Thermodynamics of Fluid Phase Equilibria

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Lecture - 25
Thermodynamics Properties from Volumetric Data – I

Welcome back. We are going to start a new topic it is a Thermodynamic Properties from Volumetric Data, ok.

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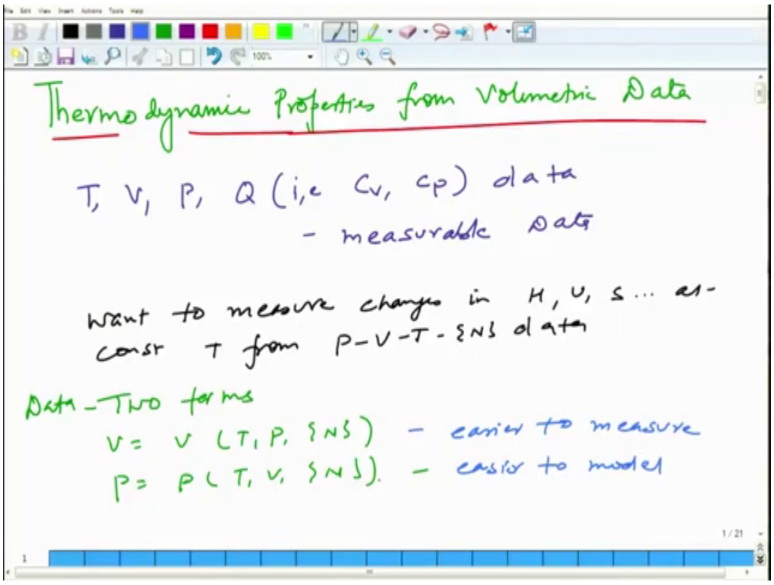

Thermodynamic Properties from Volumetric Data

T, V, P, Q (i,e C_v, c_p) data
- measurable Data

want to measure changes in H, U, S … at const T from P-V-T-{N} data

Data - Two forms

$V = V(T, P, \{N\})$ - easier to measure

$P = P(T, V, \{N\})$. - easier to model

As we have already discussed earlier that we cannot measure enthalpy entropy and all this free energy directly ok. So, these are not measurable quantities exactly, however, we can measure the difference between them. What we have accessible to the experimental data are basically in properties or in the form as in temperature, volume, pressure and heat or that is heat capacities ok. So, these are the data which we can measure.

And the interest is basically we want to find out the, want to measure changes in thermodynamic functions such as the property such as enthalpy, entropy has at constant temperature from P V T and given composition data. These are the data's which may have and our interest is to find out the changes in this property. Now, what are the typical data which I usually available? So, they are two forms.

So, the data is usually given in two forms ok, one is V as a function of T P N. Now, this is easier to measure another case is pressure is T V and N. Now, this is easier to do model ok. That means, this second one is basically we can make use of idle gas for example, or some equation of state we can use it and thus we can make use of this data to model such system ok. So, let me just start first with thermodynamic fun properties, with T P as in here as independent variables.

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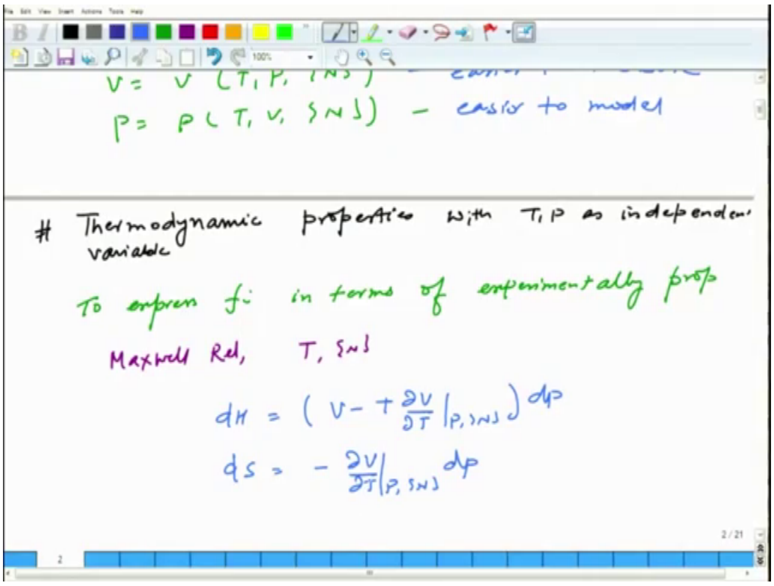

$V = V(T, P, \{N\})$

$P = P(T, V, \{N\})$ – easier to model

Thermodynamic properties with T, P as independent variable

To express f_i in terms of experimentally prop

Maxwell Rel, $T, \{N\}$

$$dH = \left(V - T\frac{\partial V}{\partial T}\Big|_{P,\{N\}}\right)dP$$

$$dS = -\frac{\partial V}{\partial T}\Big|_{P,\{N\}}dP$$

So, let me start with this first. And what is our goal? Our goal is basically to express fugacity in terms of experimental obtainable properties so, to express fugacity in terms of experimentally obtainable properties ok. Now, as we know from the Maxwell relation that at constant temperature and composition we have the following expression for the enthalpy in differential form and as well as we can write entropy in differential form, ok. So, this is directly from the Maxwell relations second one particularly. Now, we can integrate this expression.

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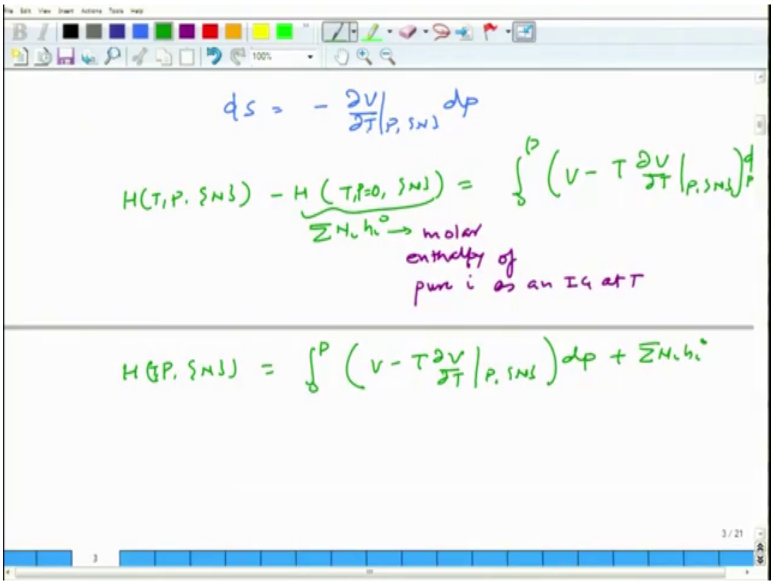

$$dS = -\left.\frac{\partial V}{\partial T}\right|_{P,\{N\}} dp$$

$$H(T,P,\{N\}) - \underbrace{H(T,P=0,\{N\})}_{\sum N_i h_i^0 \rightarrow \text{molar enthalpy of pure } i \text{ as an IG at } T} = \int_0^P \left(V - T\left.\frac{\partial V}{\partial T}\right|_{P,\{N\}}\right) dP$$

$$H(T,P,\{N\}) = \int_0^P \left(V - T\left.\frac{\partial V}{\partial T}\right|_{P,\{N\}}\right) dp + \sum N_i h_i^0$$

So, if I integrate the enthalpy expression. So, we have this minus H. So, if we integrating from pressure 0 to P. So, P equal to 0 and constant composition this is going to be 0 to P V minus T del V by del T at constant pressure and here is going to be d p.

Now, this is nothing, but at a 0 pressure we can approximate this to be another gas and thus in that case the partial molar enthalpy is nothing, but molar enthalpy. So, we can write this expression as summation N i h i 0 where this is nothing, but the molar enthalpy of pure I as an ideal gas at temperature T ok. So, we can rewrite this expression and I can get the following. So, I can take this term to the right hand side and this is the expression of enthalpy at temperature T P with the mole compositions here ok.

Now, similarly the way we have done for enthalpy we can also try to integrate the case for entropy ok. So, let me try to do that here. So, if you integrate this second expression which will written based on the Maxwell relation.

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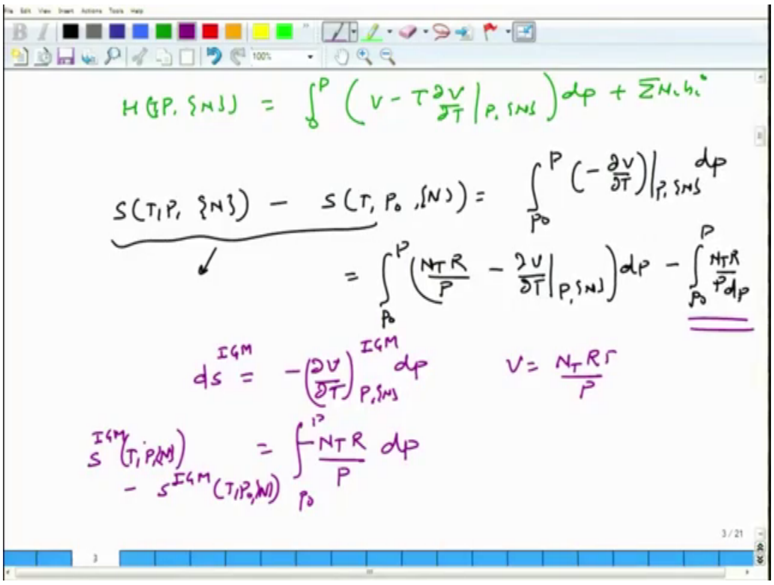

$$H(T,P,\{N\}) = \int_0^P \left(V - T\frac{\partial V}{\partial T}\Big|_{P,\{N\}}\right)dp + \sum N_i h_i^{\circ}$$

$$\underbrace{S(T,P,\{N\}) - S(T,P_0,\{N\})}_{\swarrow} = \int_{P_0}^{P}\left(-\frac{\partial V}{\partial T}\right)\Big|_{P,\{N\}} dp$$

$$= \int_{P_0}^{P}\left(\frac{N_T R}{P} - \frac{\partial V}{\partial T}\Big|_{P,\{N\}}\right)dp - \underline{\underline{\int_{P_0}^{P}\frac{N_T R}{P}dp}}$$

$$ds^{IGM} = -\left(\frac{\partial V}{\partial T}\right)^{IGM}_{P,\{N\}}dp \qquad V = \frac{N_T R T}{P}$$

$$S^{IGM}(T,P,\{N\}) - S^{IGM}(T,P_0,\{N\}) = \int_{P_0}^{P}\frac{N_T R}{P}\,dp$$

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We get S T P and N, minus S T P is 0 some P 0 which of course, could be close to 0 and this is from P 0 to P minus del V by del T at constant pressure and keeping N constant dp ok. So, note that this is simply the integration of this expression ok.

Now, what we can further do is we can take this right hand side ok. So, this is our right hand side and this expression comes here and I am going to play with the term. So, that I am going to insert N T R by P minus del V by del T at P dp and then since we have added here remember to subtract this term considering that this is going to be a simply ok.

The reason we have done this because this term is nothing, but the term corresponding to the ideal gas and let me just write that. So, we can go back to the original definition of this entropy again in the differential form and now, assume that to be for idle a mixture. So, ds is minus del V by del T at P N dp. Now, assume this to be for ideal gas mixture ok. Now, for ideal gas mixture of course, the equation of state we can write as V can be replaced by simply N T R T. So, here V is nothing, but dp ok. So, when you are going to differentiate with T you get nothing, but minus N T R P by dp, all right, ok.

So, if you integrate this we get the following from let us say from P 0 to P this is going to be S of IGM T P N minus S of IGM T P 0 M. Thus this expression is nothing, but this difference in the entropion ideal gas mixture from P 0 to P ok. So, I can now replace this ok.

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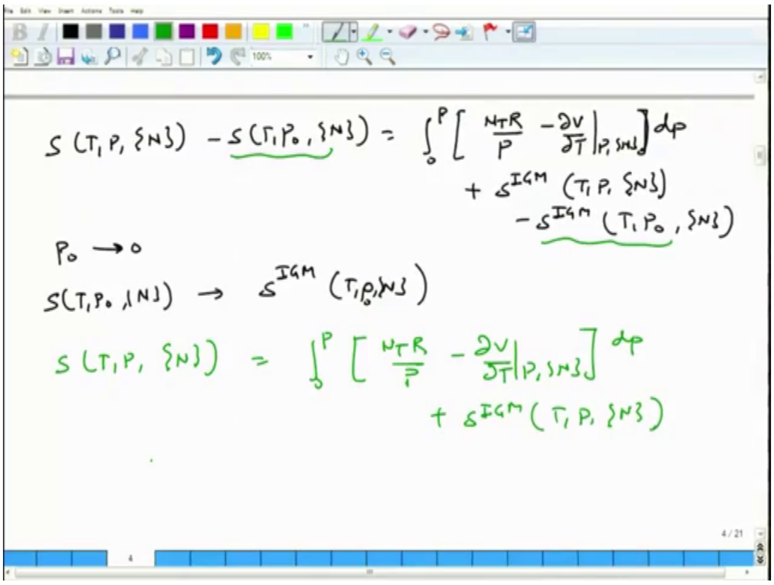

$$S(T,P,\{N\}) - \underline{S(T,P_0,\{N\})} = \int_0^P \left[\frac{N_T R}{P} - \frac{\partial V}{\partial T}\bigg|_{P,\{N\}} \right] dP + S^{IGM}(T,P,\{N\}) - \underline{S^{IGM}(T,P_0,\{N\})}$$

$$P_0 \to 0$$

$$S(T,P_0,\{N\}) \to S^{IGM}(T,P_0,\{N\})$$

$$S(T,P,\{N\}) = \int_0^P \left[\frac{N_T R}{P} - \frac{\partial V}{\partial T}\bigg|_{P,\{N\}} \right] dP + S^{IGM}(T,P,\{N\})$$

So, my left hand side expression is still S T P N minus S T P 0 N and my right hand side expression. Now, is plus S IGM T P and minus S IGM T P 0 N ok. Now, as I said P 0 now, u could be anything we can take it to be. Now, if we consider P 0 tending towards 0 ok, in this case of course, the ideal gas mixture at pressure P 0 behave as an ideal gas mixture. So, S T P 0 and is nothing, but S IGM T P 0, ok. So, it is basically ideal gas a mixture the entropy ok.

So, if that is the case then of course, this and this term should cancel each other because these are the same term because this will behave like an ideal gas at P 0 tending towards 0 ok. So, what remains now is S T P N is 0 to P plus S IGM at P. So, this is the term which we have ok.

Now, many times we take reference values of corresponding to one atmosphere. So, let me just rewrite this expression of delta S or S with reference to the pressure at one atmosphere and then we can simplify this with the data correspond to one atmosphere ok. So, what I was saying is basically that if I can write down instead of taking P 0 as 1, as 0.

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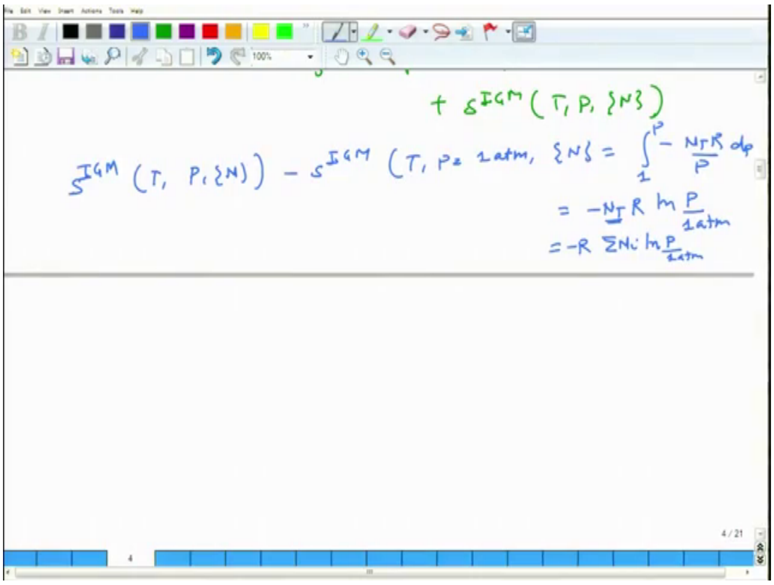

$$+ S^{IGM}(T, P, \{N\})$$

$$S^{IGM}(T, P, \{N\}) - S^{IGM}(T, P = 1\,atm, \{N\}) = \int_1^P -\frac{N_T R}{P}\,dp$$

$$= -\underline{N_T} R \ln \frac{P}{1\,atm}$$

$$= -R \sum N_i \ln \frac{P}{1\,atm}$$

We can also consider for an ideal gas as one atmosphere. Now, the right hand side expression remains the same because the ds integration here would be simply minus N T R for an ideal gas divided by P dp, but instead of P 0 we have 1 to P ok, which essentially means I can rewrite this expression as minus N T R ln P by 1 atmosphere ok. Now, N T is nothing, but summation of N i.

So, I can also write it minus R summation N i for i equal to 1 to m ln P 1 atmosphere ok. So, what we are doing going to do is we are further, so now, can make use of the expression of S IGM which we have evaluated earlier particularly for one atmosphere. So, this is going to be summation N i S i. So, I am just getting this value directly from our early expression minus R summation N i and y i, ok.

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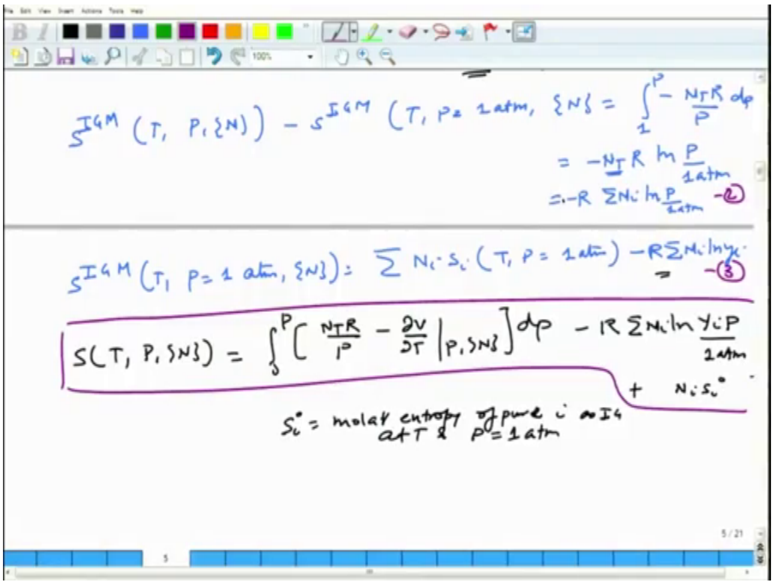

$$S^{IGM}(T, P, \{N\}) - S^{IGM}(T, P = 1\,atm, \{N\}) = \int_1^P -\frac{N_T R}{P}\,dp$$

$$= -N_T R \ln \frac{P}{1\,atm}$$

$$= -R \sum N_i \ln \frac{P}{1\,atm} \quad -②$$

$$S^{IGM}(T, P = 1\,atm, \{N\}) = \sum N_i S_i(T, P = 1\,atm) - R \sum N_i \ln y_i \quad -③$$

$$\boxed{S(T, P, \{N\}) = \int_0^P \left[\frac{N_T R}{P} - \frac{\partial V}{\partial T}\Big|_{P, \{N\}} \right] dp - R \sum N_i \ln \frac{y_i P}{1\,atm} + N_i S_i^0}$$

S_i^0 = molar entropy of pure i as IG at T & P = 1 atm

So, now, I have this expression. So, let me say this is expression number 1, this is 2 and this is 3 ok. So, if you combine this what we are going to get is S of T P summation N I, a summation sum of S of T P fall formal compositions here or number of moles here. Now, this should be equal to this term which we have written with respect to 0, 0 P, N T R by P minus del V by del T at constant pressure dp ok.

Now, we are going to use this expression here from here which depends on this pressure P 1 which is accessible pressure ok. So, I am going to take this on the right hand side and then I am going to use this expression this. So, we can combine this expression. So, let me write it here minus R summation N i ln y i P by 1 atmosphere plus summation N i, S i 0 ok.

So, what we have done is nothing but, we have combined this to this one and this one and this term we have written as simply N i is a 0 where S i 0 is nothing, but molar entropy of pure, pure i as an ideal gas at T and P is equal to 1 atmosphere ok. So, this is the expression we got ok. So, I have I have remember I combine this term and this term to get this term and this term is nothing, but this term. So, does this expression plus this expression together is this two expression. So, this is a simpler form of the entropy.

Now, given these two term which we have calculated for enthalpy and entropy. Now, you can extract other thermodynamic properties such as internal energy how much free energy in Gibbs free energy ok, with respect to this volumetric data in terms of independent variables V N R T ok.

So, let me just summarize this expression instead of deriving it ok. So, we have U is equal to H minus PV, ok.

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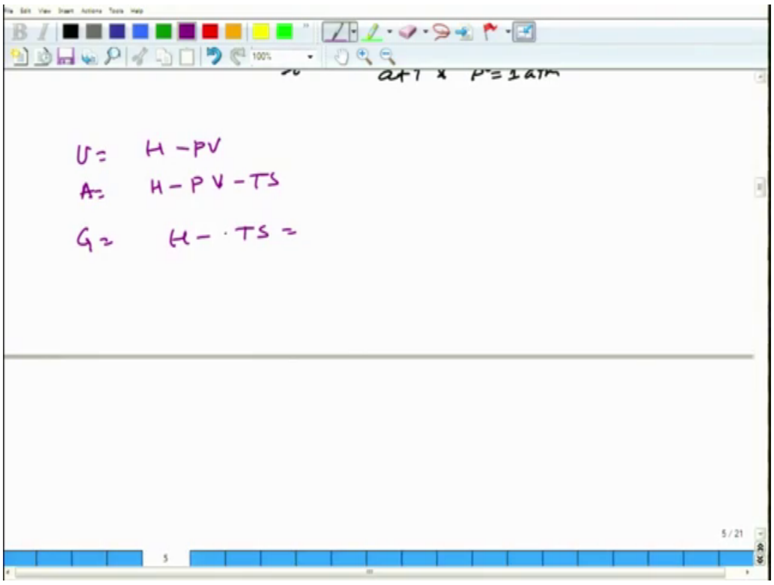

$U = H - PV$

$A = H - PV - TS$

$G = H - TS =$

So, since H we have already calculated our derived here this is the H value. So, we just have to add here minus PV ok. So, this term minus PV plus this term ok. Now, remove again, this is U minus PV similarly we can get a which is H minus PV minus TS and then you have this G which is H minus TS ok. Now, I can write this more explicitly because I will be using this G expression in calculating chemical potential.

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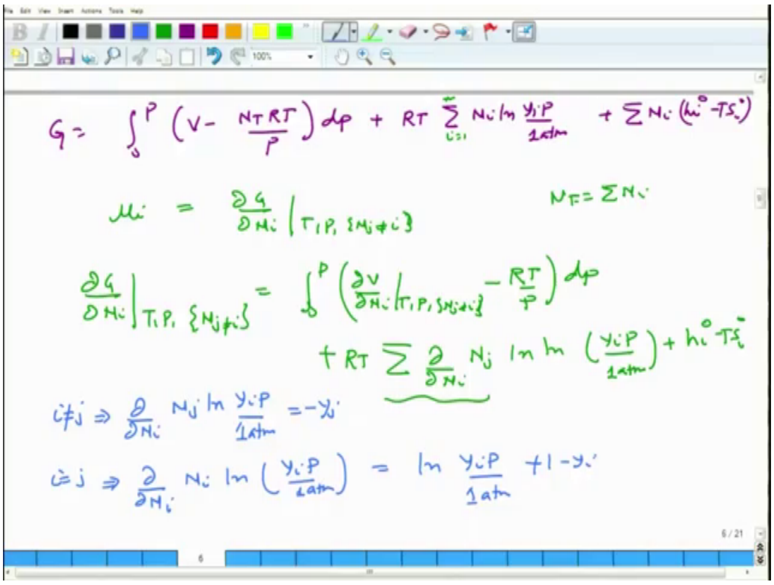

$$G = \int_0^P \left(V - \frac{N_T RT}{P}\right) dp + RT \sum_{i=1}^{m} N_i \ln \frac{y_i P}{1\,\text{atm}} + \sum N_i (h_i^0 - T s_i^\circ)$$

$$\mu_i = \left.\frac{\partial G}{\partial N_i}\right|_{T, P, \{N_{j \neq i}\}} \qquad N_T = \sum N_i$$

$$\left.\frac{\partial G}{\partial N_i}\right|_{T, P, \{N_{j \neq i}\}} = \int_0^P \left(\left.\frac{\partial V}{\partial N_i}\right|_{T, P, \{N_{j \neq i}\}} - \frac{RT}{P}\right) dp + RT \underbrace{\sum \frac{\partial}{\partial N_i}}\, N_j \ln \ln \left(\frac{y_i P}{1\,\text{atm}}\right) + h_i^0 - T s_i^\circ$$

$$i \neq j \Rightarrow \frac{\partial}{\partial N_i} N_j \ln \frac{y_i P}{1\,\text{atm}} = -y_i$$

$$i = j \Rightarrow \frac{\partial}{\partial N_i} N_i \ln \left(\frac{y_i P}{1\,\text{atm}}\right) = \ln \frac{y_i P}{1\,\text{atm}} + 1 - y_i$$

So, let me first let me write down g for that how what would be the G, G is nothing, but H first I m going to write this H 0 to P V minus N T R T divided by P and the other term which is N i h i 0 will come somewhere here, plus this TS term ok. So, this will be T summation N i ln y i P divided by 1 atmosphere and minus TS i will come here ok. So, again this is the P term. So, what will happen here is basically this two terms got cancelled this term and the corresponding if you look at here V term V minus TV by T this this and this term got cancelled. So, what remain was N T R P and V term ok. So, this is how you are going to get this expression G.

Now, this expression you can make use in order to calculate the chemical potential ok. So, what is the chemical potential? Of course, chemical potential is the partial molar derivative of Gibbs free energy. So, I am going to define here del G by del N i T P for all other j's and j is constant ok. Now, we can we can evaluate this expression further. So, let us take a derivative of this. So, what is partial derivative of G with respect to N i ok. Remember this N T is summation N i ok.

So, del G by del N i is going to be 0 to P del V by del N i minus RT by P since N T is equal to summation I when I am going to take the derivative with respect to N i is going to be 1 plus RT summation del del N i. Now, here since I am using i, since i is 1 to m and here this is a specific i. So, I am going to change this to N j ln y iP by 1 atmosphere plus summation N i will be one if take the derivative of this, this would leave one. So, what remains is basically h i 0 minus TS i 0 ok.

Now, I will not derive this part this is a bit tricky ok, but this you should be able to show that for I is equal to not equal to j del N by del N i and j and then y i P by 1 atmosphere is simply minus yi j and when i is equal to j this would be N i ln y I P one atmosphere is going to be simply ln y i P by 1 atmosphere plus 1 with this and the other 1 minus y i ok. So, of course, now, this can be separate separated into two parts, one with this and other with this part ok, all right.

So, if you do this exercise what you get is that summation of this is nothing but or the derivative of this is nothing, but ln by i P 1 atmosphere is equal to 1 minus yi minus some of y i for all i not equal to j and of course, this is nothing, but simply this should be plus ok. So, this is nothing, but 1 minus y i. So, this cancels out ok. So, what remains is this ok.

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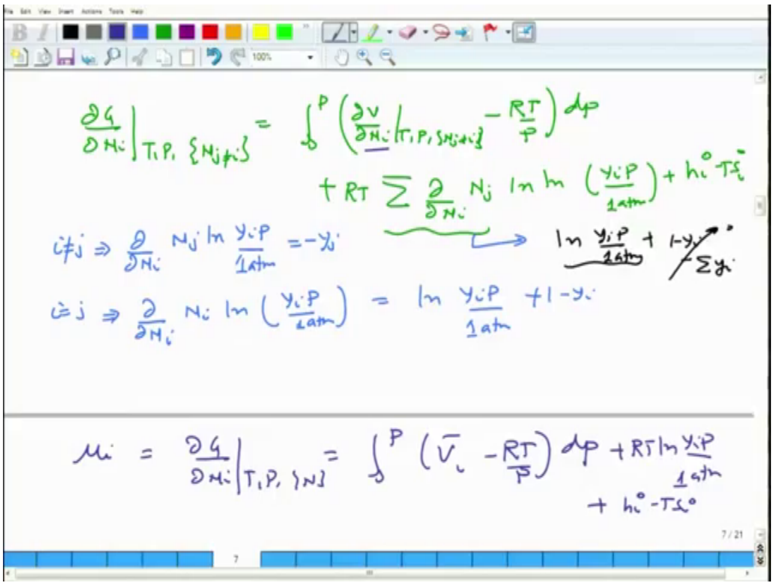

$$\left.\frac{\partial G}{\partial N_i}\right|_{T,P,\{N_{j\neq i}\}} = \int^{P}\left(\left.\frac{\partial V}{\partial N_i}\right|_{T,P,\{N_{j\neq i}\}} - \frac{RT}{P}\right)dp + RT\underbrace{\sum \frac{\partial}{\partial N_i} N_j \ln\ln\left(\frac{y_iP}{1\,atm}\right)} + h_i^0 - TS_i^0$$

$$\longrightarrow \underline{\ln\frac{y_iP}{1\,atm}} + \cancel{1-y_i}\ \cancel{\sum y_i}$$

$$i\neq j \Rightarrow \frac{\partial}{\partial N_i} N_j \ln\frac{y_iP}{1\,atm} = -y_i$$

$$i=j \Rightarrow \frac{\partial}{\partial N_i} N_i \ln\left(\frac{y_iP}{1\,atm}\right) = \ln\frac{y_iP}{1\,atm} + 1 - y_i$$

$$\mu_i = \left.\frac{\partial G}{\partial N_i}\right|_{T,P,\{N\}} = \int^{P}\left(\bar{V}_i - \frac{RT}{P}\right)dp + RT\ln\frac{y_iP}{1\,atm} + h_i^0 - TS_i^0$$

So, thus we have an expression of mu i is equal to del g by del N i T P which is 0 to P this is nothing, but partial molar volume minus RT by P dp plus RT ln y i P by 1 atmosphere plus h i 0 minus T is 0 ok. So, this is the expression which we got. Now, the last leg of this derivation is to connect this expression to the fugacity ok.

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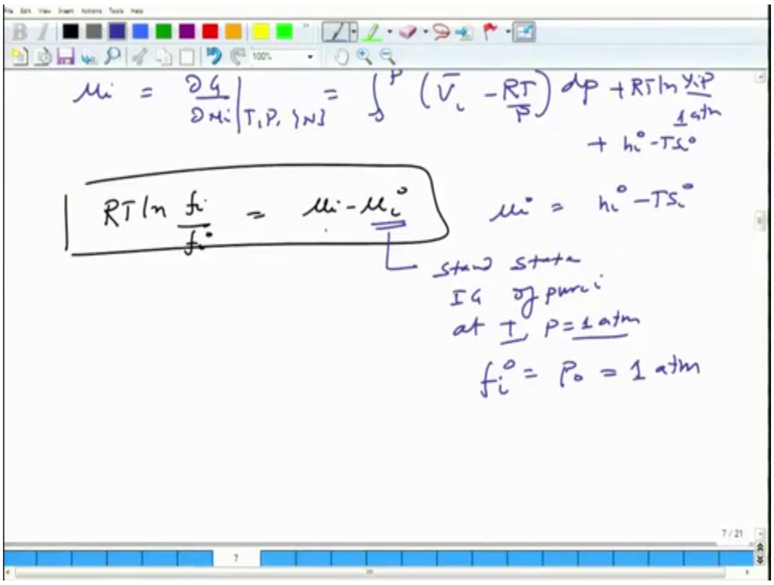

$$\mu_i = \frac{\partial G}{\partial N_i}\Big|_{T,P,\{N\}} = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dp + RT\ln\frac{y_iP}{1\,atm} + h_i^0 - Ts_i^0$$

$$\boxed{RT\ln\frac{f_i}{f_i^0} = \mu_i - \underline{\mu_i^0}}$$

$$\mu_i^0 = h_i^0 - Ts_i^0$$

stand state IG of pure i at T, P = 1 atm

$$f_i^0 = P_0 = 1\ atm$$

So, let us do that now, from fugacity definition we have RT ln fi by fi 0 ok. Now, suppose that the standard state which we are using here is a. So, this is a standard state chemical potential. So, we consider this as idle gas of pure i at T and P is equal to 1 atmosphere. So, let us assume this is a standard state in that case mu i is nothing, but for the pure nothing, but small gi which is going to be h i 0 minus T i 0 considering this to be these conditions for the pure case ok. And of course, considering the standard state is an idol gasps fi 0 is going to beat P 0 which is nothing going to be 1 atmosphere ok.

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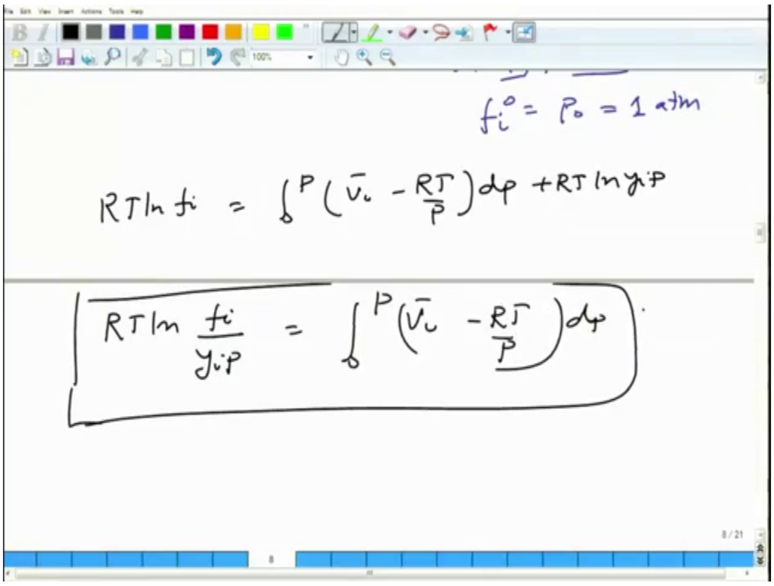

$$f_i^0 = P_0 = 1\ atm$$

$$RT\ln f_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dp + RT\ln y_iP$$

$$\boxed{RT\ln\frac{f_i}{y_iP} = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dp}$$

Now, given this we can plug our mu here ok. So, RT ln fi because fi 0 is equal to 1 this is going to be 0 to P V i bar minus RT by P dp plus RT ln y i P. So, I am removing this 1 atmosphere because that gets cancelled by fi 0 and mu i 0 gets cancelled by h i minus T i. So, what remains is only this term. This further can be simplified as T ln fi y i P 0 to P V i bar minus RT by P dp ok.

So, I have taken out this expression here and this comes out in the denominator. So, I have this expression for fugacity or in this case is going to be fugacity coefficient this ratio which relates to the volumetric property as V i bar minus RT by P integration from 0 to P dp, ok.

I will stop here and then I will continue this exercise by taking certain assumptions and connecting with some experimental information or data ok. So, I will see you in the next lecture.