Phase Equilibria

Part 7 – Phase Equilibria at Low Pressures

As you recall

$$\boxed{y_i \hat{\phi}_i P = x_i \gamma_i f_i} \quad (i = 1, 2, \ldots, N) \qquad \text{Eq. (13.12)}$$

or,

$$\boxed{y_i \Phi_i P = x_i \gamma_i P_i^{sat}} \quad (i = 1, 2, \ldots, N) \qquad \text{Eq. (13.13)}$$

Either of these expressions can be used for calculating phase equilibrium. Often the greatest non-ideality is in the activity coefficient, and it's worth isolating it.

As mentioned, if what we want to know is the value of γ_i then

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^{sat}} \quad (i = 1, 2, \ldots, N)$$

If we assume that $\Phi_i \approx 1$, which is true for low pressures (low pressures are pressures for which $\Phi_i \approx 1$ is true), then

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}} \quad (i = 1, 2, \ldots, N)$$

The rearranged version is known as the modified Raoult's law:

$$y_i P = x_i \gamma_i P_i^{sat} \quad (i = 1, 2, \ldots, N) \qquad \text{Eq. (13.19)}$$

For those cases where the modified Roult's law holds the task is how to develop models for calculating the activity coefficients.

We saw before that the activity coefficients were related to the excess Gibbs energy.

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

We need to spend some time developing these relationships further.

For a binary solution

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

becomes

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad \text{Eq. (13.54)}$$

As a side note

$$\frac{G}{RT} = x_1 \ln \hat{a}_1 + x_2 \ln \hat{a}_2$$

For all solutions

$$\lim_{x_i \to 1} \gamma_i = \lim_{x_i \to 1} \frac{y_i \Phi_i P}{x_i P_i^{sat}} = \frac{(1)(P_i^{sat})}{(1)(P_i^{sat})} = 1$$

So Raoult's law applies to species i, in the limit as x_i approaches 1.

What should happen to the excess Gibbs energy as x_i approaches 1?

$$\lim_{x_i \to 1} \frac{G^E}{RT} = \lim_{x_i \to 1} \left(x_i \ln \gamma_i + x_{\bar{i}} \ln \gamma_{\bar{i}} \right) = (1)(0) + (0) \ln \gamma_{\bar{i}}^{\infty} = 0$$

Using the Gibbs/Duhem equation to evaluate activity coefficients

$$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_2} = 0 \quad (\text{const } T, P) \qquad \text{Eq. (13.55)}$$

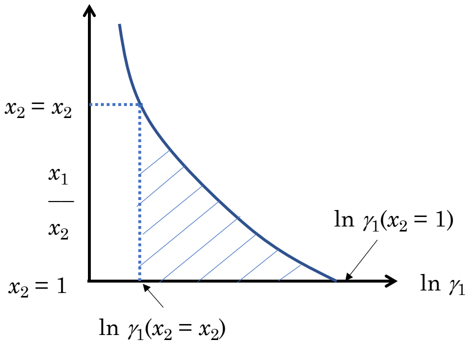
or rearranged

$$d\ln\gamma_2 = -\frac{x_1}{x_2} d\ln\gamma_1$$

which can be integrated to

$$\ln\gamma_2(x_2) = -\int_{\ln\gamma_1(x_2=1)}^{\ln\gamma_1(x_2=x_2)} \frac{x_1}{x_2} d\ln\gamma_1$$

What happens as x_2 approaches 0?

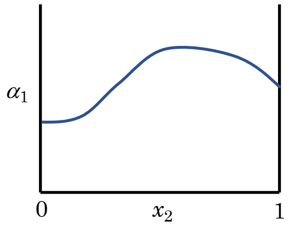


To get around this difficulty, let's define a new function, the α-function,

$$\alpha_i = \frac{\ln\gamma_i}{(1-x_i)^2}$$

For a binary system

$$\alpha_1 = \frac{\ln\gamma_1}{x_2^2} \quad \text{and} \quad \alpha_2 = \frac{\ln\gamma_2}{x_1^2}$$



Using this function, we can evaluate the ln γ_2 as

$$\ln\gamma_2(x_2) = -x_1 x_2 \alpha_1 - \int_{x_2=1}^{x_2=x_2} \alpha_1 \, dx_2$$

The argument of this integral remains finite at all compositions.

The simplest (non-zero) functional form for the alpha function is for α to be a constant. It can be shown for a binary that if α_1 and α_2 are constant at a given temperature, then

$$\alpha_1 = \alpha_2$$

and

$$\begin{aligned}\frac{G^E}{RT} &= x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad \text{Eq. (13.54)} \\ &= x_2 \alpha x_2^2 + x_2 \alpha x_1^2 \\ &= x_1 x_2 \alpha\end{aligned}$$

A solution for which the above equation holds, and for which

$$\alpha \propto \frac{1}{T}$$

is called a regular solution (solutions for which α is constant with composition but is not inversely proportional to temperature are sometimes called sub-regular solutions).

For a regular solution

$$\frac{G^E}{x_1 x_2 RT} = \alpha = \text{a constant}$$

If α is not constant but varies linearly with composition, then

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

which can be written as

$$\frac{G^E}{RT} = \left(A_{21}x_1 + A_{12}x_2\right)x_1 x_2 \qquad \text{Eq. (13.39)}$$

If we remember that

$$\frac{G^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \qquad \text{Eq. (13.54)}$$

and solve for ln γ_1 and ln γ_2, then,

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2\left(A_{21} - A_{12}\right)x_1\right] \qquad \text{Eq. (13.40)}$$

and

$$\ln\gamma_2 = x_1^2\left[A_{21} + 2\left(A_{12} - A_{21}\right)x_2\right] \qquad \text{Eq. (13.41)}$$

which are known as the *Margules equations*.

(Actually there is a whole family of Margules equations. They are all based on series expansions of the form

$$\ln\gamma_i = \beta_1 x_i + \frac{1}{2}\beta_2 x_i^2 + \frac{1}{3}\beta_3 x_i^3 + \cdots.$$

They differ in the number of terms that they include.

Table 1 Some Models for Excess Gibbs Energy and Activity Coefficients

Name	G^E	**Binary Parameters**	**$\ln\gamma_1$ and $\ln\gamma_2$**
Two-suffix Margules	$\frac{G^E}{RTx_1x_2}=A$	A	$\ln\gamma_1=Ax_2^2$ $\ln\gamma_2=Ax_1^2$
Three-suffix Margules	$\frac{G^E}{RTx_1x_2}=A_{21}x_1+A_{12}x_2$	A_{12},A_{21} or A,B	$\ln\gamma_1=x_2^2\left[A_{12}+2\left(A_{21}-A_{12}\right)x_1\right]$ $\ln\gamma_2=x_1^2\left[A_{21}+2\left(A_{12}-A_{21}\right)x_2\right]$
Four-suffix Margules	$\frac{G^E}{RTx_1x_2}=A_{21}x_1+A_{12}x_2-Cx_1x_2$	A_{12},A_{21},C	$\ln\gamma_1=x_2^2\left[A_{12}+2\left(A_{21}-A_{12}-C\right)x_1+3Cx_1^2\right]$ $\ln\gamma_2=x_1^2\left[A_{21}+2\left(A_{12}-A_{21}-C\right)x_2+3Cx_2^2\right]$
Van Laar	$\frac{G^E}{RTx_1x_2}=\frac{A'_{12}A'_{21}}{A'_{12}x_1+A'_{21}x_2}$	A'_{12},A'_{21}	$\ln\gamma_1=A'_{12}\left(1+\frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}$ $\ln\gamma_2=A'_{21}\left(1+\frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}$
Wilson	$\frac{G^E}{RT}=-x_1\ln\left(x_1+x_2\Lambda_{12}\right)-x_2\ln\left(x_2+x_1\Lambda_{21}\right)$	$\Lambda_{12},\Lambda_{21}$ See Eq 12.24	$\ln\gamma_1=-\ln\left(x_1+x_2\Lambda_{12}\right)+x_2\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right)$ $\ln\gamma_2=-\ln\left(x_2+x_1\Lambda_{21}\right)-x_1\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right)$
NRTL	$\frac{G^E}{RTx_1x_2}=\frac{G_{21}\tau_{21}}{x_1+x_2G_{21}}+\frac{G_{12}\tau_{12}}{x_2+x_1G_{12}}$	α,b_{12},b_{21}	$\ln\gamma_1=x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\frac{G_{12}\tau_{12}}{\left(x_2+x_1G_{12}\right)^2}\right]$ $\ln\gamma_2=x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2+\frac{G_{21}\tau_{21}}{\left(x_1+x_2G_{21}\right)^2}\right]$ $G_{12}=\exp\left(-\alpha\tau_{12}\right),G_{21}=\exp\left(-\alpha\tau_{21}\right),\tau_{12}=\frac{b_{12}}{RT},\tau_{21}=\frac{b_{21}}{RT}$
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What about the limits for G^E/RT and G^E/x_1x_2RT as $x_1\to 0$ or 1?

We already did

$$\lim_{x_1\to 1}\frac{G^E}{RT}=0$$

G^E/x_1x_2RT is indeterminate, so

$$\lim_{x_1\to 0}\frac{G^E}{x_1x_2RT}=\lim_{x_1\to 0}\frac{G^E}{x_1RT}=\lim_{x_1\to 0}\frac{d\left(G^E/RT\right)}{dx_1}$$

To evaluate the final limit

Where do we get the minus sign?

$$\frac{d\left(G^E/RT\right)}{dx_1}=x_1\frac{d\ln\gamma_1}{dx_1}+\ln\gamma_1+x_2\frac{d\ln\gamma_2}{dx_1}-\ln\gamma_2$$

If we apply the Gibbs/Duhem equation, then

$$\frac{d\left(G^E/RT\right)}{dx_1} = \ln\frac{\gamma_1}{\gamma_2}$$

If we take the limit

$$\lim_{x_1\to 0}\frac{d\left(G^E/RT\right)}{dx_1} = \lim_{x_1\to 0}\ln\frac{\gamma_1}{\gamma_2} = \ln\gamma_1^\infty$$

where the ∞ means *at infinite dilution*.

So finally

$$\lim_{x_1\to 0}\frac{G^E}{x_1x_2RT} = \ln\gamma_1^\infty$$

and by symmetry

$$\lim_{x_1\to 1}\frac{G^E}{x_1x_2RT} = \ln\gamma_2^\infty$$

One final note: Gibbs/Duhem tells us about the slopes of the curves

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

Quoting the text:

it requires the slope of the ln γ_1 curve to be everywhere of opposite sign to the slope of the ln γ_2 curve. Furthermore, when $x_2 \to 0$ (and $x_1 \to 1$), the slope of the ln γ_1 curve is zero. Similarly, when $x_1 \to 0$, the slope of the ln γ_2 curve is zero. Thus, each ln γ_i (i = 1, 2) curve terminates at zero with zero slope at $x_i = 1$.

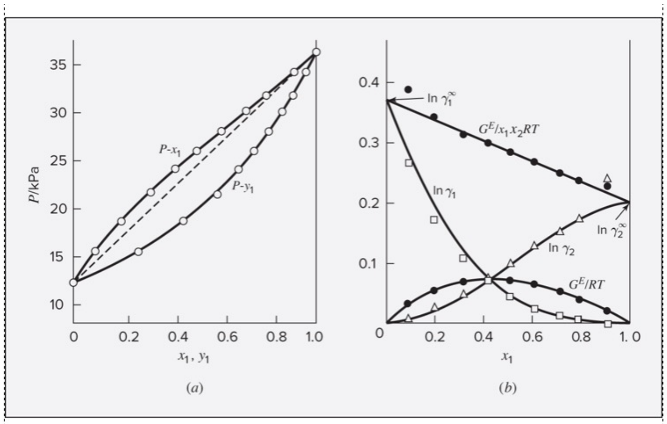

FIGURE 13.6 The methyl ethyl ketone(1)/toluene(2) system at 50°C. (***a***) ***Pxy*** data and their correlation. (***b***) Liquid-phase properties and their correlation.

Summary

Using the modified Raoult's law

$$y_i P = x_i \gamma_i P_i^{sat} \quad (i = 1,2,\ldots,N)$$

to calculate phase equilibria requires some model for the activity coefficients and the excess Gibbs energy.

The most common ones are found in the table on Slide 13.

The Gibbs/Duhem equation puts constraints on the values and slopes of the log activity coefficient curves that can be useful when evaluating data and models.