Chemical Engineering Thermodynamics

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Lecture – 25
Excess Properties

Hello and welcome back. In this previous lecture, we try to understand how a mixture of chemical species behave or how we can calculate thermodynamic properties for a mixture of chemical species. In today's lecture we start working with what are known as Excess Properties. But, before we do that, as usual, let us quickly recap what we have done so far in this section.

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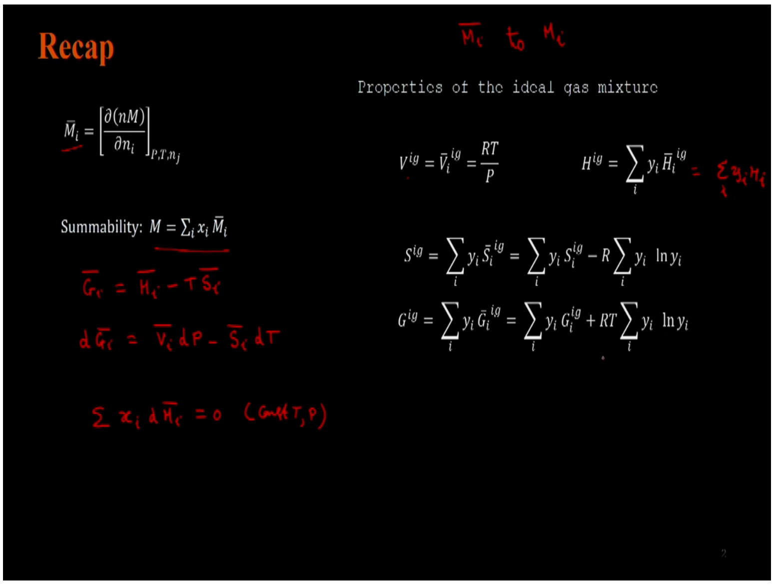

Recap

$\bar{M}_i$ to M_i

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

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

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

$$d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$$

$$\sum x_i d\bar{H}_i = 0 \quad (\text{Const } T, P)$$

Properties of the ideal gas mixture

$$V^{ig} = \bar{V}_i^{ig} = \frac{RT}{P} \qquad H^{ig} = \sum_i y_i \bar{H}_i^{ig} = \sum_i y_i H_i$$

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

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

In a mixture of chemical species we have defined a quantity known as the partial molar property M i bar, right and then we have related it to the total property of the mixture we are the summability relation weighted with the mole fraction of that particular species. And then we have interdependency among various thermodynamic properties in terms of partial molar properties such as G i bar which we also call as chemical potential by the way was H i bar minus TS i bar similar to G is H minus TS and so on.

And in addition the change in this property dG i bar is at constant composition is V i bar dP minus S i bar dT. This is similar to dG's VdP minus SdT. In addition to these relationships amongst the partial molar properties we also had interdependency we are the Gibbs Duhem equation which leads x i d M i bar or summation of x i d M i bar is 0 at constant temperature and pressure. So, in that sense in a binary mixture M 1 bar and M 2 bar are going to be related to one another. Once we identify these relationships we went on to look at how a mixture or how the partial molar properties in a mixture themselves are going to be related to the properties of the pure species or in other words how M i bar is going to be related to M i.

And we worked out way through this by first considering ideal gas mixtures wherein we said for an ideal gas mixture the molar volume or the partial molar volume and the partial molar enthalpy are going to be same as the pure component values and hence in a mixture V ig, V for the mixture is going to be same as V i bar ig and h for the mixture is going to be summation of y i H i bar ig. So, this will be summation of y i H i right. And for entropy and Gibbs free energy; however, there are going to be additional terms these are the additional terms in addition to the pure component values S i ig and G i ig.

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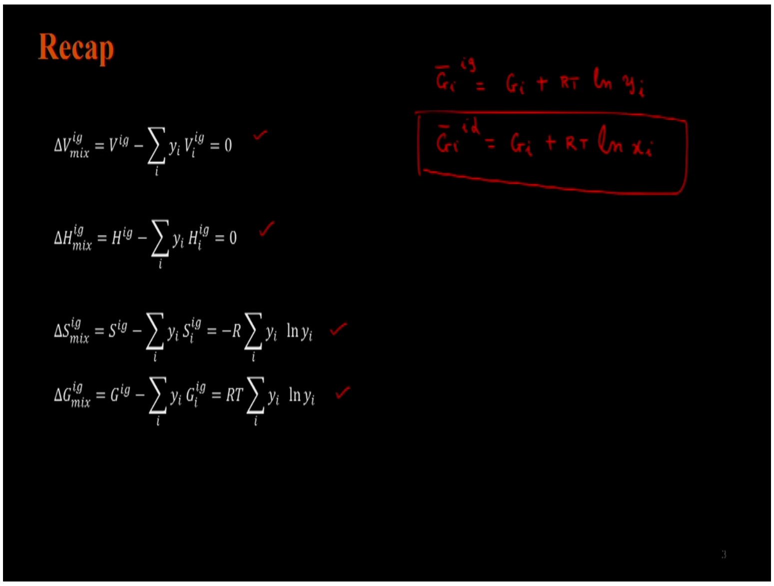

Recap

$\Delta V^{ig}_{mix} = V^{ig} - \sum_i y_i V^{ig}_i = 0$ ✓

$\Delta H^{ig}_{mix} = H^{ig} - \sum_i y_i H^{ig}_i = 0$ ✓

$\Delta S^{ig}_{mix} = S^{ig} - \sum_i y_i S^{ig}_i = -R \sum_i y_i \ln y_i$ ✓

$\Delta G^{ig}_{mix} = G^{ig} - \sum_i y_i G^{ig}_i = RT \sum_i y_i \ln y_i$ ✓

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

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

And we also defined quantities known as the property changes upon mixing and for ideal gases. The property change upon mixing for volume and enthalpy are 0 whereas, they are not 0 for entropy change upon mixing and Gibbs free energy change upon mixing.

Once we know the mole fractions we can calculate these quantities. This is for an ideal gas mixture and we said we are going define ideal solution such that it behaves in a similar fashion of the Gibbs free energy change upon mixing or rather the partial molar

Gibbs free energy change whichever way we want to look at it is going to be related to the pure species Gibbs free energy through a similar equation as that in case of an ideal gas. For example, in an ideal gas G i bar ig is plus RT ln y i and we said in an ideal solution G i bar id is going to be related through an analogous equation G i plus RT ln x i.

This ideal solution can be applied to dense phases, dense gases or liquids as well the only requirement is that the partial molar Gibbs free energy for species i for each species i in a mixture is related to the pure component Gibbs free energy we have this equation. And once that happens it turns out all the property changes upon mixing we have identified for ideal gas mixtures are going to be same for ideal solutions also. The only difference is that these are not ideal gases they can be dense phases liquid phases, but as long as this property is satisfied then all the property changes upon mixing are going to be exactly same as in case of an ideal gas mixture.

Now, of course, in real life we will not have ideal solutions. Always ideal solutions occur as we said when we have molecular species or the constituents of the mixture if the constituents of the mixture have all the species in the mixture have similar molecular size and similar chemical nature. For example, adjacent species in a homologous series or isomers etcetera where they are likely to occur. On the other hand real mixtures can be non ideal just like we have ideal gases and non ideal gases we can have mixtures which do not form ideal solutions then how do we quantify such mixtures.

We are going to resort to a similar exercise as we have done for real gases. For real gases recall that we have identified a property known as residual property which is the difference between the property of the real gas minus that of the ideal gas. So, this property in a sense indicates how far away from ideality we are. So, we are going to define a similar property so that we identify the deviation from an ideal solution.

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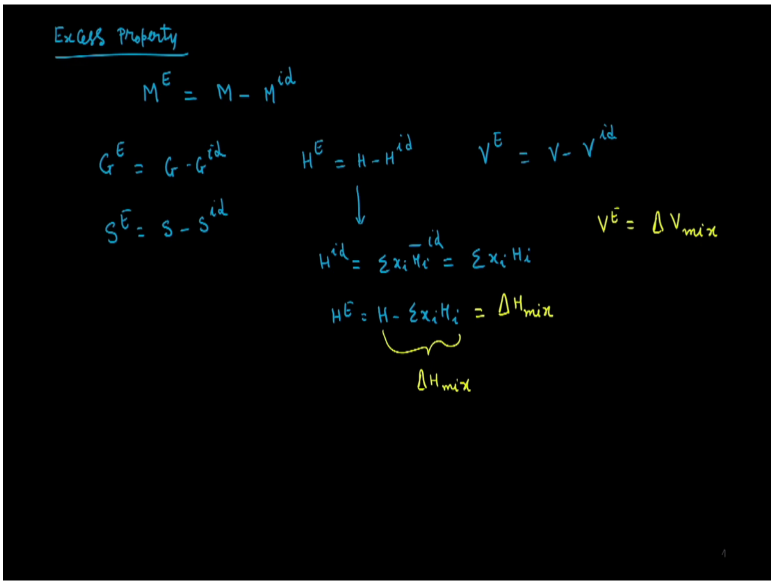

Excess Property

$$M^E = M - M^{id}$$

$$G^E = G - G^{id} \qquad H^E = H - H^{id} \qquad V^E = V - V^{id}$$

$$S^E = S - S^{id} \qquad V^E = \Delta V_{mix}$$

$$\downarrow$$

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

$$H^E = \underbrace{H - \Sigma x_i H_i}_{\Delta H_{mix}} = \Delta H_{mix}$$

This property is known as excess property. We define excess property M E; E be in the excess property as M the property of the solution minus the property in an ideal solution. This M can be anything for example, it can be Gibbs free energy. So, G E is going to be G minus G ideal any thermodynamic property or H E the excess enthalpy is going to be H minus H ideal. The excess volume is going to be V minus V ideal and so on and of course, S E let us write that also is S minus S for the ideal solution.

If you recall H for the ideal solution is sigma x i H i bar id, this is the summability relation and in an ideal solution H i bar id is same as x i H i for the pure species. So, that implies H E is going to be H minus sigma x i H i by definition and recall that this quantity we have also called it as delta H mixing. So, in that sense H E is going to be exactly identical to delta H mixing and similarly V E is going to be exactly identical to delta V mixing this is because V for an ideal is also sigma x i V i, but G E and S E of course, are not going to follow this follow this relationships they are simply G minus G ideal and S minus S ideal.

So, we have identified excess properties now. These are defined as the differences between the property and that of a property of an ideal solution. Let us also try to get some relationships with respect to excess properties and what we will do is a we will try to identify commonality in the relationships between the total properties, the residual properties and excess properties so that it is easy to comprehend all the three of them put together, but before we do that let us quickly derive the fundamental property relationship based on Gibbs free energy one more time.

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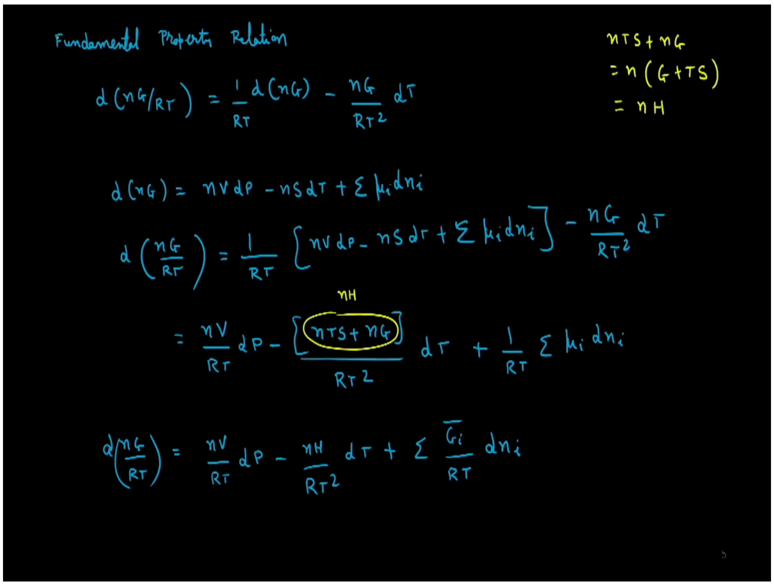

Fundamental Property Relation

$$d(nG/RT) = \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT$$

$$nTS + nG$$
$$= n(G + TS)$$
$$= nH$$

$$d(nG) = nV dP - nS dT + \Sigma \mu_i dn_i$$

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\left[nV dP - nS dT + \Sigma \mu_i dn_i\right] - \frac{nG}{RT^2} dT$$

$$= \frac{nV}{RT} dP - \frac{\left[\overset{nH}{\boxed{nTS + nG}}\right]}{RT^2} dT + \frac{1}{RT} \Sigma \mu_i dn_i$$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT} dP - \frac{nH}{RT^2} dT + \Sigma \frac{\bar{G}_i}{RT} dn_i$$

The fundamental property relation in terms of Gibbs free energy if I want to write d nG over RT then it will be d of nG 1 over RT minus nG by RT square dT and for an open system if you recall d nG is nV dP minus nS dT plus sigma mu i d n i.

What I will do is I will use this relation in the first equation so that I get d of nG over RT is going to be 1 over RT n V dP minus nS dT plus sigma over i mu i d n i minus nG by RT square dT is the last term. We will simplify this what we get is nV over RT dP minus n times TS plus nG all of it over RT square dT plus 1 over RT sigma of mu i d n i, right and if you notice n times if you notice n times TS; n times TS plus nG is n of G plus TS and because G is H minus TS this will turn out to be nH.

So, what I can do is substitute an H here. So, this will turn out to be nV by RT dP minus nH by RT square dT plus sigma over I am going to replace chemical potential with partial molar Gibbs free energy both are identical d n i and this is the quantity d of nG over RT. This is going to be our fundamental property relationship in terms of G as the generating function.

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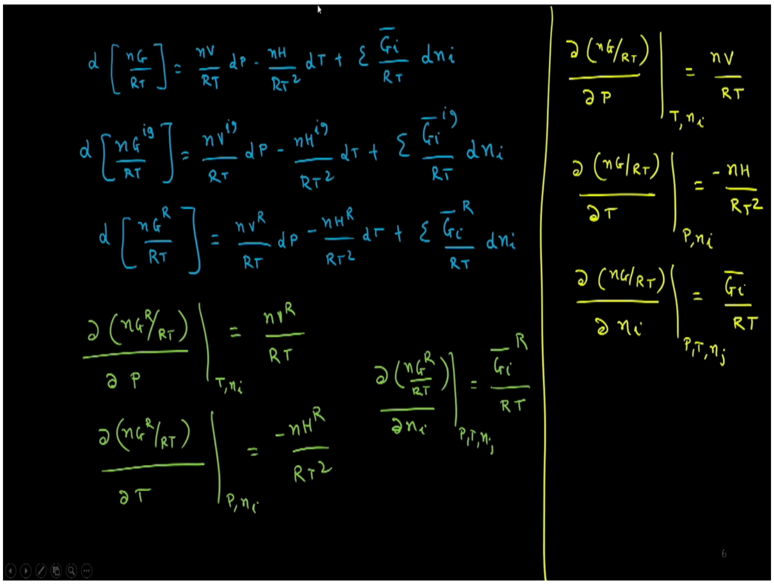

$$d\left[\frac{nG}{RT}\right] = \frac{nV}{RT}dP - \frac{nH}{RT^2}dT + \sum \frac{\bar{G}_i}{RT}dn_i$$

$$d\left[\frac{nG^{ig}}{RT}\right] = \frac{nV^{ig}}{RT}dP - \frac{nH^{ig}}{RT^2}dT + \sum \frac{\bar{G}_i^{ig}}{RT}dn_i$$

$$d\left[\frac{nG^{R}}{RT}\right] = \frac{nV^{R}}{RT}dP - \frac{nH^{R}}{RT^2}dT + \sum \frac{\bar{G}_i^{R}}{RT}dn_i$$

$$\left.\frac{\partial (nG^R/RT)}{\partial P}\right|_{T,n_i} = \frac{nV^R}{RT}$$

$$\left.\frac{\partial (nG^R/RT)}{\partial T}\right|_{P,n_i} = \frac{-nH^R}{RT^2}$$

$$\left.\frac{\partial (\frac{nG^R}{RT})}{\partial n_i}\right|_{P,T,n_j} = \frac{\bar{G}_i^R}{RT}$$

$$\left.\frac{\partial (nG/RT)}{\partial P}\right|_{T,n_i} = \frac{nV}{RT}$$

$$\left.\frac{\partial (nG/RT)}{\partial T}\right|_{P,n_i} = -\frac{nH}{RT^2}$$

$$\left.\frac{\partial (nG/RT)}{\partial n_i}\right|_{P,T,n_j} = \frac{\bar{G}_i}{RT}$$

So, we will take this relation d of nG over RT is nV by RT dP minus nH by RT square dT plus sigma over i G i bar by RT d n i. Once we look at this relationship a few derivatives need to be easily written. Derivative of nG over RT with respect to the pressure at constant T and n i is going to be nV over RT, right. We are holding T constant and we are holding n i constant.

So, both these terms disappear and the derivative will turn out to be nV over RT. Similarly derivative of nG over RT with respect to temperature at constant P and n i is going to be negative nH by RT square, in this case we are holding the pressure constant. So, this term disappears and n i constant. So, this term disappears all n i in fact, constant. So, this term disappears and we have negative nH by RT square and finally, derivative of nG over RT with respect to n i when I hold the temperature pressure and all the n j's that are not equal to i constant will be G i bar by RT which essentially is the definition for the partial molar Gibbs free energy anyway.

So, these are the 3 derivatives one can easily write looking at this equation. What we can also do is write this equation for an ideal gas nG ig by RT is nV ig by RT dP minus nH ig by RT square dT plus sigma G i bar ig by RT d n i. I can subtract one from the other, so that I get d of nG R by RT this is the residual Gibbs free energy if you recall the definition of residual Gibbs free energy is G minus G i j is nV R by RT dP minus nH R by RT square dT plus sigma G i bar R by RT d n i, right.

So, now if I look at equation 3 I can easily write again these equations derivative of nG R by RT over pressure at constant T and n i or T and x if n i is constant or the composition x itself is constant is going to be nV R by RT. Now, compare this equation with the one for the total property.

These are identical except that I have replace the total property M with residual property M R similarly derivative of nG R by RT with respect to T at constant P and n i is going to be negative nH R by RT square and finally, derivative of nG R by RT with respect to n i is going to be G i bar R, the partial molar residual Gibbs free energy G i bar R over RT. This is the scenario for the residual properties. What we can do is we can also take and write similar expressions for excess properties.

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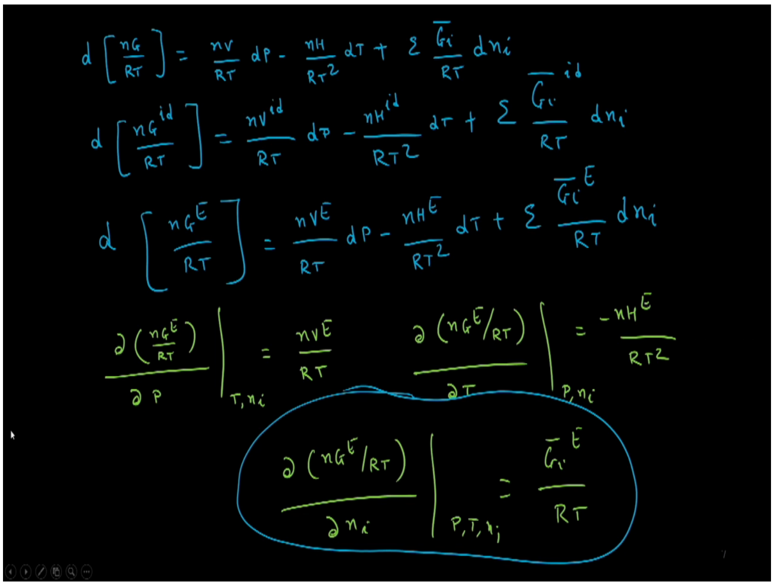

$$d\left[\frac{nG}{RT}\right] = \frac{nV}{RT}dP - \frac{nH}{RT^2}dT + \sum \frac{\bar{G}_i}{RT}dn_i$$

$$d\left[\frac{nG^{id}}{RT}\right] = \frac{nV^{id}}{RT}dP - \frac{nH^{id}}{RT^2}dT + \sum \frac{\bar{G}_i^{id}}{RT}dn_i$$

$$d\left[\frac{nG^E}{RT}\right] = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum \frac{\bar{G}_i^E}{RT}dn_i$$

$$\left.\frac{\partial\left(\frac{nG^E}{RT}\right)}{\partial P}\right|_{T,n_i} = \frac{nV^E}{RT} \qquad \left.\frac{\partial\left(nG^E/RT\right)}{\partial T}\right|_{P,n_i} = \frac{-nH^E}{RT^2}$$

$$\boxed{\left.\frac{\partial\left(nG^E/RT\right)}{\partial n_i}\right|_{P,T,n_j} = \frac{\bar{G}_i^E}{RT}}$$

We will start with the fundamental relation property relation d nG by RT is nV by RT dP minus nH by RT square dT plus sigma G i bar by RT d n i and I can write it for an ideal solution also it will be nV id by RT dP minus nH id by RT square dT plus sigma G i bar by RT for ideal solution d n i. I subtract one from the other. What I get is d nG E by RT; the excess Gibbs free energy is going to be related to the excess volume times dP excess enthalpy dT plus sigma G i bar E by RT d n i. G i bar E being the partial molar excess Gibbs free energy.

Now, compare this equation for excess property with the previous equation for residual property the equations look identical, the excess property simply needs to be replaced with the residual property. And as in this case I can again write all the derivatives we have written earlier the derivative of excess Gibbs free energy over pressure at constant temperature and n i is going to be nV E by RT. Its derivative n G E by RT with respect to temperature at constant pressure and n i is going to be negative nH E by RT square and finally, the derivative of G E by RT with respect to n i at P, T and n j is going to be negative G i sorry, it is going to be G i bar E by RT.

So, again these relationships are exactly identical to the ones in residual properties or the total properties you. Just want to make one final comment before we end this discussion on the similarities between M, M a and M R in terms of fundamental property relations.

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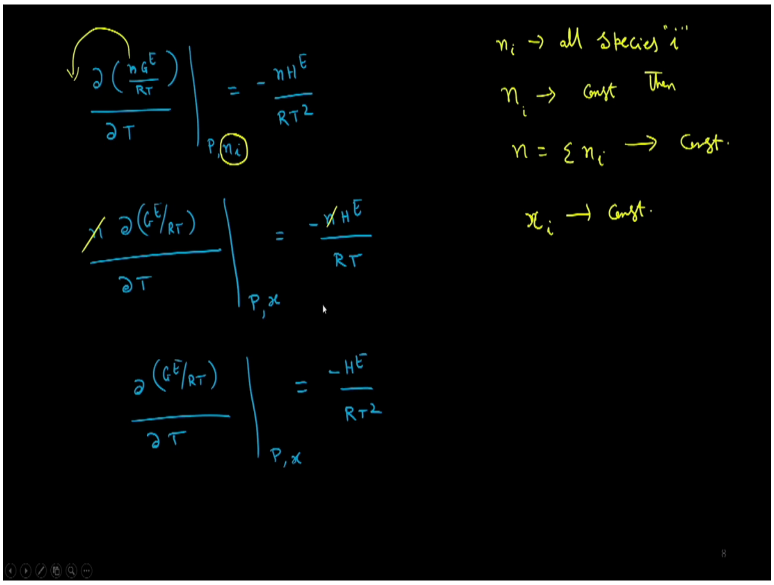

$$\left.\frac{\partial\left(\frac{nG^E}{RT}\right)}{\partial T}\right|_{P,\boxed{n_i}} = -\frac{nH^E}{RT^2}$$

$$\left.\frac{\cancel{n}\,\partial\left(G^E/RT\right)}{\partial T}\right|_{P,x} = -\frac{\cancel{n}H^E}{RT}$$

$$\left.\frac{\partial\left(G^E/RT\right)}{\partial T}\right|_{P,x} = \frac{-H^E}{RT^2}$$

$n_i \to$ all species "i"

$n_i \to$ Const Then

$n = \sum n_i \longrightarrow$ Const.

$x_i \longrightarrow$ Const.

Let us use another slide in any of these cases if you look at it we said the derivative of nG E by RT, we will take one example with respect to temperature let us say at P and n i is negative nH E by RT square. Now, if you look at this what I am holding constant when I take the derivative on the left hand side is the pressure of course and n i; n i being all species i or the moles of all species i are held constant. If moles of all species I are held constant n if n i is constant then n which is summation of n i will also be constant.

If n is constant then this can come out of the derivative here, right and on this side also I have n. So, that will cancel out n times derivative of G E by RT over dou T and because n i is constant x i is also constant; n i is constant n is constant so, x i the mole fraction needs to be constant. So, instead of calling it as at constant n i we can also say it is at constant x will be negative nH E by RT square and n on both sides can be omitted.

So, what I have in a fact is the derivative of G E over RT at constant temperature sorry, with respect to temperature at constant pressure and mole fraction is going to be equal to negative H E by RT square. So, I can write use this fundamental property relation and also write the dependencies of molar properties themselves, I do not have to use the total property all the time.

The only place where total property needs to be used is when we define the partial molar properties. So, for example, in the last equation here one of the n is changing all the other n j’s are constant over here I cannot say that n is constant because one of the n i's is changing, but in the first two equations when all the n i's are constant I can write that equation either for the total property or the molar property, right.

So, that is the takeaway from this particular exercise we can write the fundamental property relation with Gibbs free energy as the generating function and the total property, the residual property, as well as the excess property all follow analogous relationships. Now, in addition to this there are other auxiliary properties one can define in terms of excess properties, right.

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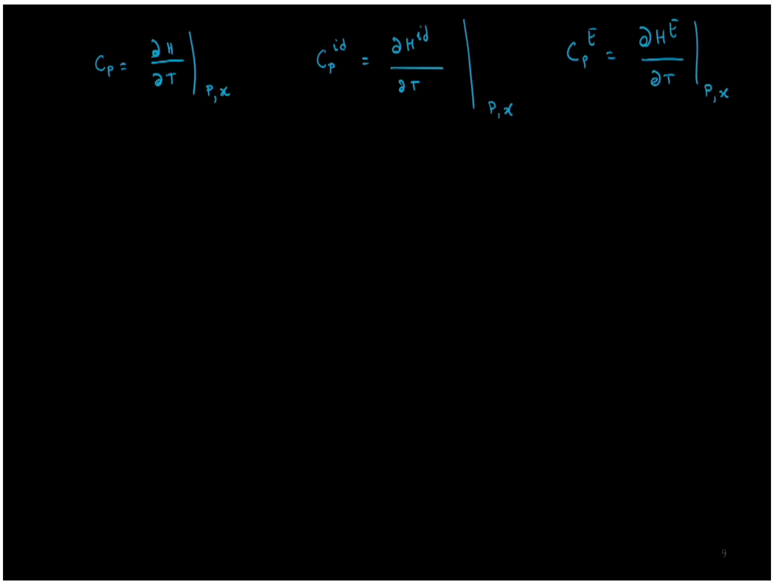

$$C_p = \left.\frac{\partial H}{\partial T}\right|_{P,x} \qquad C_p^{id} = \left.\frac{\partial H^{id}}{\partial T}\right|_{P,x} \qquad C_p^{E} = \left.\frac{\partial H^{E}}{\partial T}\right|_{P,x}$$

For example, if you recall, right C P was derivative of H with respect to temperature at constant pressure and in a multi component mixture not just pressure even the mole fraction for that mixture needs to be held constant. This is the definition for the specific heat capacity C P. One can write it for an ideal solution derivative of H for the ideal solution over derivative of temperature at constant P and x and C P E will then be derivative for the excess enthalpy with respect to temperature at constant P and x.

So, this is called as the heat excess specific heat capacity at constant pressure. We can write similar relationships as we did earlier for specific heat capacity.

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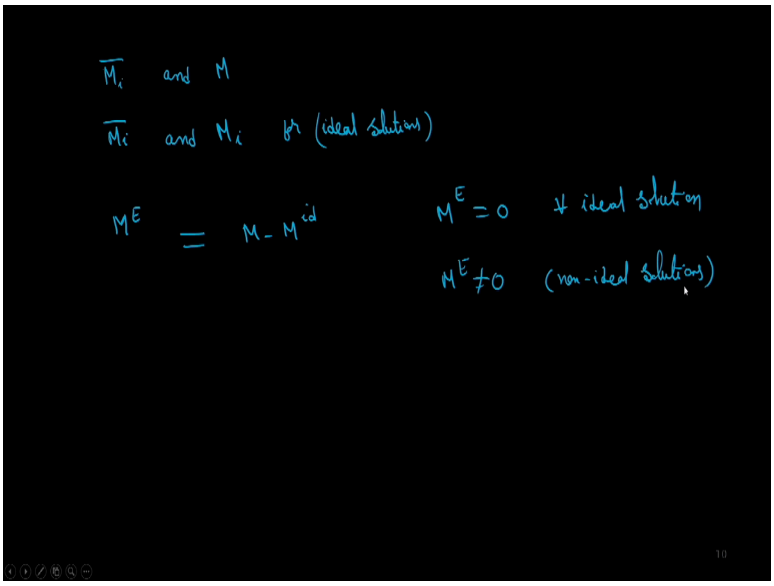

$\bar{M}_i$ and M

$\bar{M}_i$ and M_i for (ideal solutions)

$M^E = M - M^{id}$

$M^E = 0$ ∀ ideal solution

$M^E \neq 0$ (non-ideal solutions)

Now, having said this what we have done then is we have identified relationship between the property right; what we have so far is we have identified a relationship between M i bar and M that is the summability relation and we have also identified a relationship between M i bar and M i for ideal solutions or mixture of ideal gases.

So, I know how M i bar is related to M i for ideal solutions. In addition we have also defined a quantity known as the excess quantity which is M minus M ideal. So, M E will be 0 for all ideal solutions because of this definition and if the solution is non-ideal M E is not going to be 0 for non ideal solutions, right. Correctly some of the M E's are not going to be 0 for non ideal solutions. Then the next thing we want to do is there were ideal gases and then we have non-ideal gases, we have defined residual properties to characterize non ideal gases and we used equation of state Pitzer correlations or Lee Kesler tables etcetera to obtain residual properties.

Similarly, how does one obtain excess properties? If I have an ideal solution and if I want to quantify thermodynamic properties then to quantify thermodynamic properties in non ideal solutions we need some information about the excess properties if we are going to take this route. So, how does one get excess properties? Will for most of our cases in chemical engineering applications we are going to use Gibbs free energy as our generating function. So, what we are interested in is obtaining excess Gibbs free energy.

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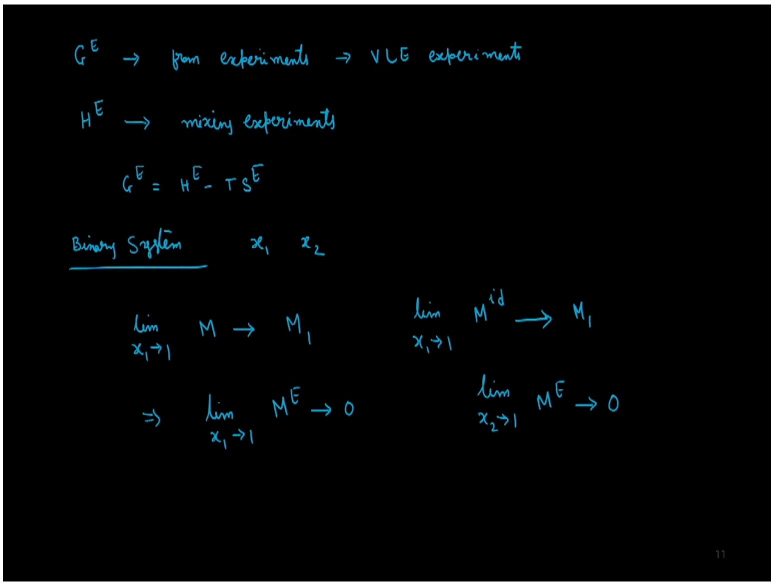

$G^E \rightarrow$ from experiments $\rightarrow$ VLE experiments

$H^E \rightarrow$ mixing experiments

$$G^E = H^E - TS^E$$

Binary System $\quad x_1 \quad x_2$

$$\lim_{x_1 \to 1} M \rightarrow M_1 \qquad \lim_{x_1 \to 1} M^{id} \longrightarrow M_1$$

$$\Rightarrow \lim_{x_1 \to 1} M^E \rightarrow 0 \qquad \lim_{x_2 \to 1} M^E \rightarrow 0$$

So, then we are looking for models for excess Gibbs free energy. So, usually it turns out that the excess Gibbs free energy data G E is obtained from experiments and typically from VLE experiments or Vapor Liquid Equilibrium experiments and H E if you recall is the excess enthalpy and we also said because of the property of ideal solutions H E will also be same as delta H mixing or the enthalpy change upon mixing. So, H E is usually obtained from mixing experiments. Once we have G E and H E we can readily calculate S E from the relation G E is H E minus TS E. So, we have G E and S H E so, we can calculate S E the excess entropy.

This is the usual route that is followed to get the excess properties. How do these excess properties can we broadly talk about, how these excess properties are going to behave? Let us see. Let us consider a binary system for this discussion. We have 2 components and the mole fractions of the 2 components are x 1 and x 2 and at the limit of x 1 going to 1, right M any thermodynamic property M if you recall we said is going to approach the pure component property M 1. At this limit M in an ideal solution also will approach M 1 which implies at the pure component limit the excess property will go to 0.

This is true for all excess properties right and not just for pure component limit of 1. In fact, this logic should also hold for pure component limit of 2. The excess property should go to 0; of course, at that limit M will approach M 2, M id will also approach M 2 the pure component property of 2. Other than that there is no particular thermodynamic restriction on how excess properties such as G E or H E need to behave.

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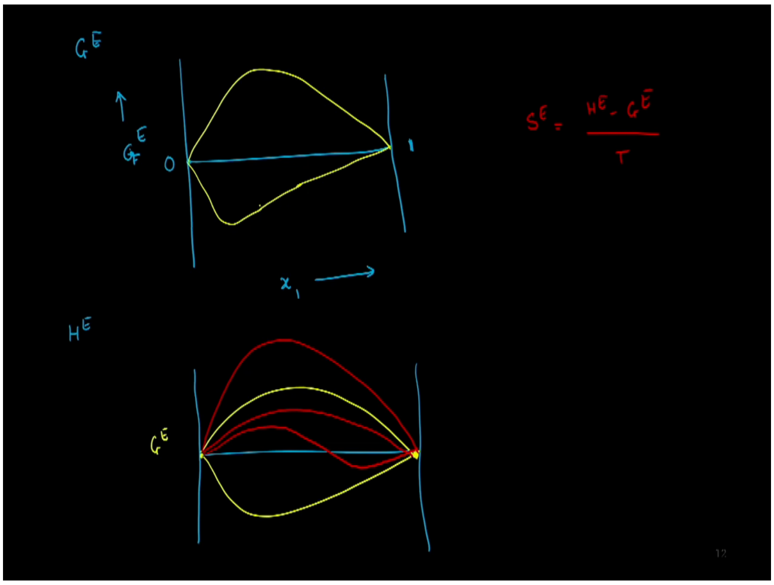

For example G E can be greater than 0. Let us say this is 0, I have G E on y axis and x 1 this is a binary mixture on x axis going from 0 to 1 and G E is 0 at the horizontal line I have drawn there.

So, G E in some cases can be greater than 0, in some other cases it can be less than 0. Usual experience says that it is parabolic in shape, but there can be variation. Of course, that is not a thermodynamic requirement, but mostly it is parabolic in shape; it can be greater than 0 or less than 0, it can show positive deviations from ideal solution behavior or negative deviations from ideal solution behavior.

If we talk about H E in relation to G E, H E can be greater than G E, H E can be less than G E. So, I am going to draw G E using the yellow curve there notice that at both the ends of pure component limits at x 1 equal to 0 or x 1 equal to 1, the excess property is going to 0. So, this is the yellow one is G E; G E for the yellow one and with respect to G E H E can be greater or it can be smaller than G E, it can in fact, for a part of the composition, it can be positive and for the other part it can be negative and so on.

So, with respect to G E there can be a lot of variations in terms of H E and of course, once we have G E and H E, S E has to obey the difference between G E and H E right S E was as we said earlier H E minus G E over temperature. So, depending on that S E is going to vary. So, as you see the only thermodynamic restriction is that at both the pure component limits both G E and H E have to go to 0, other than that there can be a wide variety of shapes one can observe in terms of G E and H E. Although like I said the most common trend is that G is parabolic in nature with respect to composition.

Now, having looked at these shapes the next question to ask is if I want to quantify the excess properties or non ideality in a solution, we need to somehow model the behavior of the Gibbs free energy or enthalpy how does one do that? Like I said the most common way is to obtain G E from vapor liquid equilibrium data. So, in general to be able to understand this whole scheme of things we first need to look at vapor liquid equilibrium, right or phase equilibrium in general.

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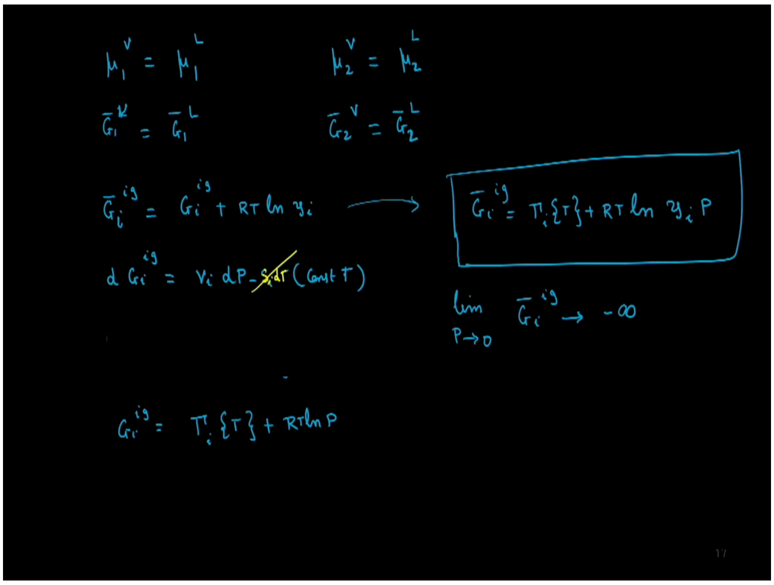

$\mu_1^V = \mu_1^L \qquad \mu_2^V = \mu_2^L$

$\bar{G}_1^V = \bar{G}_1^L \qquad \bar{G}_2^V = \bar{G}_2^L$

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

$d G_i^{ig} = V_i \, dP - \cancel{S_i \, dT} \; (\text{Const } T)$

$\lim_{P \to 0} \bar{G}_i^{ig} \to -\infty$

$G_i^{ig} = \Gamma_i\{T\} + RT \ln P$

So, let us talk a little bit now about vapor liquid equilibrium and for this discussion we are going to introduce a concept known as fugacity and let us see the origin or the reason for this thermodynamic variable. If you recall for vapor liquid equilibrium we said the requirement is that the chemical potential of the species need to be same of each species needs to be same in both the phases.

If we use the superscript V for vapor and L for liquid and we have a binary mixture then the chemical potential of 1 in the vapor phase needs to be equal to the chemical potential of 1 in the liquid phase. Similarly, the chemical potential of the species 2 in the vapor phase also needs to equal to chemical potential of species 2 in the vapor phase. One can write this chemical potentials, instead of using chemical potentials we can also say that the partial molar Gibbs free energies of 1 in the vapor and liquid phases need to be same partial molar Gibbs free energies of 2 in the vapor and liquid phases need to be same for vapor liquid equilibrium.

So, somehow to be able to characterize vapor liquid equilibrium we need to relate this chemical potential or partial molar Gibbs free energy in both the phases. Now, let us take a break here and go back to partial molar Gibbs free energy and see how it is related to the pure component property. Let us talk about an ideal gas mixture and in an ideal gas mixture if you recall we said that the partial molar Gibbs free energy of species 1 or in general for species i is related to the pure component Gibbs free energy G i we are this relation plus RT ln y i.

Now, if you recall the derivative of G i ig is V i dP, this is at constant temperature. In general it is V dP minus S i dT, but at constant temperature this term drops out and it is simply V i dP this is dG ig, right and we can integrate this from 0 pressure and we can rework this integral to get G i ig is going to be some constant with respect to temperature for that species i plus R ln RT rather ln P.

So, what I will do is I will take this equation for G i ig and substitute it back in this expression, so that what we get is an expression for G i bar ig as the constant plus RT ln y i times P. This is an expression for partial molar Gibbs free energy of species i in an ideal gas mixture. Now, if I take if we take look at this equation for a minute and ask a question what would be it is value as pressure P goes to 0? At the 0 pressure limit, right it turns out G i bar ig needs to go to negative infinity only then this equation is going to be satisfied. We can recall G i bar ig is also same as the chemical potential mu i g.

So, in general either the Gibbs free energy or chemical potential tend towards negative infinity at the 0 pressure limit although by itself it is not a mathematical problem. Chemical potential and partial molar Gibbs free energies are rather abstract variables one cannot easily relate to. So, what we do is we will try to use a variable which one can easily relate to and working with phase equilibrium problems rather than working with chemical potentials and towards that end what we will do is this.

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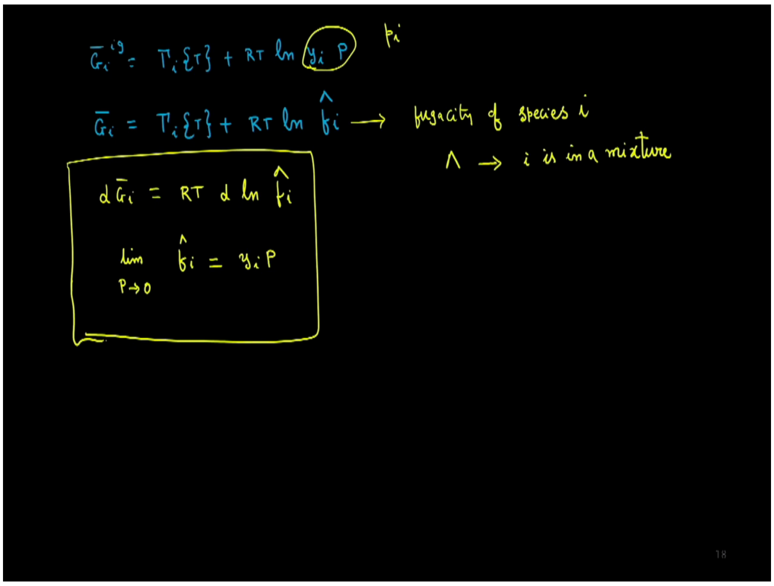

$\bar{G}_i^{ig} = \Gamma_i\{T\} + RT \ln (y_i P)$ p_i

$\bar{G}_i = \Gamma_i\{T\} + RT \ln \hat{f}_i \longrightarrow$ fugacity of species i

$\wedge \rightarrow$ i is in a mixture

$$\boxed{\begin{gathered} d\bar{G}_i = RT \, d \ln \hat{f}_i \\ \lim_{P \to 0} \hat{f}_i = y_i P \end{gathered}}$$

We will take this expression for G i bar ig and we said it is the constant plus RT ln y i P this is true for an ideal gas mixture right. But, in general even if we do not have an ideal gas we will simply write G i bar as this constant plus RT ln f i hat. So, we are replacing y i P which by the way is partial pressure, right, y i P is the partial pressure p i we are replacing that quantity p i with a quantity known as f i hat and we will call this f i hat as fugacity of species i and the hat on top represents that i is in a mixture. So, this is fugacity of species i in a mixture.

So, the way we define fugacity of species i in a mixture is G i bar is this or in more general terms d G i bar is RT d ln f i hat. This is a more general definition for fugacity of species i in a mixture; in addition to this because we also need to define a boundary condition if you will and what we do is we will say that limit of P going to 0 at this limit we will say that f i hat will be equal to y i P. These two equations together define what we called as fugacity of species i.

We will come back in the next class and see how this fugacity of species can be used and how it is more convenient to use rather than working with a chemical potentials.

Thank you.