

**Chemical Engineering Thermodynamics**  
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**Lecture – 31**  
**Models for Excess Gibbs free energy- Part 2**

So, far we looked at Models for activity coefficients which have very little theoretical foundation right using the Redlich Kister's expansion. But then, there are other models which are based on the idea of local composition.

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Local Composition

(1) Wilsons Equation  $\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right]$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) + x_1 \left[ -\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} + \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right]$$

$$\ln \gamma_1^{\infty} = \lim_{x_1 \rightarrow 0} \ln \gamma_1 = -\ln \Lambda_{12} + (1 - \Lambda_{21})$$

By local composition we mean that the mixing of the liquids is not completely random, there are short range interactions that are present when we mix two liquids. And also, the molecular orientation depends on the neighbourhood where in that particular molecule exists because of the influence of the other molecules surrounding it because of this we call that the molecular orientation is non-random. Based on these concepts models for local composition can be developed and these concepts can be used to propose models for the excess Gibbs free energy and the activity coefficients.

Some of the models which utilize these ideas include what is known as Wilson's equation. In case of Wilson's equation the excess Gibbs free energy  $G^E$  by  $RT$  is given by negative  $x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$ . These parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  only has 2 parameters,  $\Lambda_{12}$  and  $\Lambda_{21}$

and both these parameters are independent of composition. Now, if one takes the partial derivative of the excess Gibbs free energy to obtain  $G_1^E$  by  $RT$  and hence  $\ln \gamma_1$  what we end up getting is  $\ln \gamma_1$  to be negative  $\ln x_1$  plus  $x_2 \lambda_{12}$  plus  $x_2$  times  $\lambda_{12}$  by  $x_1 x_2 \lambda_{12}$  minus  $\lambda_{21}$  over  $x_2$  plus  $x_1 \lambda_{21}$ .

And similarly,  $\ln \gamma_2$  will be a symmetric equation which looks like  $x_2$  plus  $x_1 \lambda_{21}$  plus  $x_1$ , this is of course, only for a binary mixture  $\lambda_{12}$  by  $x_1$  plus  $x_2 \lambda_{12}$  minus  $\lambda_{21}$  by  $x_2$  plus  $x_1 \lambda_{21}$  or rather this is plus and this is minus.

Now, from these models we can also write the expression for  $\ln \gamma_1$  infinity, turns out to be limit of  $x_1$  going to 0  $\ln \gamma_1$  and when  $x_1$  goes to 0 what we end up in here is negative  $\ln \lambda_{12}$  plus 1 minus  $\lambda_{21}$ . And similarly, we get expression for the other activity coefficient,  $\ln \gamma_2$  to infinity at infinite dilution.

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The image shows handwritten mathematical derivations on a black background. The equations are as follows:

$$(2) \frac{G^E}{x_1 x_2 x_1} = \frac{G_{21} \gamma_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12} \gamma_{12}}{x_2 + x_1 G_{12}}$$

$$\ln \gamma_1 = x_2^2 \left[ \gamma_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \gamma_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_1^{\infty} = \gamma_{21} + \gamma_{12} G_{12}$$

$$\gamma_{12} = \frac{b_{12}}{RT} \quad \gamma_{21} = \frac{b_{21}}{RT} \quad G_{12} = \exp(-\alpha \gamma_{12})$$

$$G_{21} = \exp(-\alpha \gamma_{21})$$

So, the essential idea still remains the same, once we propose a model for the excess Gibbs free energy we are going to differentiate it to get the partial molar property and hence the activity coefficient for each of the species in that mixture, the infinite dilution limits have to be obeyed etcetera.

The other model that has been proposed based on these concepts is what is known as the NRTL equation non-random to liquid theory equation. And based on this equation  $G^E$

$\bar{I} RT x_1 x_2$  is given by an expression  $G_{21}$ , this  $G_{21}$  has nothing to do with the Gibbs free energy it is just a convenient notation plus  $G_{12} \tau_{12}$  divided by  $x_2$  plus  $x_1 G_{12}$ . Based on this the expression for  $\ln \gamma_1$  turns out to be  $x_2^2 \tau_{21} G_{21}$  by  $x_1$  plus  $x_2 G_{21}$  whole square plus  $G_{12} \tau_{12}$  by  $x_1$  plus  $x_2$  plus  $x_1 G_{12}$  whole squared, all right.

And then the infinite dilution activity coefficient that is assumed we can write a similar expression for  $\ln \gamma_2$  and the infinite dilution activity coefficient in this case turns out to be  $\tau_{21}$  plus  $\tau_{12}$  exponential  $\tau_{12}$  times  $G_{12}$ . In this case  $\tau_{12}$  and  $\tau_{21}$  are parameters that are independent of composition but dependent on the temperature. In fact, the temperature dependency for activity coefficients is included in this model. So,  $\tau_{12}$  turns out to be  $b_{12}$  by  $RT$  and  $\tau_{21}$  turns out to be  $b_{21}$  over  $RT$  that is where the temperature dependency for the parameters  $\tau_{12}$  and  $\tau_{21}$  comes from. In fact,  $G_{12}$  is exponential minus  $\alpha \tau_{12}$  and  $G_{21}$  is exponential of negative  $\alpha \tau_{21}$ .

So, once we have  $\tau_{12}$  and  $\tau_{21}$  the only other parameter in this model is  $\alpha$ . So, the 3 parameters in this model then are going to be  $\tau_{12}$ ,  $\tau_{21}$  and this parameter  $\alpha$ . Once we have these 3 parameters we can calculate  $G_{12}$ ,  $G_{21}$  and once we have  $G_{12}$  and  $G_{21}$  we can calculate the activity coefficients. Like I said again the parameter  $\alpha$  and  $\tau_{21}$  include the temperature dependency so, in fact, this can be extended over a range of temperatures there those parameters. In other models right the usually the parameters are for a particular temperature the temperature dependency of the parameters is not included in the model, but in this case it is, right.

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EXAMPLE 1       $\frac{\bar{G}_1^E}{RT} = G_1 + ax_2$        $\frac{\bar{G}_2^E}{RT} = G_2 + ax_1$   
 $G_1 = \text{pure species 1 @ } T, P$        $G_2 = \text{pure species 2 @ the same } T, P$

So, based on these concepts let us see let us try to solve a few problems. The first one it is given that the excess partial molar Gibbs free energy in a particular model is given by the expression  $\bar{G}_1^E$  is  $G_1 + ax_2$  and  $\bar{G}_2^E$  is  $G_2 + ax_1$ , right. So,  $G_1$  is pure species 1 at the same temperature and pressure and  $G_2$  is for pure species 2 at the same temperature and pressure.

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EXAMPLE 1       $\frac{\bar{G}_1^E}{RT} = G_1 + ax_2$        $\frac{\bar{G}_2^E}{RT} = G_2 + ax_1$   
 $G_1, G_2$  are the Gibbs free energies of pure species 1, 2 @ the same  $T, P$  as that of the mixture. Can this model be thermodynamically consistent -  
Solution  
(a)  $\lim_{x_1 \rightarrow 1} \bar{G}_1^E \rightarrow G_1$        $\lim_{\substack{x_1 \rightarrow 1 \\ x_2 \rightarrow 0}} \frac{\bar{G}_1^E}{RT}$

So, where  $G_1$  and  $G_2$  are the Gibbs free energies of pure species 1 and 2 at the same temperature and pressure as that of the mixture. So, the question is can this model be

thermodynamically consistent. So, we are given particular set of equations for partial molar Gibbs free energies and we are asked if this model equations are thermodynamically consistent. Now, to answer this question what we do is check if such a model satisfies the constraints we already know. The first thing is at the pure component limits the partial molar Gibbs free energies limit  $x_i$  going to 1,  $G_i$  bar E should approach  $G$  for pure one, right, that is the first requirement it needs to satisfy.

And the second requirement, now, if I look at the given expression let us work this out and then we will go to the second one after this. Limit of  $x_1$  going to 1 which means  $x_2$  is going to 0 this is a binary mixture  $G$  1 bar E over  $RT$ . So, let us look at an example. We are given that the partial molar Gibbs free energy is  $G$  1 bar E and  $G$  2 bar E are related to the pure component properties  $G$  1 and  $G$  2, along with a dependency in the mole fraction  $x_1$  or  $x_2$ .

So, this is a binary mixture I am given the relation for  $G$  1 bar E and  $G$  2 bar E based on a proposed model, where the  $G$  1 and  $G$  2 are the Gibbs free energies of the pure components at the same temperature and pressure and we are asked the question if this model can be thermodynamically consistent. Let us see if we can solve this problem.

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Example 1  $\bar{G}_1^E = G_1 + a x_2$   $\bar{G}_2^E = G_2 + a x_1$

$G_1, G_2$  are the Gibbs free energies of pure species 1, 2 @ the same  $T, P$  as that of the mixture. Can this model be thermodynamically consistent?

Solution

(a)  $\lim_{x_i \rightarrow 1} \bar{G}_i^E \rightarrow G_i$

$\lim_{\substack{x_1 \rightarrow 1 \\ x_2 \rightarrow 0}} \bar{G}_1^E = G_1 + a(0) = G_1$  ✓

$\lim_{\substack{x_2 \rightarrow 1 \\ x_1 \rightarrow 0}} \bar{G}_2^E = G_2 + a(0) = G_2$  ✓

So, for a model to be thermodynamically consistent it needs to satisfy the constraints we already know. The first one is at the pure component limit  $x_i$  going to 1,  $G_i$  bar E should approach  $G$  for pure  $i$  because it is mostly 1, so the partial molar property should be same

as the pure component property. Let us see if this particular limit is satisfied for the given relations. Limit of  $x_1$  going to 1,  $G_1$  bar E is  $G_1$  and when  $x_1$  goes to 1 recall that  $x_2$  will go to 0, so  $G_1$  plus  $a$  times  $x_2$  will be 0, so that is  $G_1$  for pure 1. No problem, it satisfies the limit we want it to. And similarly, for the other expression limit of  $x_2$  going to 1,  $G_2$  bar E is  $G_2$  plus  $a$  times  $x_1$  will go to 0,  $x_1$  will go to 0 and this will be  $a$  times 0. So, that will be  $G_2$  for pure 2.

So, at both the pure component limit its not enough if it satisfies only at 1 pure component limit, these relation we show here right needs to be satisfied at both the pure component limits and in this case for the binary mixture and in this case it does. So, this particular thermodynamic requirement has been satisfied. There is an additional requirement it needs to satisfy.

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(b) Gibbs-Duhem relation at const T, P  $\rightarrow \sum x_i d\bar{G}_i = 0$

$$x_1 \frac{d\bar{G}_1}{dx_1} + x_2 \frac{d\bar{G}_2}{dx_1} = 0 \quad \text{or} \quad x_1 \frac{d\bar{G}_1}{dx_2} + x_2 \frac{d\bar{G}_2}{dx_2} = 0$$

↓

$$\bar{G}_1 = G_1 + ax_2 \Rightarrow \frac{d\bar{G}_1}{dx_1} = 0 + a \frac{dx_2}{dx_1} = -a$$

$$\bar{G}_2 = G_2 + ax_1 \Rightarrow \frac{d\bar{G}_2}{dx_1} = 0 + a \frac{dx_1}{dx_1} = a$$

$$x_1 \frac{d\bar{G}_1}{dx_1} + x_2 \frac{d\bar{G}_2}{dx_1} = x_1(-a) + x_2(a) = a(x_2 - x_1) \neq 0$$

NOT SATISFIED! NOT THERMODYNAMICALLY CONSISTENT!!

If you recall we said Gibbs Duhem equation needs to be satisfied. This is the second requirement. At constant temperature and pressure, it reduces to  $\sum x_i d\bar{G}_i = 0$  in this case for a binary mixture it will be  $x_1 d\bar{G}_1$  plus  $x_2 d\bar{G}_2$ . And at constant temperature and pressure when we say derivative of  $\bar{G}_1$ ;  $\bar{G}_1$  changes only because the composition is changing, so let us write it as  $d\bar{G}_1$  bar by  $dx_1$  we could equivalently write it as  $d\bar{G}_2$  bar by  $dx_2$ . Or an equivalent equation will be, so the only thing that is changing here is composition. So,  $x_1 d\bar{G}_1$  bar by  $dx_1$  plus  $x_2 d\bar{G}_2$  bar by  $dx_1$  is 0 or

we can equivalently write this equation with a change in composition instead of  $x_1$  we could take it as  $x_2$  plus  $x_2 \frac{dG_2 \text{ bar}}{dx_2}$  should equal 0.

Notice that their derivatives have to be taken with respect to the same composition either  $x_1$  or  $x_2$  it really does not matter. Once we do that, so let us say we stick with this  $G_1 \text{ bar}$  is  $G_1$  for pure 1 plus  $a$  times  $x_2$  is the relation given to us. So,  $\frac{dG_1 \text{ bar}}{dx_1}$  for pure 1 the first term will go to 0, plus  $a$  times  $\frac{dx_2}{dx_1}$  which will be negative  $a$ . And  $G_2 \text{ bar}$  is  $G_2$  plus  $a x_1$  this implies  $\frac{dG_2 \text{ bar}}{dx_1}$  will be  $\frac{dG_2}{dx_1}$  is 0 for pure component  $a$  times  $\frac{dx_1}{dx_1}$  is 1, so that will reduce to  $a$ .

So,  $x_1 \frac{dG_1 \text{ bar}}{dx_1}$  plus  $x_2 \frac{dG_2 \text{ bar}}{dx_1}$  then will become  $x_1$  times negative  $a$  plus  $x_2$  times  $a$  that will be  $a$  times  $x_2$  minus  $x_1$  and unless  $a = 0$  there is no requirement for this particular value to go to 0, so which will not be equal to 0, all right. If that is the case; if that is the case then Gibbs Duhem equation for this particular model is not satisfied and if Gibbs Duhem equation is not satisfied it is not thermodynamically consistent model

So, whatever models we propose to fit the experimental data need to be thermodynamically consistent if it is not then we cannot use such a model, right. So, unfortunately the previous model that has been proposed to describe the experimental data for  $G_1 \text{ bar}$  and  $G_2$  are given by these relations is unfortunately thermodynamically inconsistent. So, we will not be able to use these equations to model any experimental data ok.

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(2) Given  $H^E = 1036x_1^2 - 1118x_1 - 524$  for a binary mixture at 300 K and 1 bar.

(a) Find minimum value for  $\frac{H^E}{RT}$ . At what composition does it occur?

(b) Find  $\bar{H}_1^E$  and  $\bar{H}_2^E$

(c) Draw  $H^E$ ,  $\bar{H}_1^E$  and  $\bar{H}_2^E$

Solution

(a)  $H^E = cx_1^2 + bx_1 + a$       Minima:  $\frac{dH^E}{dx_1} = 0$

$$\frac{d\left(\frac{H^E}{RT}\right)}{dx_1} = 2072x_1 - 1118 \Rightarrow \text{@ minima, } 2072x_1 - 1118 = 0$$

$$\Rightarrow x_1 = \frac{1118}{2072} = 0.58$$

$$H^E = 1036(0.58)^2 - 1118(0.58) - 524 = -200 \text{ J/mol}$$

So, we are given a model for the excess enthalpy  $H^E$  by  $RT$  in terms of the mole fraction for a binary mixture at 300 Kelvin and 1 bar and we need to find the minimum value where this occurs. We also want to find the infinite dilution activity coefficients  $H_1^E$  and  $H_2^E$ . And finally, we want to draw qualitatively draw the 3 curves  $H^E$ ,  $H_1^E$  and  $H_2^E$ .

To solve this particular problem what we are going to do first is use the given expression for  $H^E$  by  $RT$ . I am going to skip the numbers and write it as  $c x_1^2 + b x_1 + a$ , use this to derive the expressions and we will substitute the numerical values at the end. Now, to find the minimum value if it occurs at that particular minima the derivative with respect to either  $x_1$  or  $x_2$  will be equal to 0. So, what we will do is we will take the derivative of  $H^E$  by  $RT$  with respect to  $x_1$  of course, when we take the derivative we automatically mean temperature and pressure are constant is going to be  $2072 x_1 - 1118$  which implies at minima  $2072 x_1 - 1118$  will be equal to 0 or  $x_1$  is going to be  $1118 / 2072$ , which is about 0.58.

So, the minima is going to occur for this particular curve at a mole fraction of about 0.58. We can find the value of that particular minima. It is going to be simply  $0.58^2$  minus  $1118$  times  $0.58$  minus  $524$  and that value turns out to be about negative 200, well Joules per mole.



So, in this problem we were given an expression for  $H^E$  and we are asked to find at a given temperature and pressure and we are asked to find a minimum value for  $H^E$ , at what composition it occurs and the infinite dilution activity coefficients  $H_1^E$  and  $H_2^E$  and we are also required to draw qualitatively the curves for  $H^E$ ,  $H_1^E$  and  $H_2^E$ . In fact, since we are given the numbers we can actually draw the numerical value itself. This particular data is at a particular temperature and pressure 300 Kelvin and 1 bar.

So, finding the minimum is pretty straightforward what we will do is we will take the derivative like I have shown here, we will take the derivative with respect to  $x_1$  and the derivative needs to go to 0 for the extrema. So, in this case minima and once we equate the derivative to 0 we can get the  $x_1$  at which this minima occurs in this case it turns out to be about 0.58. Once we have that number we can go back and substitute it back in the expression given to us to get  $H^E$ . So, that is a pretty straightforward mathematics problem, all right.

Now, the second part is a little bit more involved we want to find the infinite dilution enthalpies  $H_1^E$  and  $H_2^E$ . To be able to do that the first thing we need to do is find  $H_1^E$  and  $H_2^E$ .

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(b)  $\bar{H}_1^E = \left. \frac{\partial(nH^E)}{\partial n_1} \right|_{P, T, n_2}$

$H^E = cx_1^2 + bx_1 + a$

$nH^E = \frac{cn_1^2}{n} + bn_1 + an$

$\bar{H}_1^E = x_2^2(a + 2bx_1 + 3cx_1^2)$

$\bar{H}_2^E = x_1^2 [a + b(x_1 - x_2) + c(x_1^2 - 2x_1x_2)]$

$\bar{H}_1^{E^0} = \lim_{\substack{x_1 \rightarrow 0 \\ x_2 \rightarrow 1}} \bar{H}_1^E = a = -524 \text{ unit}$

$\bar{H}_2^{E^0} = \lim_{\substack{x_1 \rightarrow 1 \\ x_2 \rightarrow 0}} \bar{H}_2^E = a + b + c = -606 \text{ unit}$

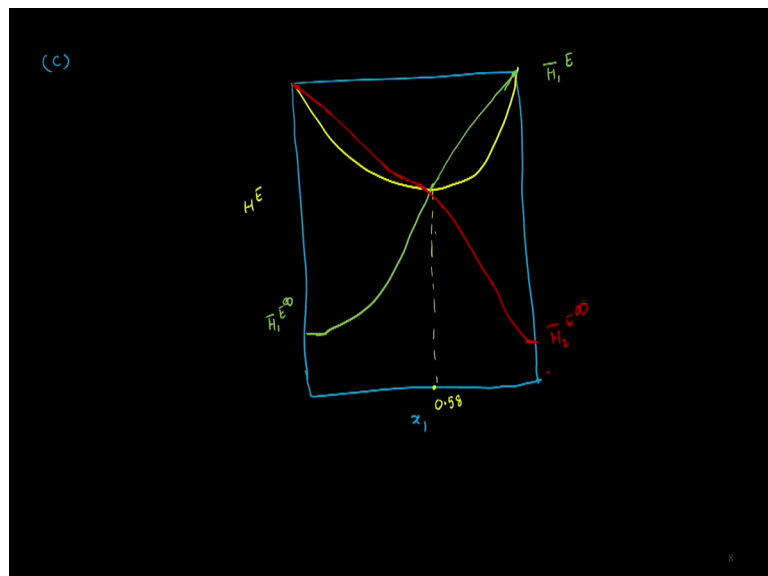
Now, if you recall  $H_1^E$  is the derivative of  $H^E$  with respect to  $n_1$  at  $P, T$  and  $n_2$ , right.  $H^E$  given to us like I said is  $cx_1^2 + bx_1 + a$  will omit the numerical

values will just show use coefficients a b and c for now, it is easier to handle the derivatives in this fashion. And n times H E as we do usually is going to be c n 1 squared over n plus b times n 1 plus a times n, plus a times n that should have been bx 1. So, it will be b times n 1 a times n. So, we have converted everything in, instead of x's we have converted into the moles n ones and n's.

And this derivative once we take the derivative and substitute it back what we end up getting is  $H_1 \bar{E}$  to be  $x_2^2 a + 2 b x_1 + 3 c x_1^2$ , right. And we can do a similar exercise to get  $H_2 \bar{E}$  and the final expression turns out to be  $H_2 \bar{E}$  is  $x_1^2 a + b x_1 - x_2^2 + c x_1^2 - 2 x_1 x_2$ . And so and once we have these two expressions it is pretty easy to find  $H_1 \bar{E}$  infinity. This will be limit of  $x_1$  going to 0  $H_1 \bar{E}$  and  $x_1$  goes to 0, remember that  $x_2$  will go to 1 and that will be simply a and in this case the value of a given to us is 524.

And similarly,  $H_2 \bar{E}$  will be limit of  $x_2$  going to 0,  $x_1$  going to 1,  $H_2 \bar{E}$  and as  $x_2$  goes to 0 it will be a plus b plus c and that value turns out to be negative 606, whatever the units are sorry. So, that is a plus b plus c which is negative 606 in the given units for the particular problem.

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Now, in the third part we are required to draw how the 3 properties H E,  $H_1 \bar{E}$  and  $H_2 \bar{E}$  look as functions of the mole fraction  $x_1$ . To be able to do that we will take the

given expressions and tabulate the values in excel and then maybe we can plot, but very briefly this is how it is going to look once we do that exercise.

This is  $x_1$  and this is  $H_1^E$  let us use a different colour. For a  $H_1^E$  we will use yellow and remember that about at 0.58 or so, it goes through a minima. So, it looks something like that for  $H_1^E$  at both the ends it will go to 0 and it will go through the minima at about a 0.58, right. And at both the ends the excess properties they approach the pure component limit, so the excess enthalpy will go to 0.

Similarly, if I want to plot  $H_1^{\text{bar } E}$  recall that at its pure component limit it will go to 0. So, at this end which is the pure component limit for  $H_1^{\text{bar } E}$  or  $x_1$  going to 1 will go to 0 and it will go through this point and curve off the wall, that will go through this point like that and then curve off to its infinite dilution value  $H_1^{\text{bar } \infty}$ . And for the other component  $H_2^{\text{bar } E}$  it will start here at 0 value at its pure component limit  $H_2^{\text{bar } E}$  the pure component limit is  $x_2$  going to 1 or  $x_1$  going to 0.

So, we will usually go through the same point and then approach the wall. Its pure component infinite dilution value is a little higher. So, let us change the slope a little bit probably it will look something like this. It will look something like that I do not like that shape. So, for  $H_2^{\text{bar } E}$  it will start off at its pure component limit the value will be 0 and then it should go through the same point of intersection through the minima and then reach its infinite dilution value somewhere there.

So, although the curves are not perfect, I am drawing it by hand, but then once you plot in excel you will see a shape that looks something like that that is the infinite dilution value a little lower than  $H_1^{\text{bar } \infty}$ , right. So, that completes this problem.

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Example

T	$G^E$	$H^E$
280	635.5	640
300	422.3	600
320	411.7	560

If  $H^E$  is linear function of T, find  $G^E$ ,  $H^E$  &  $S^E$  at 310 K.

Solution

$$H^E = a + bT \quad a = 1200 \quad b = -2$$

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

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

Let us try to solve one more problem ok. In this problem we are given the data for  $G^E$  and  $H^E$  as a function of temperature for a particular mixture. And at 3 different temperatures 280, 300 and 320 Kelvin and we are asked to find all the 3 values, all the 3 excess properties  $G^E$ ,  $H^E$  and  $S^E$  at 310 Kelvin.

The only information that is given to us is that  $H^E$  is a linear function of temperature. So, if  $H^E$  is a linear function of temperature then probably we can calculate a  $H^E$  at 310 Kelvin but the other two are still a challenge and we should not be interpolating it linearly this is where we will use our knowledge of thermodynamics to be able to solve the problem, right.

So, what we will do is this. The first thing we are going to do is since  $H^E$  is a linear function of temperature. In fact, you can see that, but what we could do is we can we could plot the 3 values for the given  $H^E$  at 280, 300 and 320, this is 320, this is 280. We can plot those 3 values fit a straight line because its linear function of temperature and find the equation of this straight line. In this case it turns out the slope will be negative 2, the intercept is going to be a 1200.

Once we have these two values for the slope and intercept for  $H^E$  as a function of temperature, in fact, we can straight away find  $H^E$  at 310 Kelvin we will come back to that final solution later. Let us also think about how to get  $G^E$  and  $S^E$ . Once we have the slope and intercept now the challenge is to be able to find  $G^E$  and  $S^E$ . But first let

us write the functionalities. Since,  $H^E$  is a linear function of the temperature we are going to write it as  $a + bT$  and in this case what we have is  $a$  is 1200 and  $b$  is negative 2 by feeding the given experimental data that is what we have.

Now, once  $H^E$  is known how do we find  $G^E$ ? Now, recall that the derivative of  $G^E$  over  $RT$  with respect to the temperature at a constant pressure and mole fraction  $x$  is negative  $H^E$  over  $RT^2$ . This is relation not just between excess properties its between residual properties is for the total property all of those things, but for now since we are looking at excess properties let us write this equation of course, it has to be  $RT^2$ . Once we do that and notice that  $R$  is a constant which can cancel out from both sides of this particular expression. So, what if this equation looks like is the derivative of  $G^E$  by  $T$  with respect to  $T$  at constant  $p$  and  $x$  is negative  $H^E$  by  $T^2$ .

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At const.  $p, x$

$$\frac{d(G^E/RT)}{dT} = -\frac{H^E}{T^2} = -\frac{a+bT}{T^2} = -\frac{a}{T^2} - \frac{b}{T}$$

$$\Rightarrow \frac{G^E}{T} = \frac{a}{T} - b \ln T + C \Rightarrow G^E = a - bT \ln T + CT$$

$$(G^E - a + bT \ln T) = CT \Rightarrow C = \frac{(G^E - a + bT \ln T)}{T}$$

And since for the given model we are looking at  $H^E$  is  $a + bT$ . I am going to write these particular set of equations at constant  $p$  and  $x$  only, so the derivative of  $G^E$  by  $T$  with respect to  $T$  is negative  $H^E$  by  $T^2$  that is  $a + bT$  negative of that over  $T^2$  or negative  $a$  by  $T^2$  negative  $b$  by  $T$ . Now, what this means is I can integrate this particular equation to get  $G^E$  over  $T$ ,  $G^E$  over  $T$  as  $a$  by  $T$  minus  $b$  times  $\ln T$  plus  $C$ .

And what this means is  $G^E$  is  $a - bT \ln T + CT$ . This  $C$  is a constant addition constant because of the integration we are doing and then that carries on to the next

expression. So,  $G^E$  the functionality for  $G^E$  if  $H^E$  is a linear function of temperature then the functionality for  $G^E$  will look something like this.

Now, in this particular equation recall that I already know  $a$  and  $b$  the only thing I do not know is  $c$ . So, one of the things I can do is take this particular equation rewrite it as  $G^E$  minus  $a$  plus  $b$  times  $T \ln T$  is  $C$  times  $T$ , right. And then now  $C$  can be  $G^E$  minus  $a$  plus  $bT \ln T$  over the temperature, right. So, write  $c$  times  $T$  and what I can do from there is take the given experimental values right for  $G^E$  at 3 different temperatures. So, let us go to the previous slide. We are given  $G^E$  at 3 different temperatures here. I will take these values use the value of  $a$  and  $b$  from here and calculate the left-hand side of this equation right.

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At  $G^E, P, x$

$$\frac{d(G^E/T)}{dT} = \frac{-H^E}{T^2} = \frac{-a-bT}{T^2} = -\frac{a}{T^2} - \frac{b}{T}$$

$$\Rightarrow \frac{G^E}{T} = \frac{a}{T} - b \ln T + C \Rightarrow G^E = a - bT \ln T + CT$$

$$(G^E - a + bT \ln T) = CT$$

Temp	T	$G^E$	$G^E - a + bT \ln T$
280	280		
300	300		
320	320		

$\Rightarrow C = -14$

$a = 1200 \quad b = -2$

Slope = C

So, I take the  $G^E$  values from the table and in each of the temperatures 280, 300 and 320. This is the temperature the values of  $G^E$  I can take from the table and I can calculate  $G^E$  minus  $a$  plus  $bT \ln T$  right, since  $a$  and  $b$  are known  $a$  is 1200  $b$  is negative 2. So, I can calculate these values and these values and then plot this value here versus temperature, right. And the plot will look something like this for the 3 different values. And the slope of this plot will equal the value of  $C$  I am looking for. And once I do this exercise it turns out that the value of  $C$  I will get is negative 14.

(Refer Slide Time: 33:13)

From  $H^E$  data  $a = 1200$   $b = -2$   
From  $G^E$  data  $C = -14$

$$H^E = a + bT$$
$$G^E = a - bT \ln T + CT$$
$$S^E = \frac{H^E - G^E}{T}$$

Find at 310 K

$$H^E = 580$$
$$G^E = 416.7 \text{ units}$$
$$S^E = 0.527$$

Once I have C, I have a b and c all the 3 parameters I need. So, from HD data I get the values of a and b, a is a 1200, b is negative 2. From G E data I get the value of C to be negative 14 and once I have this H E is a plus bT, G E is like we said a minus bT ln T plus CT, a minus bT ln T plus CT and S E recall is H E minus G E over temperature. Find at 310 Kelvin, that is the temperature of interest at 310 Kelvin we can find all the 3 values and it turns out that H E since it is a linear function anyway is going to be 580. G E is going to be 416.7 and S E is going to be 0.527, whatever the units that are given for those particular expressions are, right.

So, this is how we calculate the 3 thermodynamic variables H E, G E and S E. The only thing we need to appreciate in this particular problem is that I cannot do a simple linear interpolation for each temperature. We know certain functionalities that these thermodynamic variables have to obey, we are going to work around those equations obtained, how they depend on temperature, they dependent composition etcetera and based on those concepts we will interpolate suitably and calculate those numbers. So, it is not going to be simple linear interpolation for each and every variable. In this case the only thing that is given to us is H E is a linear function of temperature. So, the others we need to use suitable equations to obtain values at intermediate temperatures.

With that we will end the discussion on excess properties. When we come back in the next lecture what we will do is we will start working on using the activity coefficient models and apply it to phase equilibrium problems.

Thank you.