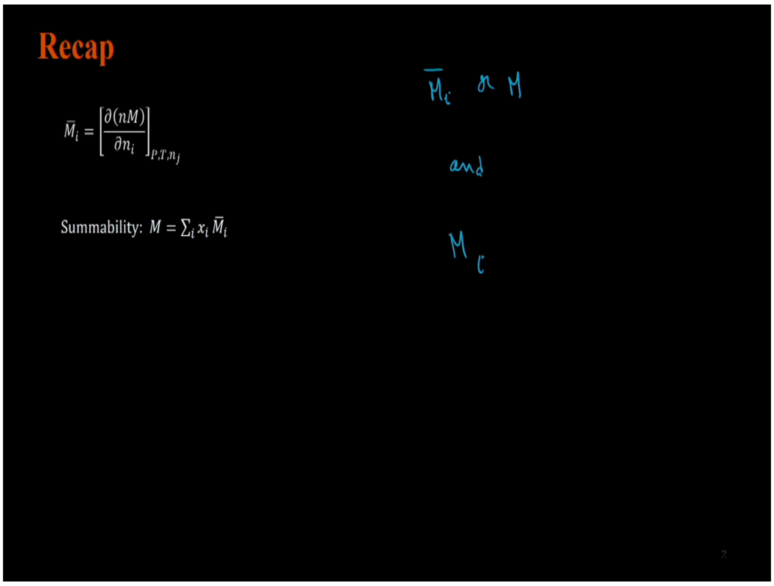
Chemical Engineering Thermodynamics
Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 23
Ideal Gas Mixtures

Hello and welcome back in the previous lectures, we were talking about solution thermodynamics and what we looked at so far, is trying to define a property known as partial molar property for a mixture.

(Refer Slide Time: 00:49)



Recap

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

Summability: $M = \sum_i x_i \bar{M}_i$

$\bar{M}_i$ or M

and

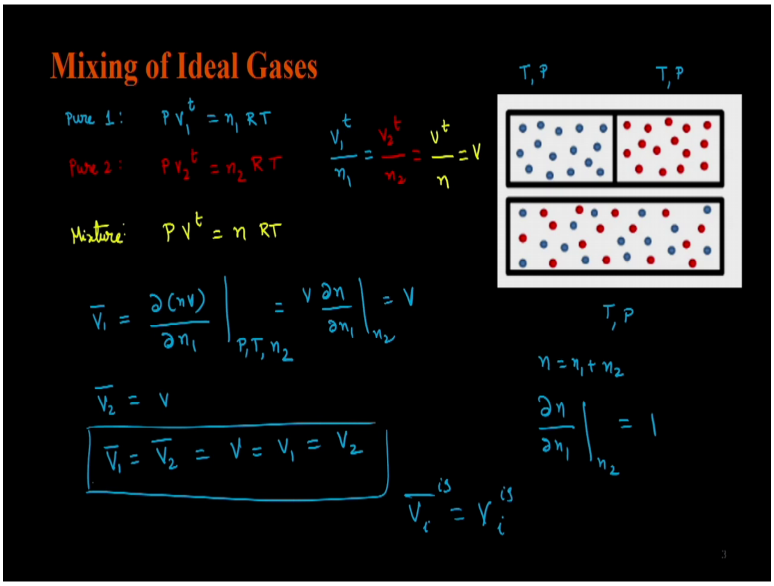
M_i

And then relate it to the total property of the mixture M, we are the summability relation and then some of the relationships amongst the partial molar properties themselves. Now while these are certainly helpful, they still do not give the complete picture of how a mixture behaves like we said earlier there are more than 22 million compounds in known in the process industry. And they form a large number of mixtures and it is very difficult to characterize each and every mixture.

So, what we like to rather do is try to somehow relate the property of a mixture to its pure component counterparts or if I can obtain a relationship or predict the relationship between either M or M i bar to M i, what I am looking for then is a relation between M i bar or M and the pure component counterparts M i. If I can somehow relate these quantities then I can at least predict how the mixture is going to likely behave. To be able to do that we start off with the easiest type of mixtures. We can predict recall how we have dealt with P V t relationships, we introduce the ideal gases first where the P V t relationships are fairly linear and then we extended it to real gases.

So, we will do a similar exercise here. When we talk about mixtures the first thing we will try to analyze is how the pure component M i is related to the partial molar property M i bar in case of ideal gas mixtures.

(Refer Slide Time: 02:49)



Mixing of Ideal Gases

Pure 1: $PV_1^t = n_1RT$

Pure 2: $PV_2^t = n_2RT$

$$\frac{V_1^t}{n_1} = \frac{V_2^t}{n_2} = \frac{V^t}{n} = V$$

Mixture: $PV^t = nRT$

$$\bar{V}_1 = \left.\frac{\partial(nV)}{\partial n_1}\right|_{P,T,n_2} = V\left.\frac{\partial n}{\partial n_1}\right|_{n_2} = V$$

$$n = n_1 + n_2$$

$$\left.\frac{\partial n}{\partial n_1}\right|_{n_2} = 1$$

$$\bar{V}_2 = V$$

$$\boxed{\bar{V}_1 = \bar{V}_2 = V = V_1 = V_2}$$

$$\bar{V}_i^{is} = V_i^{is}$$

So, let us look at a example what exactly we mean by an ideal gas mixture over here, we have two gases which are separated by a wall in between. And at some time T equal to 0, we decide to remove this wall and then the gases are going to mix freely. Before mixing, we have pure species 1 and the P V t relationship for this pure species 1 is P 1 sorry, P V 1 t is n 1 R T.

So, both these gases are at the same temperature and pressure even before mixing and they are at the same temperature and pressure after mixing. Let us say these are ideal gases. Then for pure 1, P V 1 t will be n 1 R P V 1 t being the total volume for gas 1. And for pure species 2, P V 2 t will be equal to the number of moles for 2 n 2 R T. T and P are same. So, now after I mix all I have is a mixture, right.

And for the mixture P V t is n times R T, because the temperature and pressure are same and both gases are ideal. Note that V 1 t over n 1 is the molar volume for gas 1 should be equal to the molar volume of gas 2, because temperature and pressure are same and both gases are ideal. And that should also equal V t over n and let us call this as the molar volume V. All the three molar volumes for the pure individual pure species as well as for the final mixture is same let us call it as V, right.

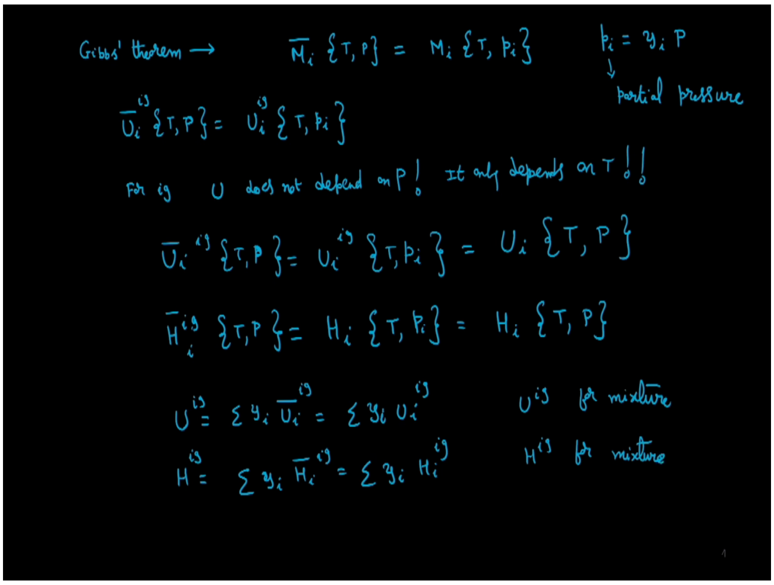
Now, if this is a mixture and I want to calculate the partial molar volume for this mixture, how do I get that? For the mixture, the partial molar volume V 1 bar is the derivative of the total volume n times V over n 1, I have only two components. So, it is at constant temperature pressure and n 2 is held constant, right and recall that n is n 1 plus n 2.

So, derivative of n with respect to n 1 at constant n 2 is 1. So, if I take this the molar volume V is constant anyway it comes out. Once, the temperature and pressure constant molar volume V is constant, it comes out. And then I have derivative of n with respect to n 1 at constant n 2 which will be V, right.

And similarly V 2 bar will also be equal to V and notice that then for this ideal gas mixture V 1 bar will be equal to V 2 bar will be equal to V which is also same as the individual molar volumes for 1 n to V 1 and V 2. So, this is an example for a binary gas mixture, we can extend it in general V i bar will simply be equal to V i for an ideal gas mixture.

Now, we have demonstrated that the partial molar volume of an ideal gas may of component i in an ideal gas mixture is same as the pure component molar volume. It does not depend whether there is other gas or not. Intuitively, it makes sense, because ideal gas by definition has no size the molecules of an ideal gas have zero, occupy zero volume and they do not interact with one another. So, the molar volume will not change as long as the temperature and pressure are same. Now, what happens to something like internal energy, enthalpy or entropy, etcetera?

(Refer Slide Time: 07:17)



Gibbs' theorem $\longrightarrow$ $\bar{M}_i\{T,P\} = M_i\{T,p_i\}$

$p_i = y_i P$ $\downarrow$ partial pressure

$\bar{U}_i^{ig}\{T,P\} = U_i^{ig}\{T,p_i\}$

For ig U does not depend on P! It only depends on T!!

$\bar{U}_i^{ig}\{T,P\} = U_i^{ig}\{T,p_i\} = U_i\{T,P\}$

$\bar{H}_i^{ig}\{T,P\} = H_i\{T,p_i\} = H_i\{T,P\}$

$U^{ig} = \sum y_i \bar{U}_i^{ig} = \sum y_i U_i^{ig}$ U^{ig} for mixture

$H^{ig} = \sum y_i \bar{H}_i^{ig} = \sum y_i H_i^{ig}$ H^{ig} for mixture

To answer this question, we resort to what is known as the Gibb's Theorem. And according to the Gibb's theorem the partial molar property M i bar in a mixture at T and P is given by the pure component property at the same temperature, but at its partial pressure p i. So, this partial pressure p i is essentially the mole fraction times the total pressure, right .We call this as the Gibb's theorem essential idea behind this theorem is that one's an ideal gas is in a mixture and because of the properties of an ideal gas having zero volume and no interactions with one another.

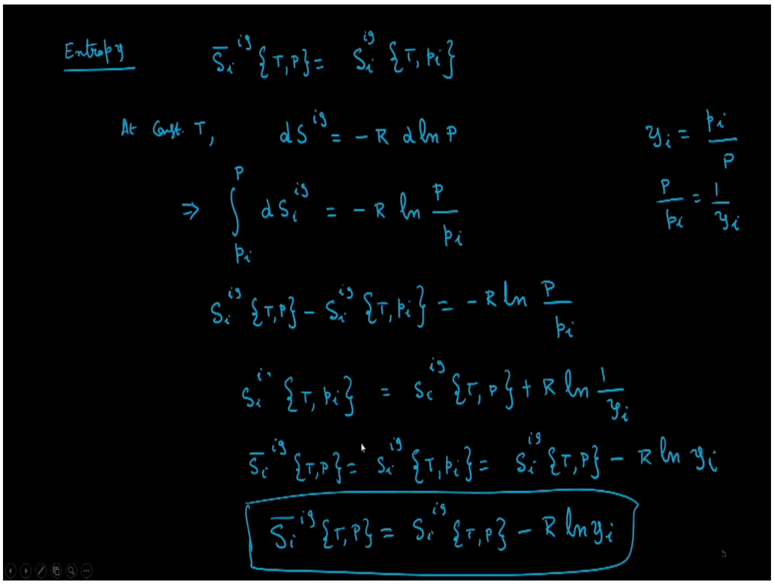
Although the ideal gas is in a mixture, it behaves as if, it is an individual component with its own partial pressure, it is not going to interact with the other species that is present in there. That is the idea behind the Gibb's theorem and then the partial molar property is given by the pure component property, but at it is partial pressure.

Now, we will take this idea to estimate the other partial molar properties or thermodynamic quantities. The first one of interest is U i bar at a given temperature and pressure. This will be U i at it is partial pressure p i, right. The temperature is same, but this time in the pressure has changed to the partial pressure, but for an ideal gas, this is an ideal gas. For ideal gas U does not depend on pressure, it only depends on temperature, if you recall.

So, U i bar i g than at T and P is U i i g at T and, I according to the Gibb's theorem and this is same as U i at T and P, because it is independent of the pressure. And so, the partial molar property for component i is same as the pure component property at the temperature and pressure of the mixture, right. Going by similar logic H i bar i g at T and P, you can show that it will be same as the pure component property at T and P. And again as long as the temperature is same the enthalpy does not change, right. What these two relations for enthalpy and internal energy also mean is that for the mixture, the total molar property U according to the summability relation is x i U i bar and because U i bar is same as U i this will be same as x i U i.

Similarly, H is oh this is for an ideal gas alone, right. So, we will use this i g to denote that we are talking about an ideal gas, sorry. This we should write it as y i for mole fraction. And similarly H i i g is y i H i bar i g which will be identical to y i i H i i g. So, for an ideal gas all we need to estimate the property of the mixture is the pure component properties at the same temperature and pressure as long as I have that information. I can directly calculate what the enthalpy and internal energy for the mixture are, I do not need any additional information.

(Refer Slide Time: 11:19)



Entropy

$$\bar{S}_i^{ig}\{T,P\} = S_i^{ig}\{T,p_i\}$$

At Const. T, $dS^{ig} = -R\, d\ln P$

$$y_i = \frac{p_i}{P} \qquad \frac{P}{p_i} = \frac{1}{y_i}$$

$$\Rightarrow \int_{p_i}^{P} dS_i^{ig} = -R \ln \frac{P}{p_i}$$

$$S_i^{ig}\{T,P\} - S_i^{ig}\{T,p_i\} = -R \ln \frac{P}{p_i}$$

$$S_i^{ig}\{T,p_i\} = S_i^{ig}\{T,P\} + R \ln \frac{1}{y_i}$$

$$\bar{S}_i^{ig}\{T,P\} = S_i^{ig}\{T,p_i\} = S_i^{ig}\{T,P\} - R \ln y_i$$

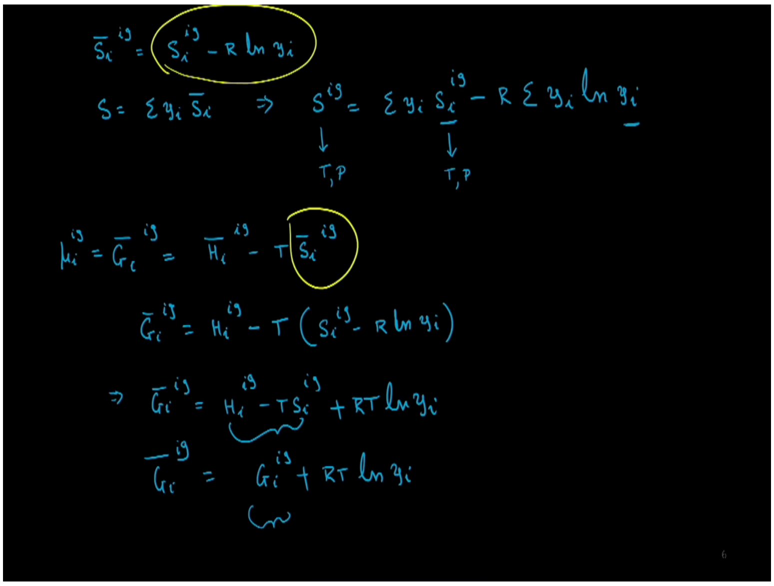
$$\boxed{\bar{S}_i^{ig}\{T,P\} = S_i^{ig}\{T,P\} - R \ln y_i}$$

Now, what about entropy? According to the Gibb's theorem, S i bar for an ideal gas at T and P is S i at T and p i, right. This is at some composition y i. Let us call this as S i i g at T and P I, right. Now, if you recall at constant temperature, if you recall d S for an ideal gas is minus R d ln P. So, what I will do is I will take this. And integrate it from the total pressure P to or from the partial pressure p i to the total pressure P. And if I do that integral going from p i to P d S i i g will be minus R ln P over p i, right. If I do the integral on the right hand side and apply the limits then it will be P over p i.

So, it will be minus R ln P over p I, right . So, on the left hand side, what I have is S i i g at T and P minus S i i g at T and p i will be this difference will be minus R ln P over p i or S i i g at T and p i will be the pure component value at T and P plus R times ln remember that mole fraction y i s p i over P. So, P over p i is 1 over y i. So, this will be 1 over y i. So, S i bar i g at T and P will be S i the pure component value at T and p i which is now the pure component value at T and P minus R ln y i. I have inverted 1 over y i and then brought the negative sign before R.

So, then for the partial molar property or partial molar entropy in a mixture of ideal gas S i bar i g will be the pure component value for entropy T and P minus R ln y i.

(Refer Slide Time: 14:21)



$$\bar{S}_i^{ig} = \boxed{S_i^{ig} - R\ln y_i}$$

$$S = \sum y_i \bar{S}_i \Rightarrow \underset{\underset{T,P}{\downarrow}}{S^{ig}} = \sum y_i \underset{\underset{T,P}{\downarrow}}{\underline{S_i^{ig}}} - R\sum y_i \ln \underline{y_i}$$

$$\mu_i^{ig} = \bar{G}_i^{ig} = \bar{H}_i^{ig} - T\boxed{\bar{S}_i^{ig}}$$

$$\bar{G}_i^{ig} = H_i^{ig} - T\left(S_i^{ig} - R\ln y_i\right)$$

$$\Rightarrow \bar{G}_i^{ig} = \underbrace{H_i^{ig} - TS_i^{ig}} + RT\ln y_i$$

$$\bar{G}_i^{ig} = \underbrace{G_i^{ig}} + RT\ln y_i$$

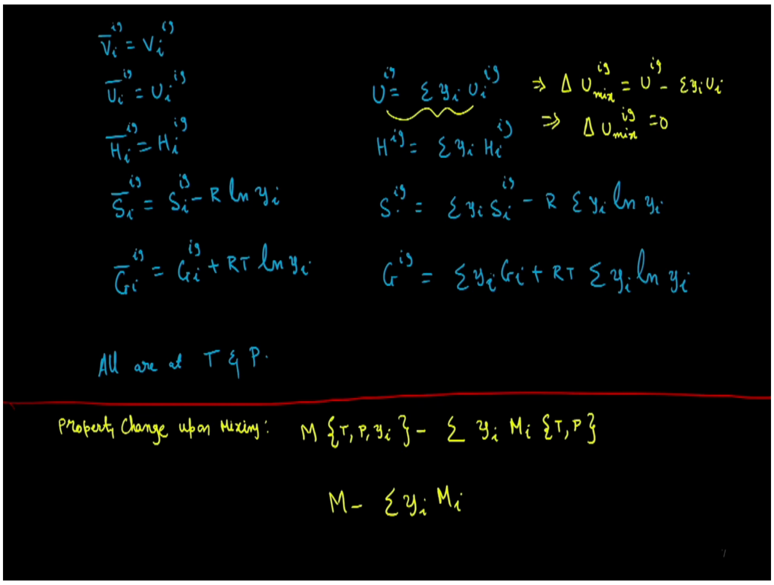
Now, we can extend this. What we had earlier is S i bar i g is S i i g at T and P minus R ln y i . Now S is sigma y i s i bar from some ability relation what this means is S i g will be sigma S i i g minus R sigma y i ln y i, right. This is the total entropy of an ideal gas mixture in terms of the pure component entropy S i i g and the mole fraction y i. Remember that this is at some temperature and pressure, this also is at the same temperature and pressure.

So, what we have done is in effect related the entropy of the mixture at a given temperature. And pressure to the pure component entropy at the same temperature and pressure and the mole fractions of course, for an ideal gas scenario. We can also write the Gibb's free energy which is of more interest to us, because it is related to chemical potential and phase equilibrium problems dependent chemical potential like we discussed earlier. The Gibb's free energy, partial molar Gibb's free energy mu i i g is same as the chemical potential as you recall. And this will be H i bar i g minus T times S i bar i g.

Now, if you recall H i bar i g was H i i g, it is same as the pure component property at the same temperature and pressure minus T times, I am going to replace this S i bar i g here with this quantity here, right. So, that will be S i i g minus R ln y i. So, G i bar i g will be H i i g minus T S i i g plus R t ln y i or this quantity here is G i for the pure component plus R T ln y i. So, the partial molar Gibb's free energy or the chemical potential is equal to the pure component Gibb's free energy G i plus R T ln y i.

So, what we have done is derived a relationship between the partial molar property and the pure component property all at the same temperature and pressure. Let us quickly summarize what we have done so far V i bar is V i U i bar is U i H i bar is H I, right. S i bar is S i minus R ln y i and G i bar is G i plus R T ln y i. Now all of these are for ideal gases.

(Refer Slide Time: 17:13)



$\bar{V}_i^{ig} = V_i^{ig}$

$\bar{U}_i^{ig} = U_i^{ig}$ $\quad U^{ig} = \underbrace{\sum y_i U_i^{ig}}$ $\Rightarrow \Delta U_{mix}^{ig} = U^{ig} - \sum y_i U_i$

$\bar{H}_i^{ig} = H_i^{ig}$ $\quad H^{ig} = \sum y_i H_i^{ig}$ $\Rightarrow \Delta U_{mix}^{ig} = 0$

$\bar{S}_i^{ig} = S_i^{ig} - R \ln y_i$ $\quad S^{ig} = \sum y_i S_i^{ig} - R \sum y_i \ln y_i$

$\bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i$ $\quad G^{ig} = \sum y_i G_i + RT \sum y_i \ln y_i$

All are at T & P.

Property Change upon Mixing: $M\{T, P, y_i\} - \sum y_i M_i\{T, P\}$

$M - \sum y_i M_i$

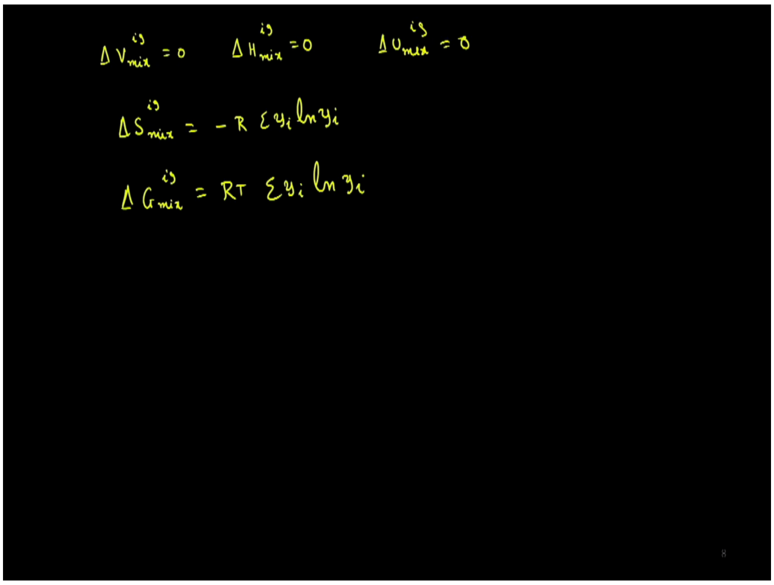
So, I am going to use the superscript i g, we have derived all these relations. For partial molar properties in terms of the pure component properties all are at T and P the temperature and pressure are same which is same as that of the mixture.

Now, following these relations we can also show that U is sigma y i U i i g, we use the summability relation over the partial molar properties to get these equations sigma y i H i i g S i g, the mixture entropy is sigma y i S i i g minus R sigma y i ln y i. And finally, the Gibb's free energy of the mixture is sigma y i G i plus R T sigma y i ln y i. So, we have derived the partial molar properties as well as the total properties for the mixture of ideal gases, right. One final thing while we are at this is to define a property called as property change upon mixing. When we mix two substances as we looked at the schematic earlier this one, I have two different species, pure species separated initially at some temperature. And pressure and what happens when I mixture how much is the total property change, we call that as the property change upon mixing.

So, let us quickly write that quantity by looking at these equations here. So, what I will do is I will, alright. And write property change upon mixing and the way we define property change upon mixing is the property of the mixture at T P and y i minus the pure component property is weighted with their mole fractions also at the same temperature and pressure, right.

So, for sake of clarity I am going to drop the functionalities, this is simply M minus sigma y i M i M as well as M i all are take are all taken at the same temperature and pressure and the corresponding mole fraction for M is y i of course, right. So, by looking at this expression I can write property change on mixing for delta U mixing of an ideal gas is U for an ideal gas minus sigma y i U i and because of this relation here this automatically implies delta U mixing for an ideal gas is 0. Going through similar steps I can also derive the following equations. Delta V mixing for an ideal gas is 0 delta H mixing for an ideal gas is 0.

(Refer Slide Time: 21:05)



$\Delta V_{mix}^{ig} = 0$ $\Delta H_{mix}^{ig} = 0$ $\Delta U_{mix}^{ig} = 0$

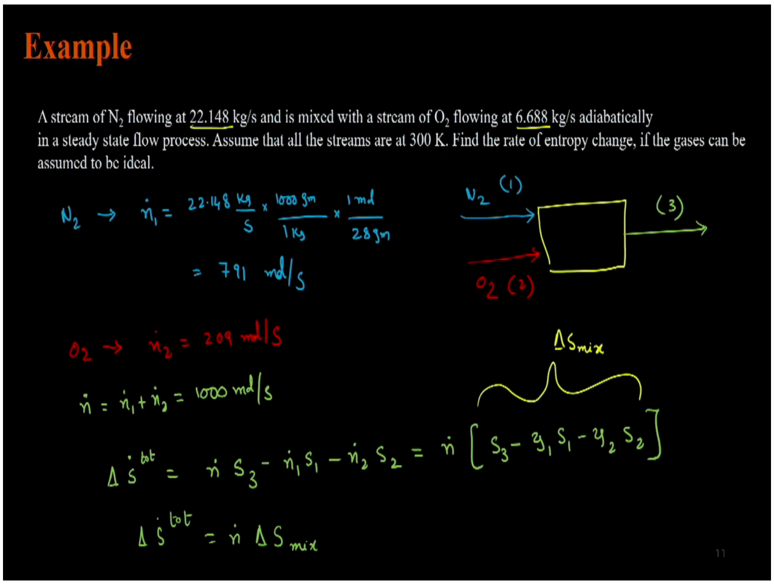
$$\Delta S_{mix}^{ig} = -R \sum y_i \ln y_i$$

$$\Delta G_{mix}^{ig} = RT \sum y_i \ln y_i$$

The entropy of mixing delta S mixing for an ideal gas mixture is minus R sigma y i ln y i. And finally, the Gibb’s free energy of mixing for an ideal gas mixture is R T sigma y i ln y i.

So, these are all the various quantities of course, in the previous slide we derived internal energy change upon mixing is 0 as well. So, these are various property changes upon mixing for an ideal gas mixture. Now that we talked about ideal gas mixtures let us quickly run through two examples on using the equations, we have just derived before we move on and extend this discussion on ideal gas mixtures to what are known as ideal solutions.

(Refer Slide Time: 22:13)



Example

A stream of N_2 flowing at 22.148 kg/s and is mixed with a stream of O_2 flowing at 6.688 kg/s adiabatically in a steady state flow process. Assume that all the streams are at 300 K. Find the rate of entropy change, if the gases can be assumed to be ideal.

$$N_2 \rightarrow \dot{n}_1 = 22.148\,\frac{kg}{s} \times \frac{1000\,gm}{1\,kg} \times \frac{1\,mol}{28\,gm} = 791\ mol/s$$

$$O_2 \rightarrow \dot{n}_2 = 209\ mol/s$$

$$\dot{n} = \dot{n}_1 + \dot{n}_2 = 1000\ mol/s$$

$$\Delta \dot{S}^{tot} = \dot{n} S_3 - \dot{n}_1 S_1 - \dot{n}_2 S_2 = \dot{n}\,\overbrace{\left[S_3 - y_1 S_1 - y_2 S_2\right]}^{\Delta S_{mix}}$$

$$\Delta \dot{S}^{tot} = \dot{n}\,\Delta S_{mix}$$

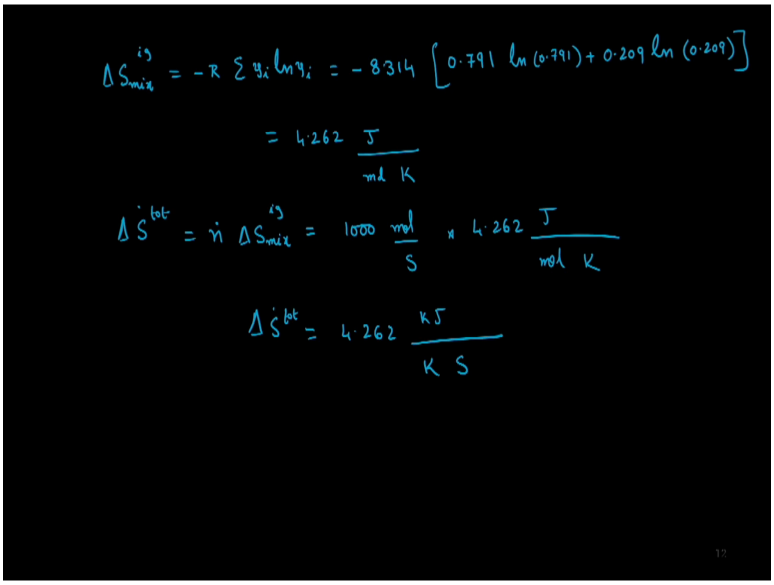
The first example says, we have a stream of nitrogen flowing at a certain flow rate and oxygen flowing as well and these two streams I have a stream of nitrogen and another stream of oxygen and what we get out is a stream of air or mixture of these two compounds. And we are interested in assuming the or sorry, we are interested in calculating the rate of entropy change for this particular process, right.

To calculate the rate of entropy change what we will do is first find the molar flow rates of the two streams, right. So, for N 2 molar flow rate n 1 dot is 22.148 kilograms per second times 1000 grams per 1 kilogram times 1 mole per 28 grams. So, that will translate to 791 moles per second. Similarly, for oxygen n 2 dot is 209 moles per second. And the total molar flow rate for the mixture n, this is n 1 dot plus n 2 dot. This will be 1000 moles per second some of 791 and 2 or 9. This is the total mixture, I am making and we are interested in finding the rate of entropy change. So, delta S total dot will be n dot times S, let us call these streams, let us give them some numbers, right.

So, let us call this as 1, this as 2 and this as 3. Then delta S total the change in total entropy or the rate of that change is n dot times S 3 minus n 1 dot times S 1 minus n 2 dot times S 2. So, this will be essentially n dot times S 3, the molar entropy of stream 3 minus y 1 S 1 minus y 2 S 2 dot. And if you look at this we can easily recognize that the quantity inside the parentheses, here is the entropy change upon mixing delta S mixing.

So, then essentially delta S total this change or rate of this changes n dot times delta S mixing the molar entropy change upon mixing. And that is what we are interested in calculating I already know n dot all I need to find is the entropy change upon mixing and I can then calculate what I need.

(Refer Slide Time: 25:53)



$$\Delta S_{mix}^{ig} = -R \sum y_i \ln y_i = -8.314 \left[0.791 \ln(0.791) + 0.209 \ln(0.209)\right]$$

$$= 4.262 \frac{J}{mol\ K}$$

$$\Delta \dot{S}^{tot} = \dot{n}\, \Delta S_{mix}^{ig} = 1000 \frac{mol}{s} \times 4.262 \frac{J}{mol\ K}$$

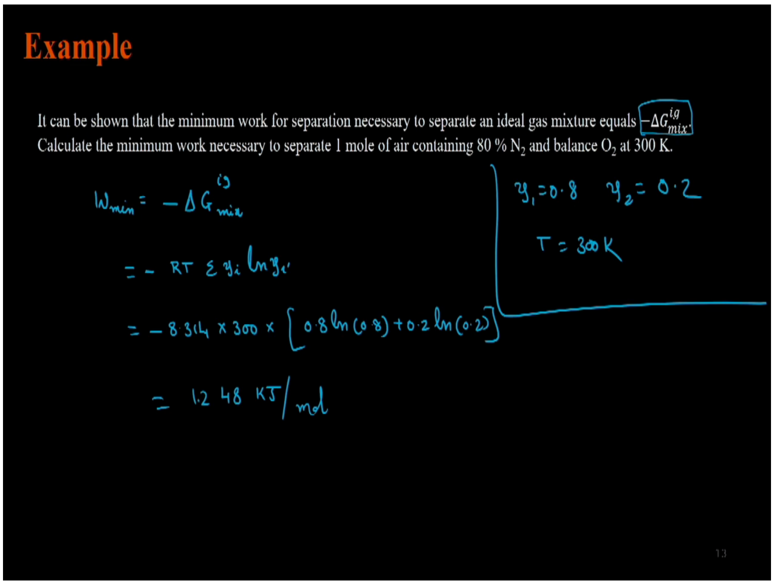
$$\Delta \dot{S}^{tot} = 4.262 \frac{kJ}{K\ s}$$

Now, by definition if you recall for an ideal gas mixture, we can assume that this is an ideal gas mixture delta S mixing for an ideal gas mixture is minus R sigma y i ln y i. So, this will be negative 8.314 times y 1 which is 0.791 ln y 1 n which is again 0.791 plus 0.209 ln of 0.209.

And this quantity, right here turns out to be 4.262 Joule per mole Kelvin, right. And if I am interested in the total entropy change, rate of total entropy change total dot. Then it is n dot multiplied with delta S mixing for an ideal gas, because we can assume the streams to be ideal gas streams. In this scenario, this turns out to be 1000 moles per second multiplied with 4.262 Joule per mole Kelvin.

So, that would be 4.262 kilo Joules per Kelvin second. This is the rate of entropy change for this particular process. I noticed that the entropy change is positive which it should be for a process, it should be positive it is greater than 0.

(Refer Slide Time: 27:37)



Example

It can be shown that the minimum work for separation necessary to separate an ideal gas mixture equals $\boxed{-\Delta G_{mix}^{ig}}$. Calculate the minimum work necessary to separate 1 mole of air containing 80 % N_2 and balance O_2 at 300 K.

$$W_{min} = -\Delta G_{mix}^{ig}$$

$$= -RT \sum y_i \ln y_i$$

$$= -8.314 \times 300 \times \left[0.8 \ln(0.8) + 0.2 \ln(0.2)\right]$$

$$= 1.248 \ KJ/mol$$

$y_1 = 0.8 \quad y_2 = 0.2$

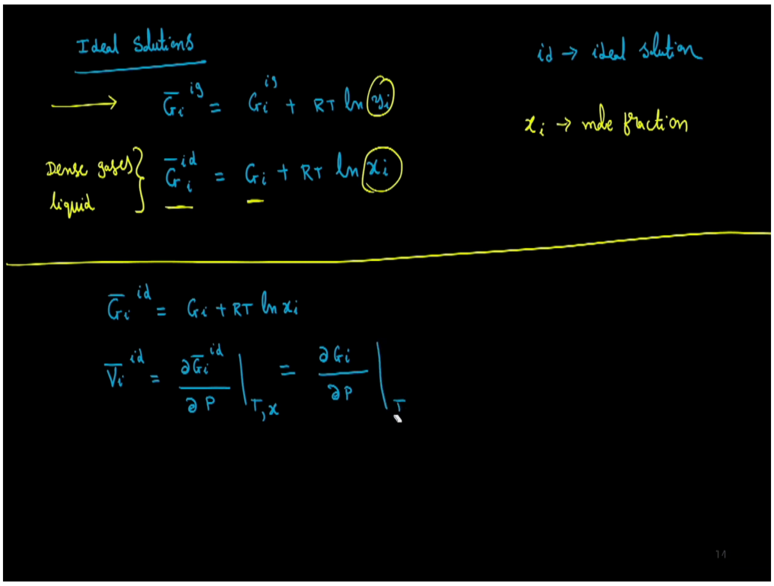
$T = 300 K$

Let us look at another example can be shown that the minimum work of separation necessary to separate an ideal gas mixture is negative delta G mixing, this is a minimum work required to separate an ideal gas mixture.

Now, calculate the minimum works necessary to separate 1 mole of air containing 80 percent nitrogen and the balance oxygen of course, we can assume that in this particular scenario, we are talking about ideal gas mixtures. So, if we have to calculate the minimum work required W minimum then is negative delta G mixing of an ideal gas, right.

And we are given that y 1 is 0.8, y 2 for oxygen is 0.2 and the temperature is 300, Kelvin right. Now, for an ideal gas mixture delta G mixing is RT, right sigma y i ln y i so that will be negative 8.314, 300 times 0.8 ln 0.8 plus 0.2 ln 0.2. So, value right here turns out to be, so, delta G mixing is a molar quantity. So, the minimum work required is the minimum work per 1 mole of gas. So, that is how we can use the concepts about ideal gas mixtures .We learnt earlier and do some quick calculations on entropy changes upon mixing and Gibb’s free energy changes upon mixing. What we will do next is we will continue this discussion on ideal gas mixtures and extend it to a larger class of mixtures. The idea being some of the characteristics of ideal gas mixtures can also be translated to dense phases. If we get denser mixtures of gases or even liquids and solids for that matter, right. So, let us extend our discussion on ideal gas mixtures to a new class of mixtures known as Ideal Solutions.

(Refer Slide Time: 29:59)



Ideal Solutions

id → ideal solution

x_i → mole fraction

$$\longrightarrow \quad \bar{G}_i^{ig} = G_i^{ig} + RT\ln \boxed{y_i}$$

Dense gases, liquid

$$\bar{G}_i^{id} = G_i + RT\ln \boxed{x_i}$$

$$\bar{G}_i^{id} = G_i + RT\ln x_i$$

$$\bar{V}_i^{id} = \left.\frac{\partial \bar{G}_i^{id}}{\partial P}\right|_{T,x} = \left.\frac{\partial G_i}{\partial P}\right|_{T}$$

In an, an ideal gas mixture recall that the partial molar Gibb's free energy or the chemical potential is related to its pure component value via this equation.

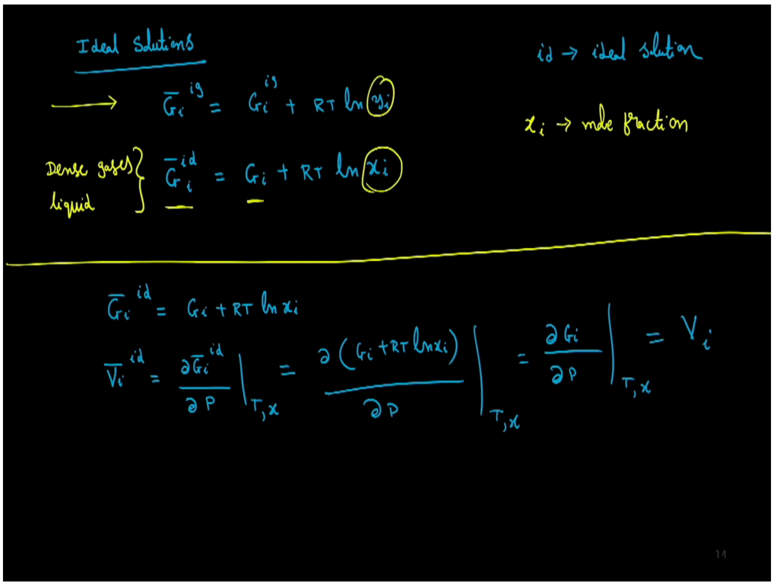
What we will do is a define a class of solutions or mixtures known as ideal solutions which exhibit similar relationship between the partial molar Gibb's free energy or the chemical potential and the pure component Gibb's free energy. So, G i bar in an ideal solution i d standing for an ideal solution is related to G i the pure component, Gibb's free energy in exactly similar relationship.

Notice that I have changed the mole fraction y i to x i, y i is something we usually use for a gaseous phase x i is something we use for liquid phase. This class of mixtures is typically a used to define liquid solutions. So, I am using x i in this case, but the idea is that we have extended a characteristic of ideal gas mixture that is a relationship between the chemical potential and the pure component Gibb's free energy to denser phases, right be it a denser gaseous phase or even a liquid phase. In this case the ideal gas relationship P V equal to n RT or other characteristics of non interaction between the molecules or zero size of the molecules may not hold, but still the partial molar Gibb's free energy is related to the pure component Gibb's free energy in a similar fashion as that in an ideal gas mixture.

So, what this does is it gives the composition dependency for the partial molar property in terms of the mole fraction in a similar fashion as that in a ideal gas mixture. Now it serves well for dense gases liquids or even mixtures of solids as long as we call them as ideal solutions. And typically it works well when, when the liquid mixtures have species that contain molecules of similar sizes and similar chemical nature. For example, adjacent species in a homologous series or isomers can be well defined using a ideal solution behavior.

Now, because of this reason, right, so we can use the relationships, we have developed earlier to calculate the other thermodynamic properties for an ideal solution. Now we know that G i bar i d is G i plus R T ln x i, x i can be mole fraction either for gas or a liquid phase like I said earlier. Now if I want to calculate V i bar ideal then recall that V is the derivative of the Gibb's free energy with respect to the pressure at constant T and x, right.

(Refer Slide Time: 33:53)



Ideal Solutions

id → ideal solution

$$\longrightarrow \quad \bar{G}_i^{ig} = G_i^{ig} + RT\ln \boxed{y_i}$$

x_i → mole fraction

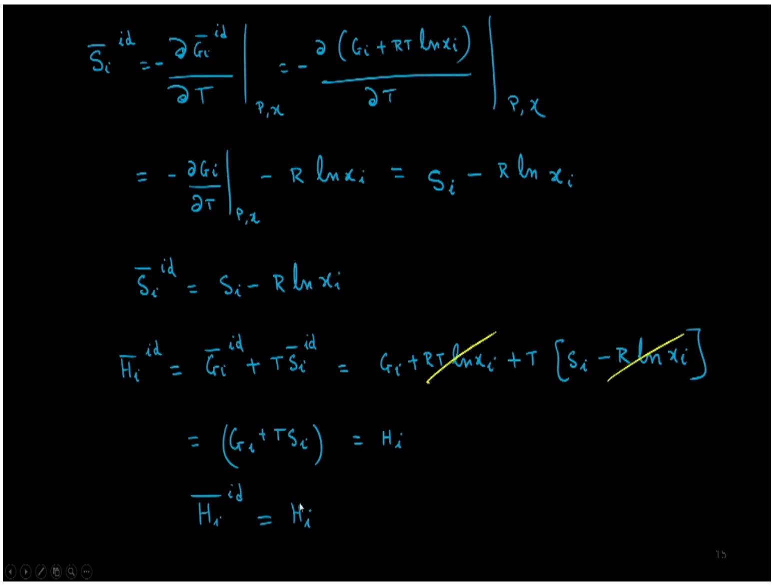
$$\text{Dense gases, liquid} \Big\} \quad \underline{\bar{G}_i^{id}} = \underline{G_i} + RT\ln \boxed{x_i}$$

$$\bar{G}_i^{id} = G_i + RT\ln x_i$$

$$\bar{V}_i^{id} = \left.\frac{\partial \bar{G}_i^{id}}{\partial P}\right|_{T,x} = \left.\frac{\partial\left(G_i + RT\ln x_i\right)}{\partial P}\right|_{T,x} = \left.\frac{\partial G_i}{\partial P}\right|_{T,x} = V_i$$

And once T and x are constant then this will simply be the derivative of G i with respect to pressure at constant. Well, let me write that explicitly this will be derivative of G i plus R T ln x i with respect to pressure at constant T and x. Now, because temperature and x are constant the second term drops out and all I have left is derivative of G i with respect to P at T n x which is essentially the molar volume for component i V i. Now notice that this molar volume does not have to be ideal gas volume, it is whatever the molar volume for component pure component i at that temperature and pressure is.

(Refer Slide Time: 34:29)



$$\bar{S}_i^{id} = -\frac{\partial \bar{G}_i^{id}}{\partial T}\Big|_{P,x} = -\frac{\partial (G_i + RT\ln x_i)}{\partial T}\Big|_{P,x}$$

$$= -\frac{\partial G_i}{\partial T}\Big|_{P,x} - R\ln x_i = S_i - R\ln x_i$$

$$\bar{S}_i^{id} = S_i - R\ln x_i$$

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id} = G_i + \cancel{RT\ln x_i} + T\left[S_i - \cancel{R\ln x_i}\right]$$

$$= (G_i + TS_i) = H_i$$

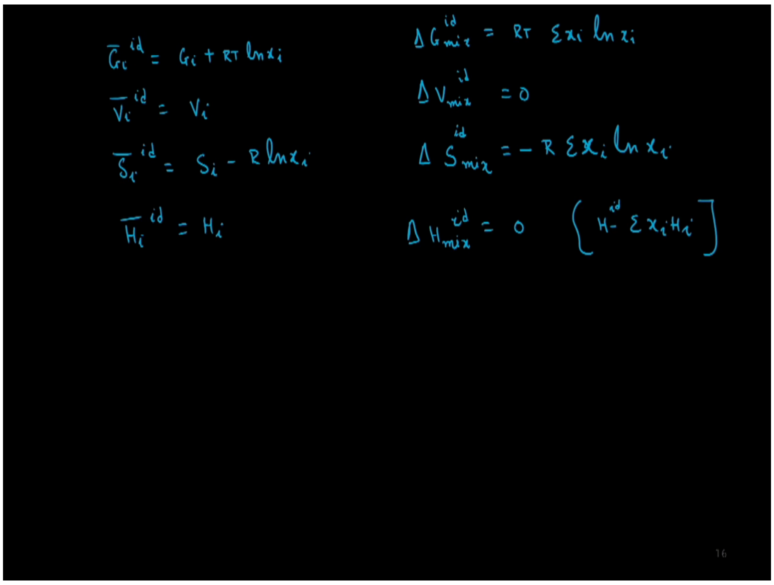
$$\bar{H}_i^{id} = H_i$$

Next thing we want to calculate is the partial molar entropy in an ideal solution S i bar i d. This is derivative of the partial molar Gibb’s free energy with respect to the temperature at constant P and x. So, this will be derivative of G i plus R T ln x i with respect to temperature at P and x. In fact, this is negative of that quantity, right.

So, that would be negative derivative of G i with respect to temperature at P and x for the pure component minus R times ln x i all of them are constant, we only have temperature. So, the derivative of temperature with respect to temperature is 1. The first term of course, is the entropy of the pure species i minus R ln x i, right. So, what we have then is S i bar i d is S i minus R l n x i. And finally, we can calculate the enthalpy H i bar i d, it is since G is H minus T S, H is G plus T s or it is G i bar plus T s i bar i d. So, that is G i plus R T ln x i plus T times S i minus R l n x i.

So, that will be G i plus T S i that is for the pure species and the other two terms cancel out. So, that quantity will then be equal to H i. So, H i bar id is same as H i. So, now, let us quickly summarize what we have derived so far for an ideal solution.

(Refer Slide Time: 36:45)



$\bar{G}_i^{id} = G_i + RT \ln x_i$

$\bar{V}_i^{id} = V_i$

$\bar{S}_i^{id} = S_i - R \ln x_i$

$\bar{H}_i^{id} = H_i$

$\Delta G_{mix}^{id} = RT \sum x_i \ln x_i$

$\Delta V_{mix}^{id} = 0$

$\Delta S_{mix}^{id} = -R \sum x_i \ln x_i$

$\Delta H_{mix}^{id} = 0 \quad \left\{ H^{id} - \sum x_i H_i \right]$

The first thing is G i bar i d, this is by definition of an ideal solution is G i plus R T ln x i. Then we have derived that V i bar i d is V i. S i bar i d is S i minus R ln x i. And finally, H i bar i d is H i Now we can also write the property changes upon mixing delta H mixing for an ideal solution will be equal to 0, because it is H minus sigma x i H i.

Similarly, delta V mixing for an ideal solution will also be equal to 0, delta S mixing will be minus R sigma x i ln x i and delta G mixing of an ideal solution will be equal to R T sigma x i ln x i. So, notice that all these property changes upon mixing are same as that for an ideal gas mixture. So, what we have done is extended the concept of an ideal gas mixture to a class of solutions known as ideal solutions and it turns out that the various thermodynamic property changes for ideal solutions are similar to what we have observed for ideal gas mixtures.

So, like I said what it gives us is a handle on how to relate the property changes upon mixing or the partial molar properties to either the pure component properties or the mole fractions, right. So, with that we will stop the lecture today when we come back in the next class, what we will do is try to extend this discussion on ideal solutions and see how we can apply them to real life problems.

Thank you.