Chemical Engineering Thermodynamics
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Lecture - 30
Activity Coefficients

Hello and welcome back. In the previous lectures, we were looking at solution thermodynamics and how we can model various thermodynamic properties for a mixture of chemical species. Along that discussion we introduced the concept of ideal solution and we said to account for non ideality we use what are known as activity coefficients, one of the ways to account for non ideality that is.

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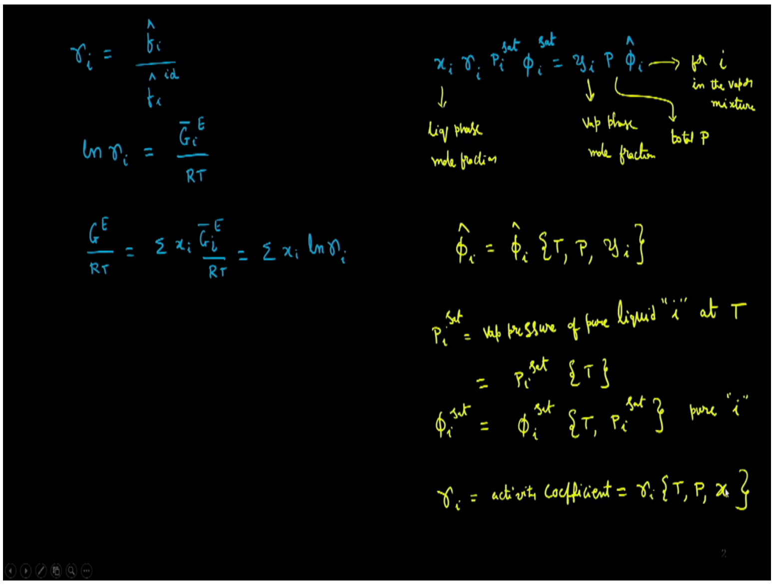

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{id}}$$

$$\ln \gamma_i = \frac{\bar{G}_i^E}{RT}$$

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT} = \sum x_i \ln \gamma_i$$

$$x_i \gamma_i P_i^{sat} \phi_i^{sat} = y_i P \hat{\phi}_i \rightarrow \text{for } i \text{ in the vapor mixture}$$

x_i ↓ Liq phase mole fraction

y_i ↓ Vap phase mole fraction

P ↓ total P

$$\hat{\phi}_i = \hat{\phi}_i \{T, P, y_i\}$$

$$P_i^{sat} = \text{Vap pressure of pure liquid "i" at } T$$

$$= P_i^{sat} \{T\}$$

$$\phi_i^{sat} = \phi_i^{sat} \{T, P_i^{sat}\} \quad \text{pure "i"}$$

$$\gamma_i = \text{activity coefficient} = \gamma_i \{T, P, x\}$$

And, these activity coefficients if you recall we have defined it as gamma i for species i is the ratio of fugacity of that species in the solution or the mixture over the fugacity if that solution were ideal. So, it is ratio of f i hat over f i hat for an ideal solution of an ideal solution, right and it turns out because of this definition and the relationship between the fugacity of species in the mixture to the chemical potential or the partial molar Gibbs free energy. This ratio will actually yield the relation that the logarithm of the activity coefficient is partial molar excess Gibbs free energy over RT for that particular species G i bar E over RT. Moreover because of this summability relation the total excess Gibbs free energy of the solution G E over RT is sigma x i G i bar E over RT and because G i bar r E over RT is related to the activity coefficient this equation will become sigma x i ln gamma i.

In addition to this, we have also derived the criteria for phase equilibrium using the equality of chemical potentials and hence the fugacities. And, we expressed fugacities in terms of fugacity coefficients and the activity coefficient and the final relation we and yesterday was for the liquid phase the fugacity of species in the mixture is x i gamma i P i sat where it P i sat is the vapor pressure at the temperature we are interested in times phi i sat that is the fugacity coefficient for the pure species at the temperature of interest.

And, this will be equal to the fugacity of the vapor phase which is y i times P, the partial pressure, multiplied by the fugacity of species i; fugacitycoefficient for species i in the vapor phi i hat, right. On the left hand side we have fugacity of the liquid phase on the right hand side I have fugacity of the vapor phase. Of course, this relation ignores the pointing correction factor for the liquid phase and if the total pressure of the mixture is not too far away from the vapor pressure P i sat then this is a fair approximation, right.

Let me reemphasize each of these terms here. This is the liquid phase mole fraction and y i is the vapor phase mole fraction total pressure and this is the fugacity coefficient for species i in the vapor mixture. So, if I were to write the functionalities for the vapor phase; this will be a function of the temperature T, the pressure P as well as the mole fraction y i. I can use any suitable equation of state be it we virial equation of state or a cubic equation of state to obtain the vapor phase fugacity.

Now, for the liquid phase I have x i which is the liquid phase mole fraction, let us see P i sat is the vapor pressure of pure liquid in this case i at temperature T. It will be only the function of temperature because it is pure liquid. So, P i sat is only a function of temperature there is the vapor pressure of that species i and phi i sat is the fugacity coefficient at the saturation conditions and so, it will be a function of the temperature and the corresponding vapor pressure which is P i sat, but this is still for pure species i alone, it is not in the mixture. So, it is independent of that composition x i.

And, gamma i is the activity coefficient as in case of all other thermodynamic properties this activity coefficient because it is related to partial molar Gibbs free energy in strict sense it will be a function of the temperature, the pressure, as well as the liquid phase composition x, but in real life the effect of pressure is somewhat weak it does not affect the liquid phase activity coefficients that much. So, usually we ignore that functionality of pressure, but nevertheless thermodynamically it is a function of the temperature pressure as well as the liquid phase mole fraction.

So, this is the phase equilibrium relation we have looked at yesterday.

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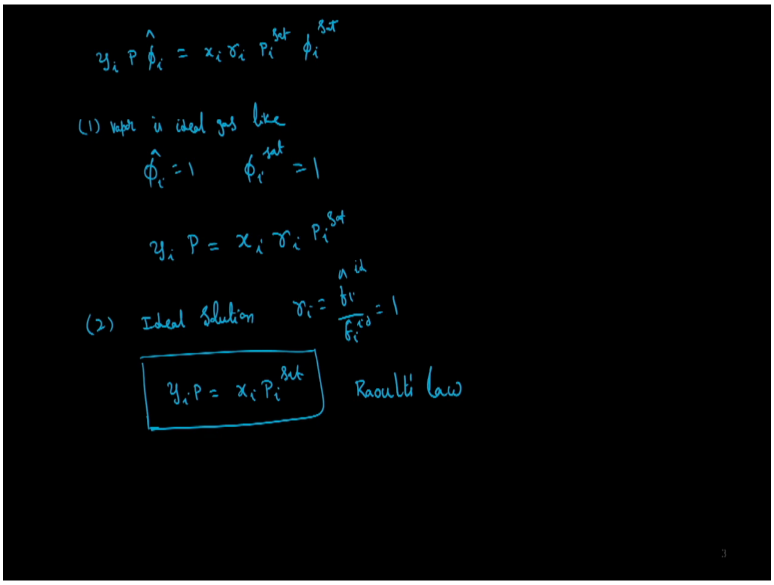

$$y_i P \hat{\phi}_i = x_i \gamma_i P_i^{sat} \phi_i^{sat}$$

(1) vapor is ideal gas like

$$\hat{\phi}_i = 1 \qquad \phi_i^{sat} = 1$$

$$y_i P = x_i \gamma_i P_i^{sat}$$

(2) Ideal Solution $\gamma_i = \frac{\hat{f}_i^{id}}{f_i^{id}} = 1$

$$\boxed{y_i P = x_i P_i^{sat}}$$

Raoult's law

Now, one can simplify this phase equilibrium relation by making certain assumptions. It turns out that if the vapor phase is ideal well let me write what we had in the previous slide y i P phi i hat is x i gamma i P i sat times phi i at the saturation condition.

Now, if the vapor phase is ideal gas line then phi i hat will be 1, phi i sat we will also be equal to 1 and I can write it that equation reduces to y i P is x i gamma i P i sat and in addition to this if we have an ideal solution recall for an ideal solution gamma i will be f i hat over f i hat for the ideal solution and because it is an ideal solution in itself this will both of them will be f i hat ideal or that ratio will turn out to be 1 which means y i P is going to be equal to x i P i sat. This is for an ideal solution and the vapor phase behaving as an ideal gas. This equation at the end is more commonly known as Raoult's law. Of course, we know the underlying assumptions to be able to use Raoult's law, right.

So, in any of these equations we have seen here all of them relate on one side the fugacity of the liquid phase to the fugacity of the vapor phase on the other side. Depending on the conditions we are at, the temperature, the pressure conditions we are at we can use one or the other form of these equations. Of course, neglecting the activity coefficients or assuming the solution to be ideal off also requires knowledge of the chemical species and if those chemical species do form an ideal solution or an ideal mixture or not.

So, with that what we will look at next is how I can use the vapor liquid equilibrium information to calculate the excess Gibbs free energy.

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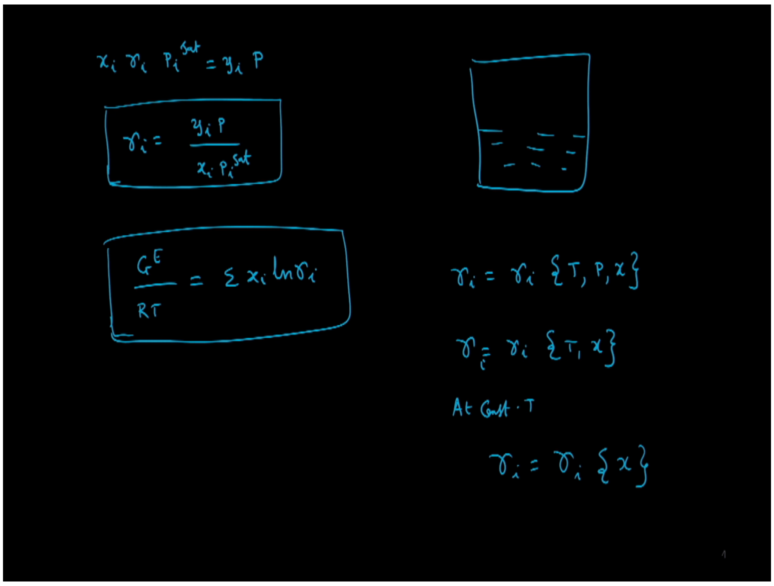

$$x_i \gamma_i P_i^{sat} = y_i P$$

$$\boxed{\gamma_i = \frac{y_i P}{x_i P_i^{sat}}}$$

$$\boxed{\frac{G^E}{RT} = \Sigma x_i \ln \gamma_i}$$

$$\gamma_i = \gamma_i \{T, P, x\}$$

$$\gamma_i = \gamma_i \{T, x\}$$

At Const. T

$$\gamma_i = \gamma_i \{x\}$$

If you recall one of the equations we have written for ideal gas like behavior for phase equilibrium is x i gamma i P i sat. For now for sake of simplicity let us assume that this equation is valid, the solution is not ideal. We have an activity coefficient that is not equal to unity. If I have this relation what I can do is rewrite this equation to get the activity coefficient in terms of the mole fractions of the vapor and the liquid phases and the vapor pressure of the species i.

So, activity coefficient is going to be related to them via this equation. We can perform an experiment like we discussed yesterday. A vapour liquid equilibrium experiment obtain the composition of the liquid phase, obtain the composition of the vapor phase, the total pressure and hands calculate the activity coefficient at equilibrium conditions for each of the species i. If I perform this at various mole fractions then I get activity coefficient as a function of the mole fraction x i. Once I have the activity coefficient recall that the excess Gibbs free energy G E by RT is sigma x i ln gamma i.

So, once I have the activity coefficients I can go back and calculate the excess Gibbs free energy for that particular mixture. The excess Gibbs free energy or the activity coefficients indicate that the solution is ideal, then things are simpler. if then; if the solution is not ideal then we need to build a model that represents the behavior of that particular solution. When we see a model if you recall we said activity coefficients are functions and G by RT for that matter are functions of temperature pressure and the mole fraction x the functionality on pressure is weak.

So, what I am looking at is a is a model for activity coefficients in terms of temperature and x or at constant temperature what we are looking for is an model for activity coefficient in terms of the mole fraction x that is applicable at that particular temperature or pressure of interest; once the temperature changes then that model of course, will change. So, we can do experiments at constant temperature and pressure conditions obtain how G E by RT or the activity coefficients behave as a function of composition and then try to model such a behavior, right.

Now, before we talk about the models let us first look at broad behavior of these activity coefficients especially as we have done in the other cases, at the ends of the or especially as we have done in the other cases when the composition approaches pure component limits.

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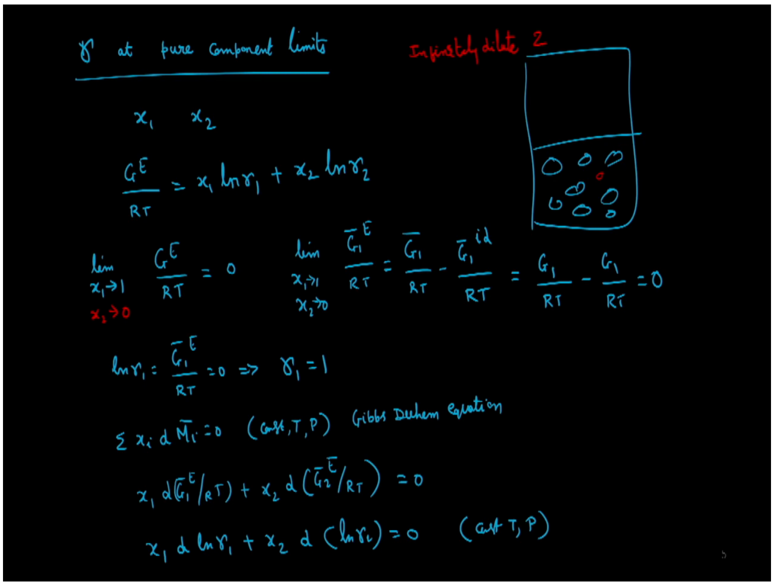

γ at pure component limits

Infinitely dilute 2

$x_1 \quad x_2$

$$\frac{G^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \frac{G^E}{RT} = 0 \qquad \lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \frac{\bar{G}_1^E}{RT} = \frac{\bar{G}_1}{RT} - \frac{\bar{G}_1^{id}}{RT} = \frac{G_1}{RT} - \frac{G_1}{RT} = 0$$

$$\ln\gamma_1 = \frac{\bar{G}_1^E}{RT} = 0 \Rightarrow \gamma_1 = 1$$

$\sum x_i \, d\bar{M}_i = 0$ (const, T, P) Gibbs Duhem equation

$$x_1 \, d(\bar{G}_1^E/RT) + x_2 \, d(\bar{G}_2^E/RT) = 0$$

$$x_1 \, d\ln\gamma_1 + x_2 \, d(\ln\gamma_2) = 0 \quad (\text{const } T, P)$$

So, to for sake of discussion let us consider a binary mixture. So, I have x 1, I have x 2 and then G E by RT is going to be x 1 ln gamma 1 plus x 2 ln gamma 2. As we approach the pure component limit, let us consider a mixture which is like this and most of it is component 1, except I have a very small amount of component 2. At such limit x 1 going to 1 which means x 2 is going to 0. At this limit of pure component 1 what we will see is that the mixture is fairly ideal because most of it is made up of only one component and the excess Gibbs free energy G E by RT will be equal to 0.

Also, if you want to look at the partial molar Gibbs free energy right I will drop the color code for now G 1 E by RT will be equal to G 1 bar by RT minus G 1 bar in an ideal solution over RT and in both cases because I am approaching the pure component limit both these terms G 1 bar as well as G 1 bar ideal will equal that of the pure component at this limit, right pure component values which is G 1 by RT minus G 1 by RT. So, that will be 0.

So, at the pure component limit the total Gibbs free energy as well as the partial molar Gibbs free energy for 1 will be equal to 0. If this is 0 what this means is ln gamma 1 which is G 1 bar E over RT equals 0 or gamma 1 equals 1, it is approaching an ideal solution behavior. So, the activity coefficient for that species will approach 1. Now, what happens to the activity coefficient of the other species 2 at this particular limit?

Now, recall that at this particular limit we said that it is the limit of pure component 1 or infinitely dilute 2; 2 is in such a small quantity that we call it as infinitely dilute. At this infinite dilution limit for 2 what happens to its activity coefficient is what I am interested in. What I will do is I will resort to the Gibbs-Duhem equation which relates a sigma x i d M i bar equals a 0 at constant temperature and pressure. This is the Gibbs-Duhem equation.

I will use this equation and I will use the partial molar Gibbs free energy G i bar E in this particular equation. So, this will read x 1 d G 1 bar E over RT plus x 2 d G 2 bar E over RT; I am just using it for a binary solution will equal 0 and recall that G 1 bar E over RT ln gamma 1. So, this is x 1 d ln gamma 1 plus x 2 d ln gamma 2 will be equal to 0 at constant temperature and pressure. This is Gibbs-Duhem equation written in terms of activity coefficients 1 and 2.

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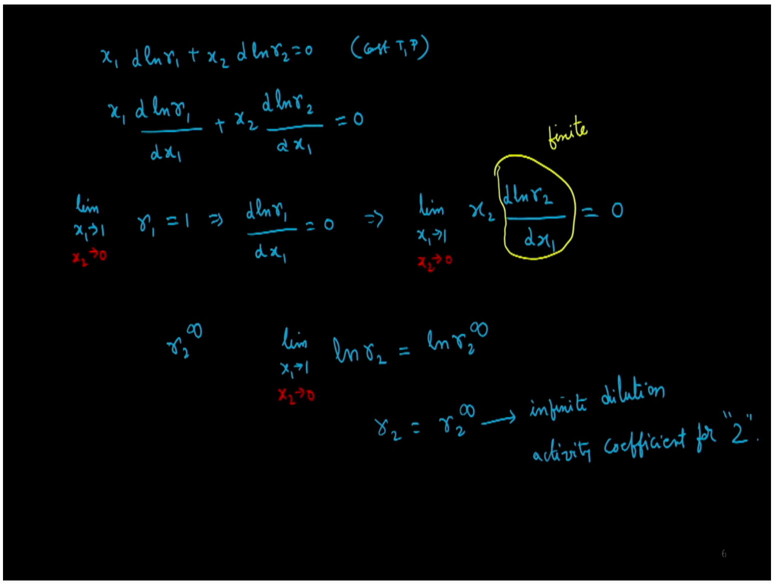

$$x_1\, d\ln\gamma_1 + x_2\, d\ln\gamma_2 = 0 \quad (\text{cst } T, P)$$

$$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = 0$$

finite

$$\lim_{\substack{x_1\to 1\\ x_2\to 0}} \gamma_1 = 1 \Rightarrow \frac{d\ln\gamma_1}{dx_1} = 0 \Rightarrow \lim_{\substack{x_1\to 1\\ x_2\to 0}} x_2 \boxed{\frac{d\ln\gamma_2}{dx_1}} = 0$$

$$\gamma_2^{\infty} \qquad \lim_{\substack{x_1\to 1\\ x_2\to 0}} \ln\gamma_2 = \ln\gamma_2^{\infty}$$

$\gamma_2 = \gamma_2^{\infty} \longrightarrow$ infinite dilution activity coefficient for "2".

Now, for this particular equation, let me rewrite that again. x 1 d ln gamma 1 plus x 2 d ln gamma 2 will equal 0 at constant temperature and pressure. Now, and constant temperature and pressure recall that we said activity coefficient will only be a function of composition that is the only thing that is left; temperature and pressure or any way have constant. So, that derivative then is taken with respect to the composition or the mole fraction.

Let us take it with respect to mole fraction of species 1. It does not matter it is a binary we could equivalently take it with respect to mole fraction of component 2 , but for now let us say it is with respect to component 1. So, this is the Gibbs-Duhem equation written in terms of activity coefficients in a binary mixture at constant temperature and pressure.

Now, if you look at this equation we said that at the limit x 1 going to 1 and x 2 going to 0, which is the infinite dilution limit for 2, the first term gamma 1 will go to 1 which means d ln gamma 1 it will go to a constant value. So, d ln gamma 1 over d x 1 will be 0 which means the first term drops out. And, if that drops out then the limit of x 1 going to 1 and x 2 going to 0 for the second term which is x 2 d ln gamma 2 over d x 1 will be equal to 0.

Now, as x 2 goes to 0 if the product of x 2 multiplied with another term in this case d ln gamma 2 by d x 1 should equal 0 then it automatically means that the second term here should be finite because x 2 is going to 0 and the product is going to 0. The only way that happens is if the second term in this product will be a finite quantity, right. And, that finite quantity then is what we are going to call it as gamma to infinity.

So, limit of x 1 going to 1 and x 2 going to 0, right ln gamma 2 will be what we call as ln gamma to infinity or gamma 2 will be what we call as gamma to infinity. This is infinite dilution activity coefficient for species 2. So, gamma 2 will be gamma to infinity or the infinite dilution activity coefficient for species 2.

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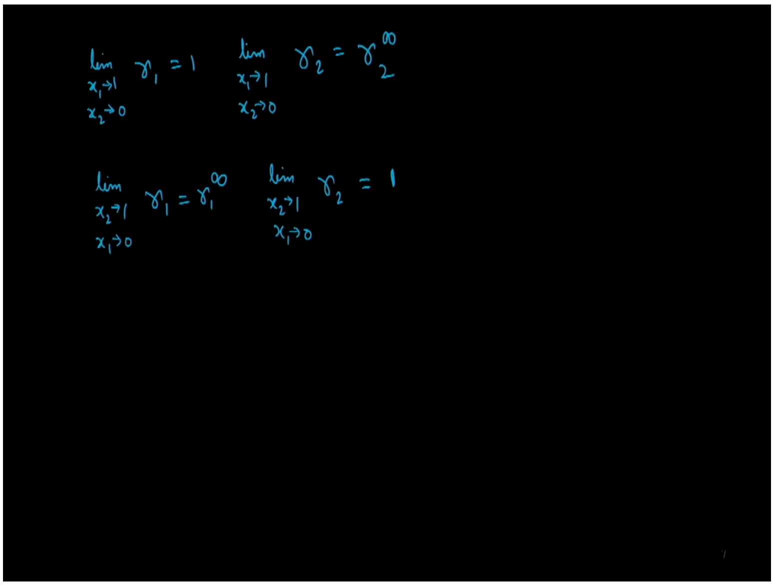

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \gamma_1 = 1 \qquad \lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \gamma_2 = \gamma_2^{\infty}$$

$$\lim_{\substack{x_2 \to 1 \\ x_1 \to 0}} \gamma_1 = \gamma_1^{\infty} \qquad \lim_{\substack{x_2 \to 1 \\ x_1 \to 0}} \gamma_2 = 1$$

So, at the pure component limit; so, let us summarize then what we just did; all we did was we have use gives you an equation to obtain this at the infinite at the pure component limit x 1 going to 1, x 2 going to 0, gamma 1 will be 1 and at the same limit x 1 going to 1, x 2 going to 0 gamma 2 will be at infinite dilution condition. So, its activity coefficient will be gamma to infinity.

Similarly, at the other limit of x 2 going to 1, x 1 going to 0 gamma 1 will be at it is infinite dilution condition. So, it will be gamma 1 infinity and at the same limit x 2 going to 1 x 1 going to 0 gamma 2 will be pure component 2. So, gamma 2 will be equal to 1. So, this is the summary of how the activity coefficients behave in a binary system as we approach the pure component limits.

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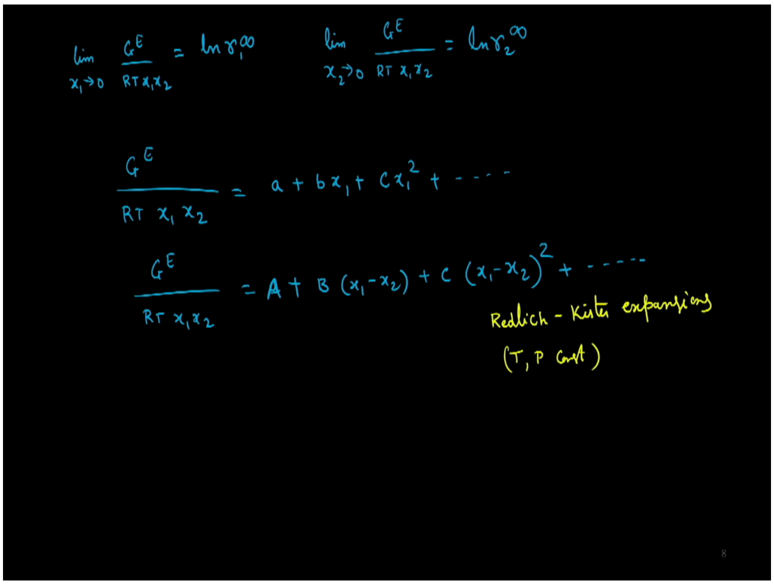

$$\lim_{x_1 \to 0} \frac{G^E}{RT x_1 x_2} = \ln \gamma_1^\infty \qquad \lim_{x_2 \to 0} \frac{G^E}{RT x_1 x_2} = \ln \gamma_2^\infty$$

$$\frac{G^E}{RT x_1 x_2} = a + b x_1 + c x_1^2 + \cdots$$

$$\frac{G^E}{RT x_1 x_2} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots$$

Redlich - Kister expansions

(T, P const)

Now, that we know how they behave at the ends of the phase diagram and to make sure that this behavior holes it turns out that the limit of x 1 going to 0 G E by RT x 1 x 2 will be equal to ln gamma 1 infinity and limit of x 2 going to 0 G E by RT x 1 x 2 will be equal to ln gamma 2 infinity, right and we can show this based on our previous discussion.

So, what we usually do is to be able to model the behavior of activity coefficients 1 and 2 with respect to composition we rather model the behavior of the excess Gibbs free energy because it incorporates both gamma 1 and gamma 2 and then take its partial derivative with respect to n 1 or n 2 to get the partial molar Gibbs free energies or the activity coefficients. In general, in a power series type of expansion the way we represent G E by RT x 1 x 2 is a function of power series either in x 1 or x 2 in a binary mixture it does not matter plus so on.

We can reduce it into a more mathematically convenient form as G E by RT x 1 x 2 is A plus B x 1 minus x 2 plus C x 1 minus x 2, let us use capital letters whole square plus so on. These expansions for G by RT where x 1 x 2 are known as Redlich-Kister expansions. These are expansions for the excess Gibbs free energy at a given temperature and pressure. So, it is only function of the mole fraction.

Now, out of these Redlich-Kister expansions then depending on our requirement we choose the first term, two terms, three terms etcetera. We can choose as many terms as we want out of this power series expansion.

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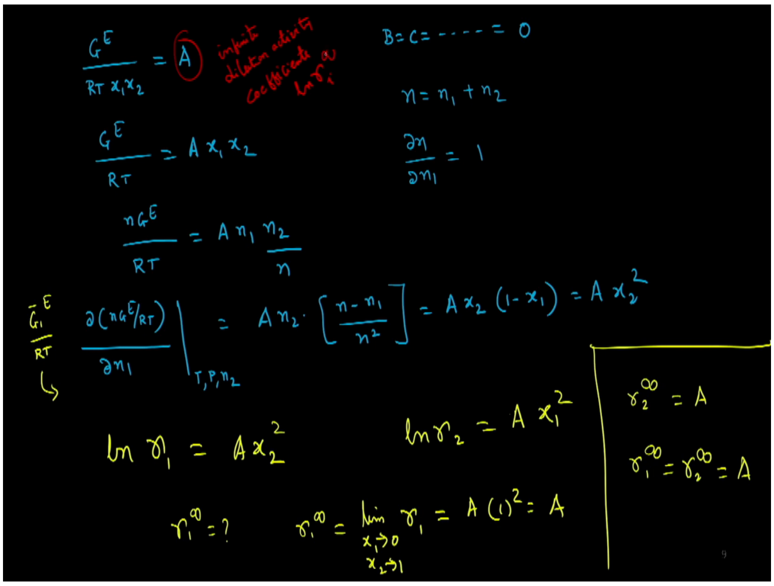

So, let us start with the simplest scenario where G E by RT let me demonstrate how we calculate the activity coefficients based on this model G E by RT x 1 x 2 is only A; every other term after be including B is 0. If this is the case then G E by RT x 1 x 2 will simply be A or G E by RT will be A x 1 x 2.

Now, if I want to find the activity coefficients from this particular model then what we do is take the derivative of all; we want to obtain G 1 bar E and G 2 bar E. So, what I will do is I will multiply it with and the total number of moles in the binary mixture and what I get on this side is n 1 n 2 over n. Recall that when we take the partial derivatives to obtain when to obtain the partial molar properties. We want to convert all the mole fractions into number of moles of each of the species.

So, when I multiply it with 1 n x 1 will change to n 1, but x 2 will remain as such. So, I am rewriting it as n 2 by n of course, remember that n is n 1 plus n 2 and derivative of n with respect to n 1 is going to be hence 1. Now, with that in mind what I will do is I will take the derivative of n G E over RT with respect to n 1 at constant temperature pressure and n 2. If I do that what I will get on this side is A; let us say it is written only for a particular temperature and pressure. So, A is A and n 2 is constant, derivative of n 1 over n is n minus n 1 divided by n square and if we simplify this; this is A x 2 and that will be 1 minus x 1. So, that will be A x 2 squared, right.

So, the quantity on the left hands if you recognize is partial molar Gibbs free energy excess partial molar Gibbs free energy for component 1 which we will call; which is related to the activity coefficient as ln gamma 1. So, ln gamma 1 using this model will be A x 2 square. We can go through a similar exercise and also show that ln gamma 2 will be A x 1 square. So, this is the simplest model we get using the Redlich-Kisters expansions for excess Gibbs free energy.

Now, if I ask a question what is gamma 1 infinity? Then we can use this model and say that gamma 1 infinity is nothing, but the limit of x 1 going to 0 for gamma 1 and as x 1 goes to 0 x 2 will go to 1. So, A times 1 squared would be simply A. So, in this model gamma 1 infinity will be A and if we actually write gamma 2 infinity this will also equal A. So, for this particular model gamma 1 infinity equals gamma 2 infinity will be equal to A. So, the infinite dilution activity coefficients are what this term A represents in this particular model. Rather, this is logarithm of infinite dilution activity coefficients to be more specific, but then that is what it is.

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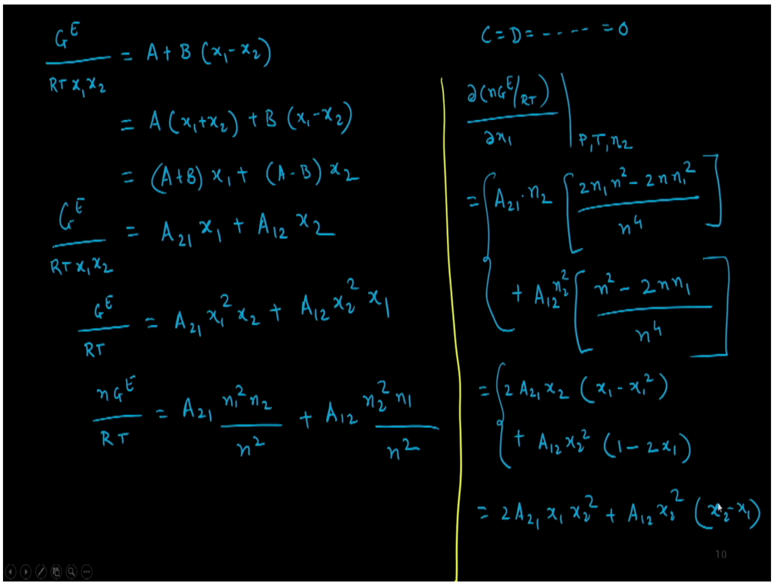

$$\frac{G^E}{RTx_1x_2} = A + B(x_1 - x_2)$$

$$= A(x_1 + x_2) + B(x_1 - x_2)$$

$$= (A+B)x_1 + (A-B)x_2$$

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

$$\frac{G^E}{RT} = A_{21}x_1^2x_2 + A_{12}x_2^2x_1$$

$$\frac{nG^E}{RT} = A_{21}\frac{n_1^2n_2}{n^2} + A_{12}\frac{n_2^2n_1}{n^2}$$

$$C = D = \text{-----} = 0$$

$$\left.\frac{\partial(nG^E/RT)}{\partial n_1}\right|_{P,T,n_2}$$

$$= \begin{cases} A_{21}\cdot n_2\left[\frac{2n_1n^2 - 2nn_1^2}{n^4}\right] \\ + A_{12}n_2^2\left[\frac{n^2 - 2nn_1}{n^4}\right] \end{cases}$$

$$= \begin{cases} 2A_{21}x_2(x_1 - x_1^2) \\ + A_{12}x_2^2(1 - 2x_1) \end{cases}$$

$$= 2A_{21}x_1x_2^2 + A_{12}x_2^2(x_2 - x_1)$$

Now, now let us look at a model which is slightly complicated than this and we call this as modules equation. What we will do is we will take Redlich-Kisters expansion up to two terms. A plus B x 1 minus x 2 and we will drop all the other terms from C onwards in the infinite series. If that happens we will readjust this a little bit and this will be A x 1 plus x 2 plus B x 1 minus x 2 x 1 plus x 2 anyways 1. So, it does not matter and then I can write it as A plus B times x 1 plus A minus B times x 2, right and we will give a name to this A plus B quantity we will call it as A 2 1 x 1 plus A 1 2 x 2.

So, I can rewrite the model equation Redlich-Kisters expansion containing 2 terms in this fashion G E by RT x 1 x 2 will be A 2 1 x 1 plus A 1 2 x 2. Now, we want to get the activity coefficient for this particular model. So, what we need to do is first get the partial molar quantities out of G E by RT; n G E by RT will be A 2 1 x 1 square x 2 plus A 1 2 x 2 squared x 1, right well this is still G E by RT not n G E by RT.

Now, if I make it n G E by RT then this will be A 2 1 n 1 squared n 2 over n squared plus A 1 2 n 2 squared n 1 over n squared. Notice that I am multiplying only with one n and I have a cubic in decomposition on the right hand side. So, I still need to multiply and divide with n square so that everything is converted in terms of n and we do not leave any compositions in there.

Now, once we have it in this form I can calculate the partial molar enthalpy. Now, once we have it in this form I can take the derivative of this quantity with respect to n 1 and obtain G 1 bar E by RT. So, the derivative of n G E by RT with respect to n 1 at P t and n 2 will be equal to A 2 1 times n 2 is constant and I have n 1 square whose derivative will be 2 n 1 times n squared minus 2 n n 1 squared over n to the power 4 and for the second term it will be A 1 2 and 2 square is constant n squared minus 2 n n 1 over n to the power 4, right.

So, this will be 2 A 2 1 x 2 multiplied with x 1 minus x 1 square plus A 1 2 x 2 squared multiplied with 1 minus 2 x 1. So, this will be 2 A 2 1 x 1 x 2 squared plus A 1 2 x 2 squared multiplied with x 2 minus x 1, right. So, that will be derivative of n G E by RT with respect to n 1.

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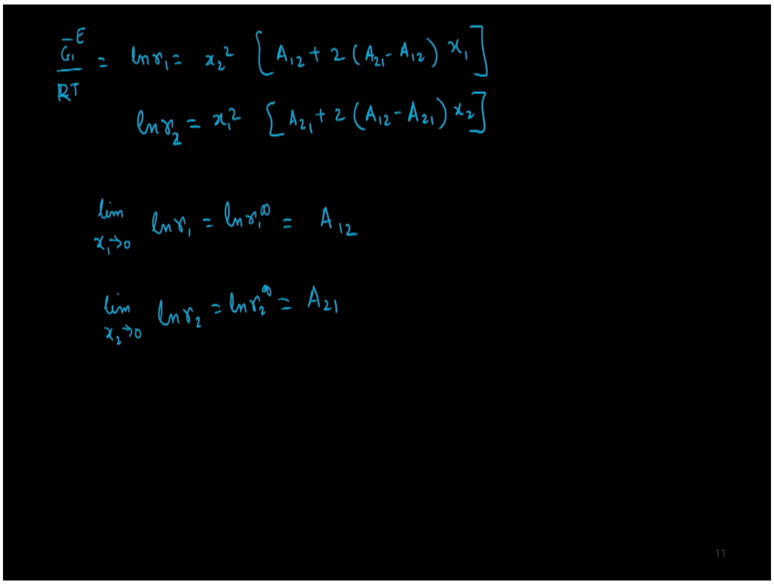

$$\frac{\bar{G}_1^E}{RT} = \ln \gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12}) x_1 \right]$$

$$\ln \gamma_2 = x_1^2 \left[A_{21} + 2(A_{12} - A_{21}) x_2 \right]$$

$$\lim_{x_1 \to 0} \ln \gamma_1 = \ln \gamma_1^\infty = A_{12}$$

$$\lim_{x_2 \to 0} \ln \gamma_2 = \ln \gamma_2^\infty = A_{21}$$

I can simplify this and rewrite it in a more convenient form it turns out that G 1 bar E by RT will be equal to ln gamma 1 and the simplified form of that will be x 2 squared A 1 2 plus 2 times A 2 1 minus A 1 2 times x 1. And, similarly if I take the derivative with respect to n 2 at constant n 1 I will get ln gamma 2 which will be x 1 squared A 2 1 plus 2 times A 1 2 minus A 2 1 times x 2 this is ln gamma 2.

Now, if I ask a question what we will be gamma 1 infinity; if we want to know what the infinite dilution activity coefficients are we simply need to take the limit as x 1 approaches 0; ln gamma 1 will give us ln gamma 1 infinity and that quantity will be simply A 1 2 and similarly, if we take the limit as x 2 approaches 0 for ln gamma 2 we get ln gamma 2 infinity and that quantity as x 2 approaches 0, notice that x 1 will approach 1 this term drops out and we are left with A 2 1.

So, as you can see in this case the infinite dilution activity coefficients for species 1 and 2 are not same, they are different. One of them is A 1 2 the other one is A A 2 1. So, once I have a model for G E over RT then I can use that model and obtain the activity coefficients from that information.

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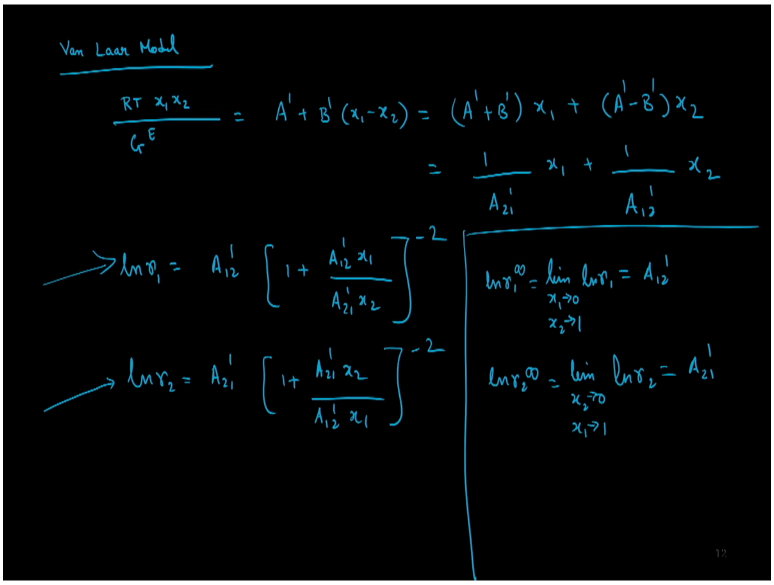

Van Laar Model

$$\frac{RT\, x_1 x_2}{G^E} = A' + B'(x_1 - x_2) = (A' + B')\, x_1 + (A' - B')\, x_2$$

$$= \frac{1}{A'_{21}}\, x_1 + \frac{1}{A'_{12}}\, x_2$$

$$\ln\gamma_1 = A'_{12}\left[1 + \frac{A'_{12} x_1}{A'_{21} x_2}\right]^{-2}$$

$$\ln\gamma_2 = A'_{21}\left[1 + \frac{A'_{21} x_2}{A'_{12} x_1}\right]^{-2}$$

$$\ln\gamma_1^\infty = \lim_{\substack{x_1 \to 0 \\ x_2 \to 1}} \ln\gamma_1 = A'_{12}$$

$$\ln\gamma_2^\infty = \lim_{\substack{x_2 \to 0 \\ x_1 \to 1}} \ln\gamma_2 = A'_{21}$$

The other popular model is what is known as Van Laar model and in this particular model what we do is we write a power series for the inverse of G by RT x 1 x 2 and that looks like A prime plus B prime x 1 minus x 2. We can rewrite this as A prime plus B prime x 1 plus A prime minus B prime x 2 just like we did it in the Margules equation case and when we do that what we have is A 2 1 prime x 1 plus 1 by A 1 2 prime x 2.

So, this is the model equation we start with and then we take partial molar derivatives and do the regular exercise and finally, what we get is an expression for ln gamma 1 as A 1 2 prime 1 plus A 1 2 prime x 1 over A 2 1 prime x 2 to the power negative 2 and ln gamma 2 will be A 2 1 prime 1 plus A 2 1 prime x 2 by A 1 2 prime x 1 also raised to the power negative 2.

And, if I want to know what the infinite dilution activity coefficients are ln gamma 1 infinity will be the limit of x 1 going to 0 ln gamma 1 and that quantity if i put x 1 to be 0 and x 2 to be 1 in this particular equation what I get is simply A 1 2 prime. And, similarly ln gamma 2 infinity will be the limit as x 2 going to 0 x 1 going to 1 ln gamma 2 and if I put the limits in this particular equation what I will get is A 2 1 prime.

So, again using the model I can calculate the activity coefficients and what will be the activity coefficients at the infinite dilution limits. Now, all these models we have looked at so far are based on power series expansion they have very little a theoretical basis behind them.

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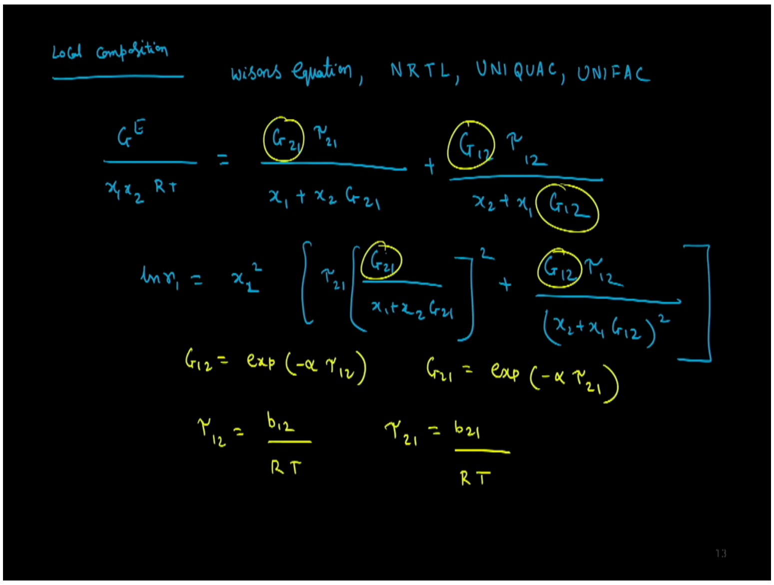

Local Composition

Wilsons Equation, NRTL, UNIQUAC, UNIFAC

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}}$$

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

$$G_{12} = \exp(-\alpha \tau_{12}) \qquad G_{21} = \exp(-\alpha \tau_{21})$$

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

The next set of models that have been developed for activity coefficients or excess Gibbs free energies are based on the concept of Local Composition. What local composition essentially means is that the liquids are not completely randomly mixed, but on a molecular level there is an influence of the short range interactions between the molecules and the molecular orientation itself is not completely random. It is based on what it is neighboring molecule or how it is neighboring molecule is oriented.

Based on these concepts are several models have been developed some of the popular ones include what are known as Wilsons equation; the nonrandom two-liquid theory model or NRTL model, the universal quasi chemical approach which is known as UNIQUAC model and finally, the universal; the UNIQUAC model and finally, a functional group type of approach known as the UNIFAC model.

Now, the approach behind calculating activity coefficients from the excess Gibbs free energy models in all these; now, the approach behind calculating the activity coefficients using any of the models is essentially the same as we have looked at in the previous scenarios when we use the Redlich-Kisters type of expansions. The only difference in using these models is there is some theoretical basis behind them and we can sort of relate the model parameters to the physics behind the interactions between molecules of various types.

So, for example, in case of NRTL equation I will just illustrate one of them for sake of an example. The NRTL equation; in case of NRTL equation G E by RT x 1 x 2 is given as and using this model for excess Gibbs free energy one can derive the relation for activity coefficient 1 as x 1 plus x 2 G 2 1 and the parameters G notice that G 1 2 here within the model equation has nothing to do with the Gibbs free energy and this G 1 2 and G 2 1 are written in terms of alpha and tau 1 2 and tau 2 1. And, tau 1 2 itself is written as a function of temperature B 1 2 and temperature B 1 2 is a parameter that is independent of temperature.

So, in addition to representing the composition dependency because the parameter is tau 1 2 and tau 2 1.