Thermodynamics of Fluid Phase Equilibria
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Lecture – 21
Ideal Gas Mixture - part 1

Welcome back in this lecture we are going to look at Ideal Gas Mixtures.

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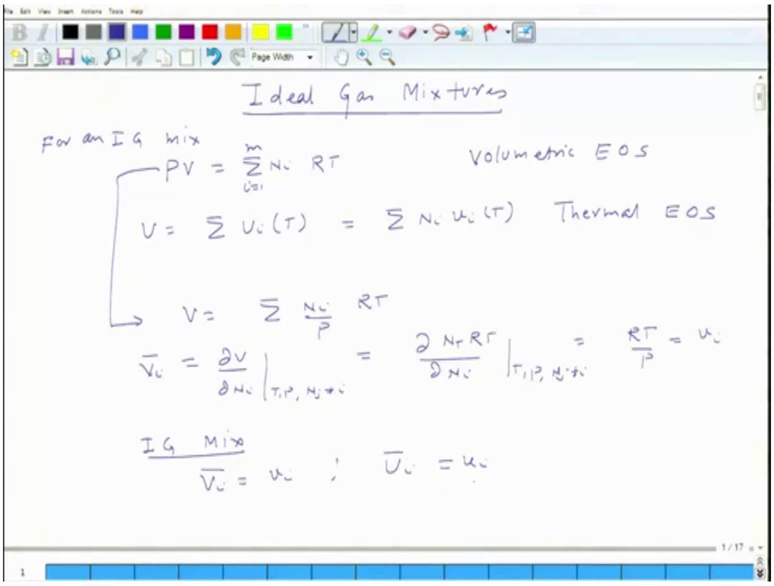

Ideal Gas Mixtures

For an I G mix

$PV = \sum_{i=1}^{m} N_i RT$ Volumetric EOS

$U = \sum U_i(T) = \sum N_i u_i(T)$ Thermal EOS

$V = \sum \frac{N_i}{P} RT$

$\bar{V}_i = \frac{\partial V}{\partial N_i}\Big|_{T,P,N_j \neq i} = \frac{\partial N_T RT}{\partial N_i}\Big|_{T,P,N_j \neq i} = \frac{RT}{P} = v_i$

I G Mix

$\bar{V}_i = v_i$; $\bar{U}_i = u_i$

And subsequently we will be looking at partial molar properties particularly how it is evaluated or calculated from the experimental data. So, for an ideal gas we are all aware of the equation of state right P v is equal to nrt.

But for ideal gas mixture we can extend that and write as P v is equal to summation of N i number of moles multiplied by RT where i is equal to 1 to m. So, this we can sometimes also call volumetric equation of state because the volume is related with temperature and pressure.

In addition since idle gas is a non interacting system which means basically they are not interacting at all you can sum up the internal energy of individual component ok. Now you know final gas internal energy is only a function of temperature so essentially this is a function of temperature.

We can also write this as summation of number of moles of each component multiplied by molar, molar internal energy of the component I which is also function of temperature ok. So, this is sometimes also called thermal equation of state ok. Now what I am interested basically is obtaining the partial molar volume for idle gas so we can use this expression and get v is equal to summation n i divided by P RT ok.

And now we can obtain vi which is a passion molar property of component i for the ideal gas as simply del v by del N i keeping temperature, pressure and all of the component mass are the moles constant ok. So, if we do this exercise I can write this v as summation and i or N T is the total number of moles multiplied by RT and this is going to be simply RT by P ok. Now which is nothing but, actually the molar volume of a component I occupying the same volume basically ok.

So, this is nothing, but vi which is a pure component molar volume which occupies the same volume having a moles N i ok. So, this is something which we have also done in our earlier thermodynamics courses ok. So, I can summarize that for ideal gas mixture vi is nothing, but vi and ui the is nothing, but ui ok.

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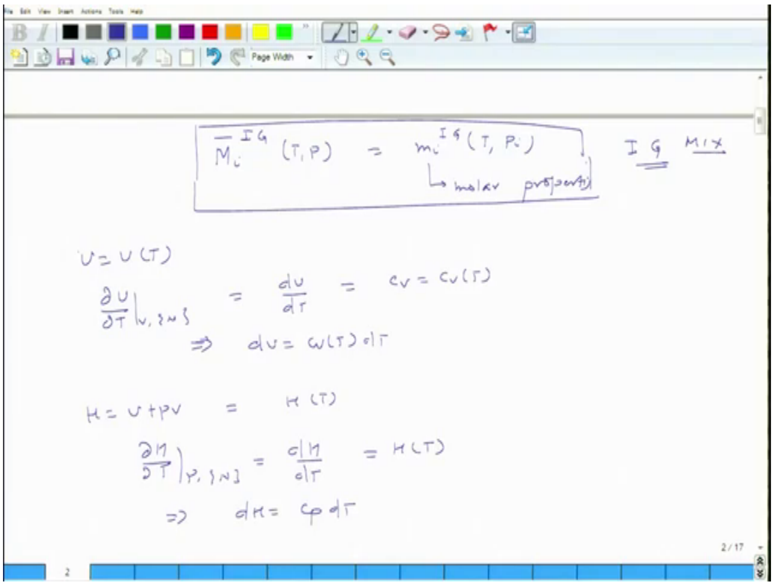

$$\boxed{\overline{M}_i^{IG}(T,P) = \underbrace{m_i^{IG}(T,P_i)}_{\text{molar property}}} \quad \underline{\underline{IG}} \ \underline{MIX}$$

$$U = U(T)$$

$$\left.\frac{\partial U}{\partial T}\right|_{V,\{N\}} = \frac{dU}{dT} = c_v = c_v(T)$$

$$\Rightarrow dU = c_v(T)\,dT$$

$$H = U + PV = H(T)$$

$$\left.\frac{\partial H}{\partial T}\right|_{P,\{N\}} = \frac{dH}{dT} = H(T)$$

$$\Rightarrow dH = c_p\,dT$$

Now in general ideal gas mixture I can generalize this what we have calculate now as for any extensive thermal adding property the partial molar property of that for an ideal gas at a given temperature in pressure is equivalent to its molar property of this pure system for a component I add the temperature, but its own partial pressure ok. So, this is a molar property ok.

So, you understand this expect that when you contain this and i component in a volume v the number of moles i for species i is basically occupying the same volume, but with a pressure P i basically ok. This we are going to use it later when we are going to derive little bit more so this is a generic property for an idle gas not for all only for ideal mixtures ok. Now I am just going to quickly do this exercise since if ideal gas u is equal to function of temperature; that means, basically the partial derivative of u with respect to T which is nothing, but C v ok.

This is only a function of temperature; that means, I can write as this and this is not even c v which is also a function of temperature this implies that for a ideal gas ok. Similarly H is equal to u plus P v which is because P v is nothing, but NT RT which is also a function of temperature. So, del H by del T at P for all, can be written also in a similar form which I which means this is ok.

So, this is something which we know and when we are going to make use of it whenever we are going to apply ideal gas approximation for mixtures we can also use this approximations to get the changes in the internal energy with respect to temperature by making use of heat capacities. Now what I am trying to obtain an expression for internal of all entropy and Gibbs free energies and those Gibbs free energies for an ideal gas mixtures ok.

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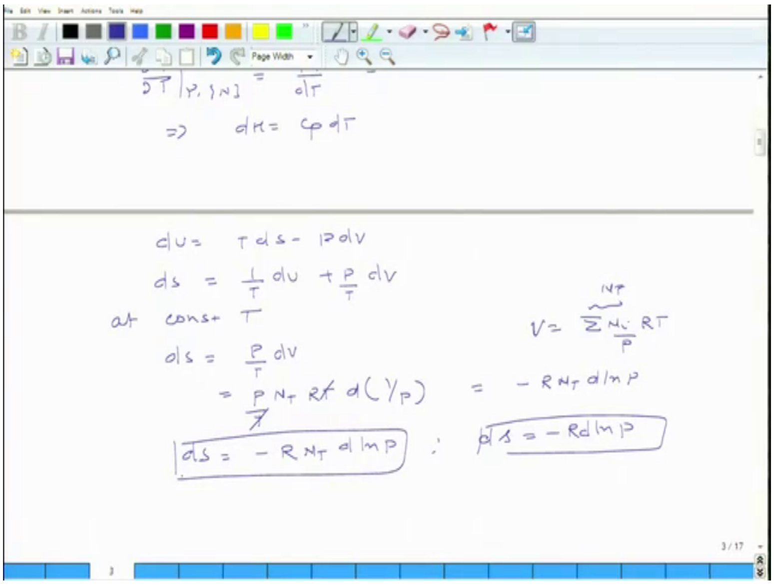

$\partial T \big|_{P,\{N\}} = dT$

$\Rightarrow \quad dH = c_p \, dT$

$dU = T\,dS - P\,dV$

$dS = \frac{1}{T} dU + \frac{P}{T} dV$

at const T

$V = \frac{\overbrace{\sum N_i}^{N_T}}{P} RT$

$dS = \frac{P}{T} dV$

$= \frac{P}{\cancel{T}} N_T R\cancel{T} \, d(1/P) = -R N_T \, d\ln P$

$\boxed{dS = -R N_T \, d\ln P}$; $\boxed{ds = -R \, d\ln P}$

So, let me just start with the first law ok. Now from here we are going to extract ideal gas so I can rearrange S in this form ds is equal to 1 by T, du plus P by T dv ok.

Now if you consider that the system is at constant temperature then I what I get this is because its constant temperature all other things are changing; that means, the internal energy is a constant why because u is a function of temperature ideal gas mixtures so, ds is nothing, but P by T dv ok. Now for an ideal gas mixtures I can write this because I know volume is summation N i by P RT. So, I can now get a derivative of this so this summation NT, I can write as n summation N i, I can write as NT so this becomes NT total number of moles RT d of 1 by P or I can rewrite as because TT can cancel.

Now, I can rewrite as minus R NT d log P in a simpler form ok. So, the ds is now if I divide by total number of moles then I can also write this expression as d small S which means molar property minus R d ln P I can also write in this form both are equivalent ok. Now what is my interest is to obtain ideal gas entropy of the ideal gas so this is the expression for an ideal gas expression in the differential form at constant temperature.

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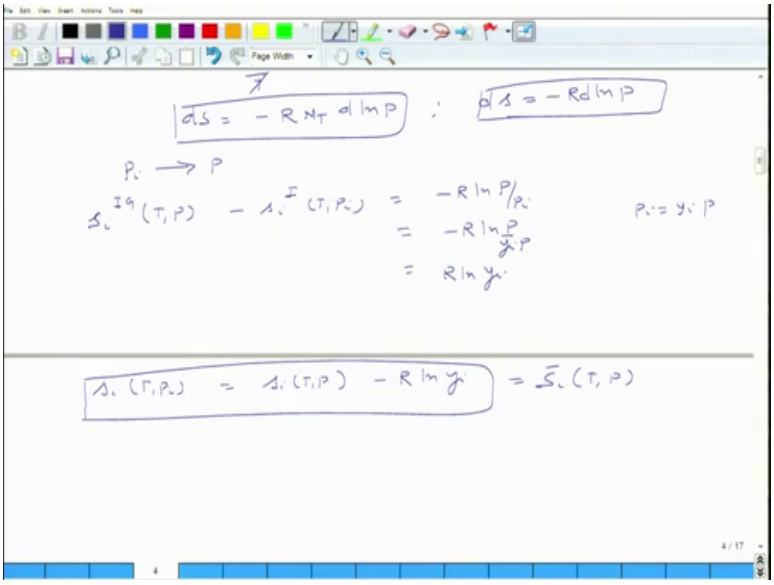

$$\boxed{dS = -R\,n_T\,d\ln P} \;;\; \boxed{ds = -R\,d\ln P}$$

$$P_i \longrightarrow P$$

$$s_i^{IG}(T,P) - s_i^{I}(T,P_i) = -R\ln P/P_i \qquad P_i = y_i P$$

$$= -R\ln\frac{P}{y_i P}$$

$$= R\ln y_i$$

$$\boxed{s_i(T,P_i) = s_i(T,P) - R\ln y_i} = \bar{S}_i(T,P)$$

So, we are going to now integrate from P i the partial pressure of component I in the mixture to P so that we are going to integrate now let us see what we get. So, considering the molar expression so I am going to get as small S i ideal gas I am going to put that temperature T P minus that is going to be equal to minus R and then P by P i because that is simpler expression which you have there is nothing else right.

So now so basically this expression holds for ideal gas mixture and this is a molar property so when we integrated we got this expression now what is P i P i is y i times P. So, I can get an expression now this as minus R ln P by y i P and this is equivalent to r ln yi ok.

So, I have an expression now I have an expression ok. So, this is the expression here of course, this is T comma P i remember that so this is for ideal gas at T P. Now if you recall this is what we talked we made a statement here that for an idle gas this expression holds for all properties extensive property we can write in this way. So, what we calculated here is basically the left hand side for if you replace m by S then mi T P i is nothing but S i T P i and this can be down replaced by the partial molar property of S.

So, this is nothing, but equivalent to saying that this is equal to S i bar T and P ok. So, this is an expression for us now.

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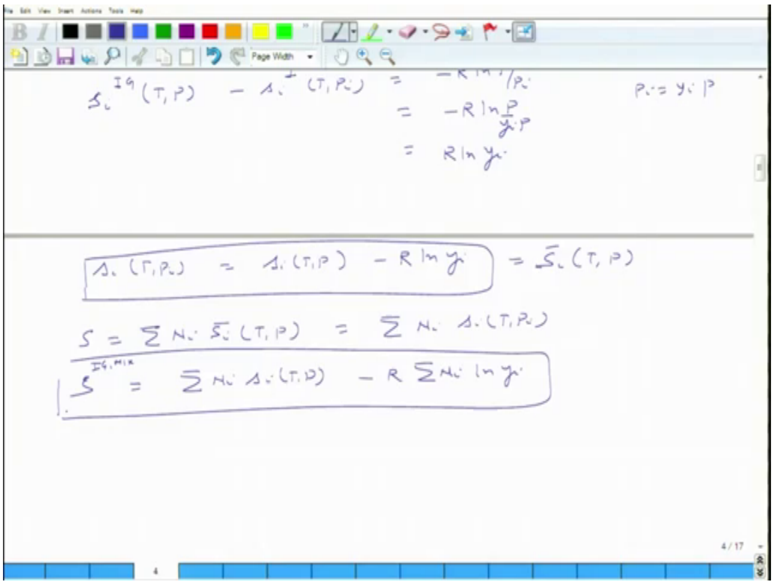

$$s_i^{IG}(T,P) - s_i^{IG}(T,P_i) = -R\ln P/P_i$$

$$= -R\ln\frac{P}{y_iP}$$

$$= R\ln y_i$$

$$P_i = y_iP$$

$$\boxed{s_i(T,P_i) = s_i(T,P) - R\ln y_i} = \bar{S}_i(T,P)$$

$$S = \sum N_i\bar{S}_i(T,P) = \sum N_i s_i(T,P_i)$$

$$\boxed{S^{IG,MIX} = \sum N_i s_i(T,P) - R\sum N_i \ln y_i}$$

Now this is a in terms of the molar property I can also write that total S for ideal gas or in general can be written as N i S i bar at the same temperature and pressure. So, this is we know this is true for in general properties and now that I can write for an ideal gas N i S i T P i so that means, this is equivalent of saying that for an ideal gas summation N i, S i T P minus R summation N i lny. So, this is basically for an ideal gas mixture ok. Now I using this expression we can derive other properties that would be your G and H.

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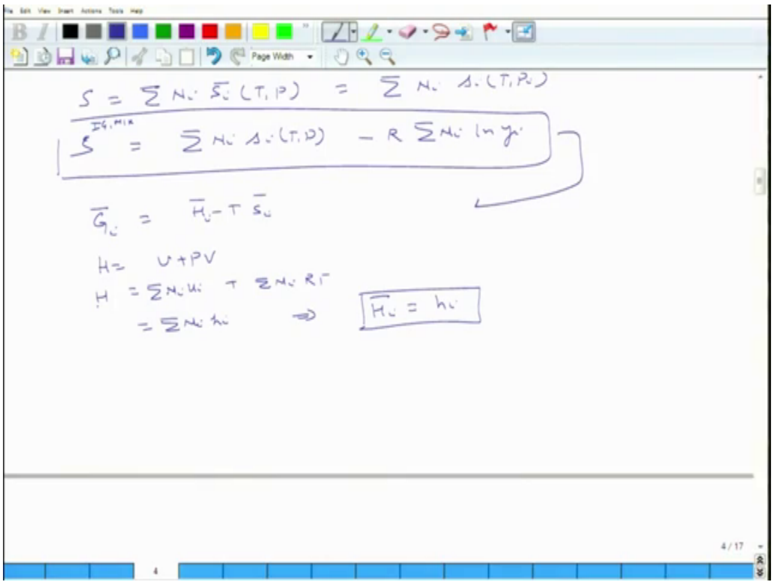

$$S = \sum N_i\bar{S}_i(T,P) = \sum N_i s_i(T,P_i)$$

$$\boxed{S^{IG,MIX} = \sum N_i s_i(T,P) - R\sum N_i \ln y_i}$$

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$H = U + PV$$

$$H = \sum N_i u_i + \sum N_i RT$$

$$= \sum N_i h_i \Rightarrow \boxed{\bar{H}_i = h_i}$$

So, let us look at first G, G is by definition is H minus T S and for a partial molar we can write this as ok. Now what would be the ideal gas what would be a H i bar. So, let us look at H, H is u plus P v u of course, we can write as N i ui because of the fact that it is an ideal gas non interacting system and T is a summation N i RT H. Now which essentially means this is nothing, but summation N i H i which essentially you can mean that if you take a partial derivative of H keeping the other moles constant then H i bar will be equal to H i.

So, this is for ideal gas system you can replace H i bar in the G expression by small h i now this S i bar the partial molar property of entropy can be replaced by this expression ok. So, this is what we are going to do in order to get G i bar. So, let me just plug in these values.

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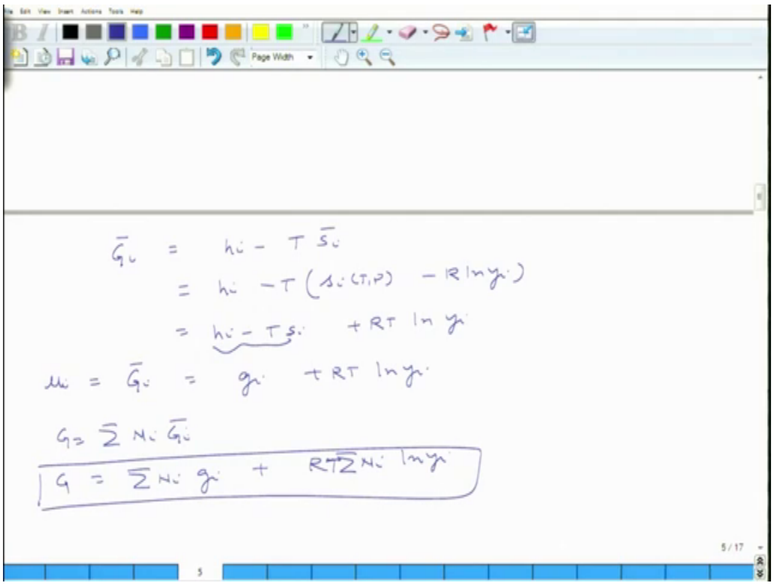

$$\bar{G}_i = h_i - T\bar{S}_i$$

$$= h_i - T\left(s_i(T,P) - R\ln y_i\right)$$

$$= \underbrace{h_i - Ts_i} + RT\ln y_i$$

$$\mu_i = \bar{G}_i = g_i + RT\ln y_i$$

$$G = \sum N_i \bar{G}_i$$

$$\boxed{G = \sum N_i g_i + RT\sum N_i \ln y_i}$$

So, G i bar is H i minus T S i bar and now I am going to replace T S i bar by this expression because S i bar is there. So, I am just going to take the one which is which is the expression which we have derived here which is small s i small s i T P minus R l n y i so this is expression.

So, this is can be written as minus because h i is also a T P s i is also a T P. So, this is written simply like this plus RT l n y i ok. Now this is nothing, but small g i plus RT l n y G i bar ok. Now what is G i bar G i bar we have already defined it earlier G i bar that partial molar Gibbs free energy for a component i is equal to chemical potential of that component I right so this is nothing, but u i ok.

So, now, I can make use of the fact that G is nothing, but summation N i G i bar. So, I can get the G as summation N i G i plus R summation RT summation N i l n y. So, this is the expression for my G ok.

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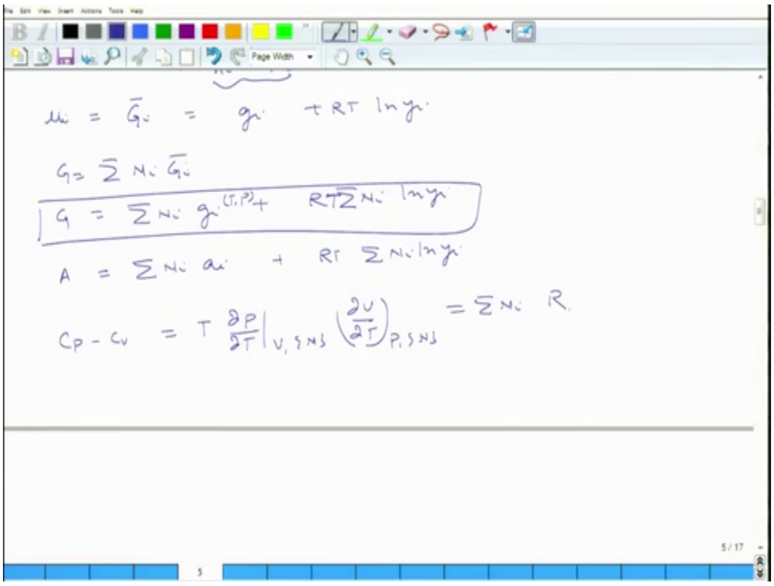

$$\mu_i = \bar{G}_i = g_i + RT \ln y_i$$

$$G = \sum N_i \bar{G}_i$$

$$\boxed{G = \sum N_i g_i^{(T,P)} + RT \sum N_i \ln y_i}$$

$$A = \sum N_i a_i + RT \sum N_i \ln y_i$$

$$C_P - C_V = T \frac{\partial P}{\partial T}\Big|_{V,\{N\}} \left(\frac{\partial V}{\partial T}\right)_{P,\{N\}} = \sum N_i R$$

Now, similarly I can actually extend this exercise for Gibbs free energy and this is going to be now in a similar way ai plus RT summation N i l n y i remember that this is at temperature T P ok. So, similarly this would be also a temperature T P ok.

Now for an ideal gas we know that C p minus C v is equal to r for that ideal gas mixture you can also derive that. So, C p minus C v can be shown to have this following expression T del P by del T at constant volume, keeping all the most constant del v by del T P and constant. So, if you plug in the equation of state for ideal gas you can show that this is nothing, but N i R ok.

So, this is something which you can derive now you may be asked like how does ideal gas properties G, A, H behaves as a function of composition for gas ok. So, I can just draw schematic form that how it looks like when you plot such a function for ideal gas mixture.

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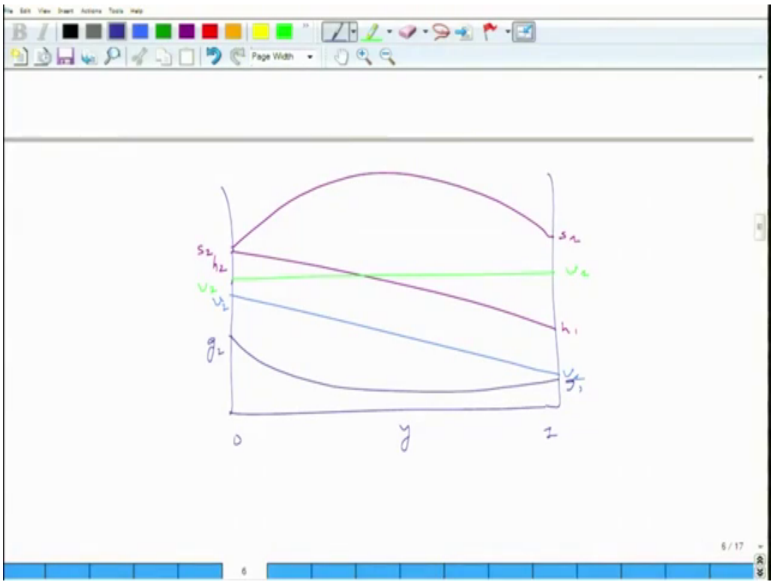

So, it is going to be a little bit messy, but let us see if we can draw it well. So, this is y from 0 to 1 for one the property would be let us say one plus for 0 it will be let us say 2. So, I am going to draw first entropy so it may look like this. So, this is like a molar property of 2 P o 2 component is the molar property of component one this may look like for enthalpy ok, this may look like for internal energy ok.

And this may look like for volume molar volume and this may look like for the Gibbs free energy G 1 G 2 ok. So, somewhere its showing minima also for G so this is a schematic form that how does this behave as a function of y for simple ideal gas mixture for binary component ok.

So, with this we will stop here we will continue this exercise in the next lecture.