constant pressure. Please remember, this is only only for perfect gas only for perfect gas, otherwise we will use the definition of C v is equal to dou u by dou T at constant volume.

So, what we have discussed in this lecture is that the equations that we have developed for the ideal gas or ideal cases ideal solutions whatever system we choose, the similar form of the equations can be retained, but some other factors can be introduced which allow deviations from ideality. We also showed in today's lecture that for an ideal gas c v is equal to dou u by dou T at constant volume and we can also use dou u by dou T at constant pressure.

These partial derivatives can further be manipulated to get many more thermodynamic relations, which will demonstrate that how we can connect one property with another. And that we will discuss further in our next lecture.

Thank you very much.