

AN INTRODUCTION TO ACTIVITY MODELS

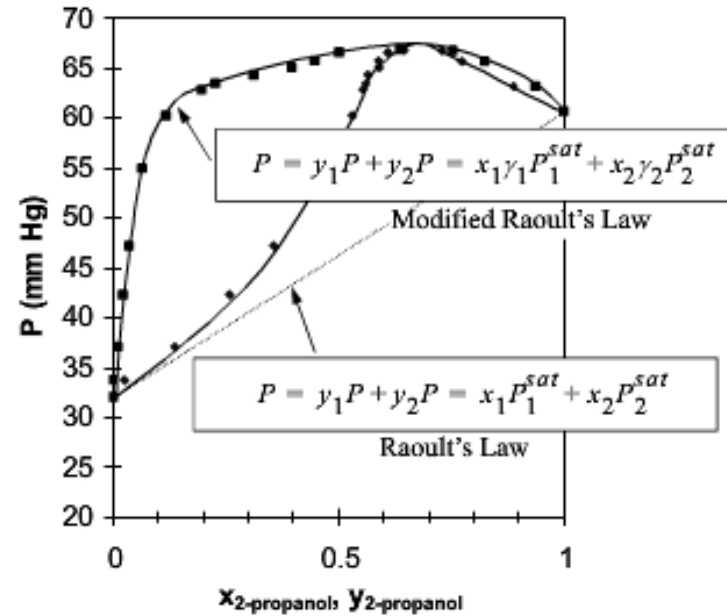


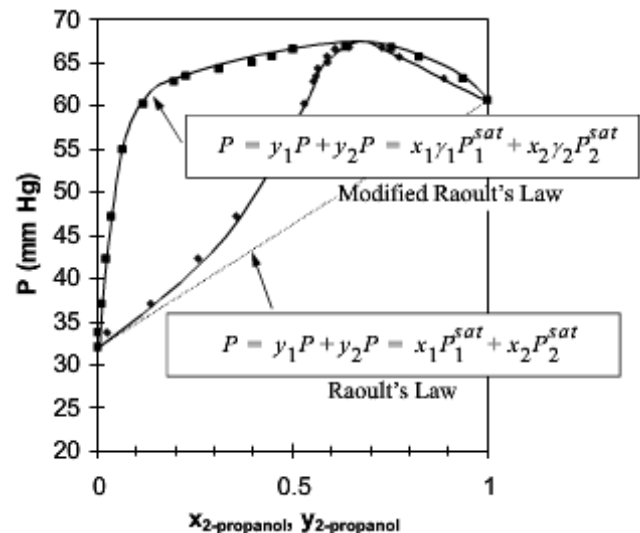
Figure 11.1 *P-x-y diagram for isopropanol-water at 30°C illustrating the rationale for activity coefficients using modified Raoult's law. Data from Udovenko, V.V., and Mazanko, T.F. 1967. Zh. Fiz. Khim. 41:1615.*

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \quad \text{“modified Raoult’s law”} \quad 11.1$$

$$P = y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

11.2  Bubble pressure calculation.

Now we can begin to see how this approach adjusts the model to the bubble pressure. When a system has **positive deviations** from Raoult’s law, the bubble line lies above the Raoult’s law bubble line ($P = x_1 P_1^{sat} + x_2 P_2^{sat}$), therefore $\gamma_i > 1$. When a system has **negative deviations**, $\gamma_i < 1$. This correction factor γ_b is referred to as the **activity coefficient**. Therefore, P - x - y data are related to the deviations of the activity coefficients from unity, or it may be helpful to consider the sign of $\ln \gamma_i$.¹ Look back at Fig. 11.1 and the figures in Section 10.7 and note that the deviations from Raoult’s law disappear as pure compositions are approached. This means that the deviations depend on composition, and that the $\gamma_i(x)$ that we have introduced in Eqn. 11.1 must go to 1 as the solution becomes pure in the i^{th} component.



$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \quad \text{“modified Raoult’s law”} \quad 11.1$$

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}} \quad 11.3$$

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad 11.4$$

As you might imagine, there are rules that we should follow to develop feasible functions. We discuss those theoretical aspects in the upcoming sections. The accepted method of modeling the system is to build a model for $\gamma_i(x)$ based in the **excess Gibbs energy**. The excess Gibbs energy is also discussed in upcoming sections, but briefly it is the Gibbs energy in “excess” of an ideal solution. It is generally positive when $\gamma_i > 1$ and negative when $\gamma_i < 1$. The model for excess Gibbs energy can be developed from a theoretical model of mixing behavior, and usually contains adjustable parameters to adjust the magnitude and skewness of the “excess” and thus fit the experiment.

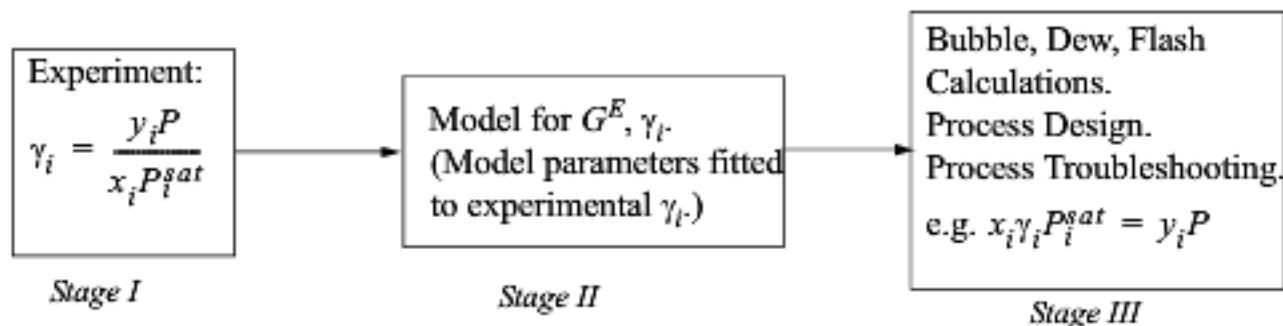


Figure 11.2 Strategy for using excess Gibbs energy models for activity coefficients. Experiments are used to determine γ_i in Stage I. A model is selected and the model is fitted in Stage II. The model is utilized to extend and extrapolate the experimental results in Stage III.

The One-Parameter Margules Equation

i The one-parameter Margules equation is the simplest excess Gibbs expression.

$$\frac{G^E}{RT} = A_{12}x_1x_2 \quad 11.5$$

i Margules one-parameter model for a binary mixture.

$$\ln\gamma_i = A_{12}(1-x_i)^2 \quad 11.6$$

Example 11.1 Gibbs excess energy for system 2-propanol + water

Using data from the 2-propanol(1) + water(2) system presented in Fig. 10.8 calculate the excess Gibbs energy at $x_1 = 0.6369$ and fit the one-parameter Margules equation. Data from the original citation provide $T = 30^\circ\text{C}$, $P_1^{sat} = 60.7$ mmHg, $P_2^{sat} = 32.1$ mmHg, and $y_1 = 0.6462$ when $x_1 = 0.6369$ at $P = 66.9$ mmHg.

Solution: The approach is to determine the activity coefficients and then relate them to the excess Gibbs energy. The Stage I step is

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{0.6462 \cdot 66.9}{0.6369 \cdot 60.7} = 1.118$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^{sat}} = \frac{0.3538 \cdot 66.9}{0.3631 \cdot 32.1} = 2.031$$

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = 0.6369 \ln (1.118) + 0.3631 \ln (2.031) = 0.328 \quad 11.7$$

If we were given more experimental data, we could repeat the calculation for each data point, thus creating a plot of G^E versus x_1 like the points shown in Fig. 11.3.

Then, we have been instructed to use the one-parameter Margules model for Stage II. Let us fit the model as given by Eqn. 11.5 and using the value from Eqn. 11.7.

$$\frac{G^E}{RT} = A_{12} x_1 x_2 = 0.328 \Rightarrow A_{12} = 0.328 / [(0.6369)(0.3631)] = 1.42 \quad 11.8$$

The curve of G^E versus x_1 is shown in Fig. 11.3 along with the two-parameter models to be discussed in Section 11.6 and Example 11.5.

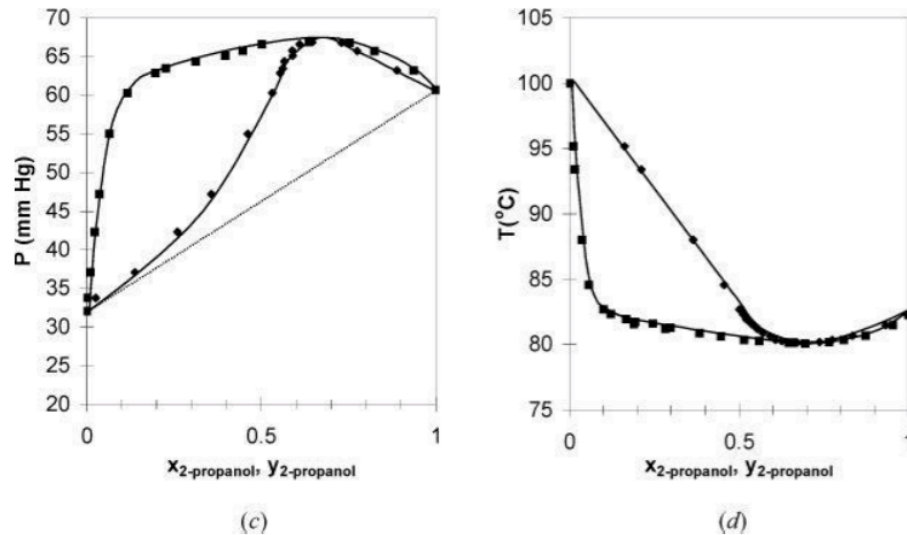


Figure 10.8. (c), (d) Phase behavior of the 2-propanol + water system. Left figure at 30°C. Right figure at 760 mm Hg. (T-x-y from Wilson, A., Simons, E.L., 1952. Ind. Eng. Chem. 44:2214, P-x-y from Udovenko, V.V., and Mazanko. T.F. 1967. Zh. Fiz. Khim. 41:1615.)

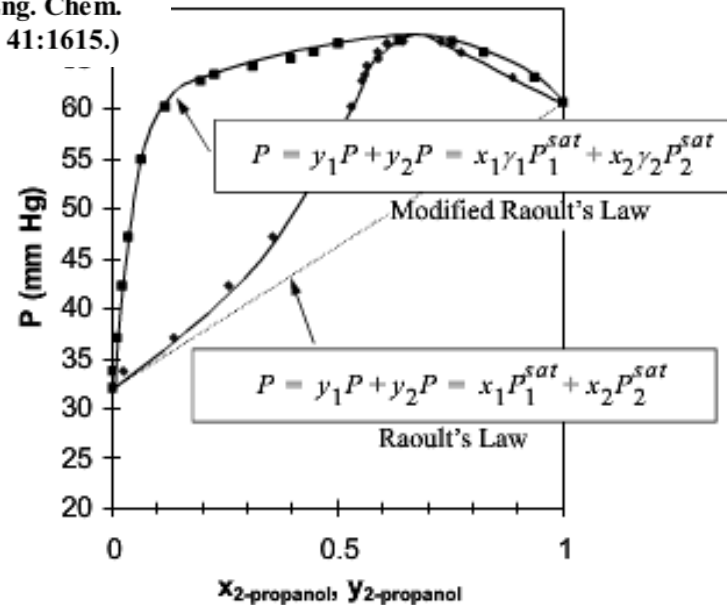


Figure 11.1 P-x-y diagram for isopropanol water at 30°C illustrating the rationale for activity coefficients using modified Raoult's law. Data from Udovenko, V.V., and Mazanko, T.F. 1967. Zh. Fiz. Khim. 41:1615.

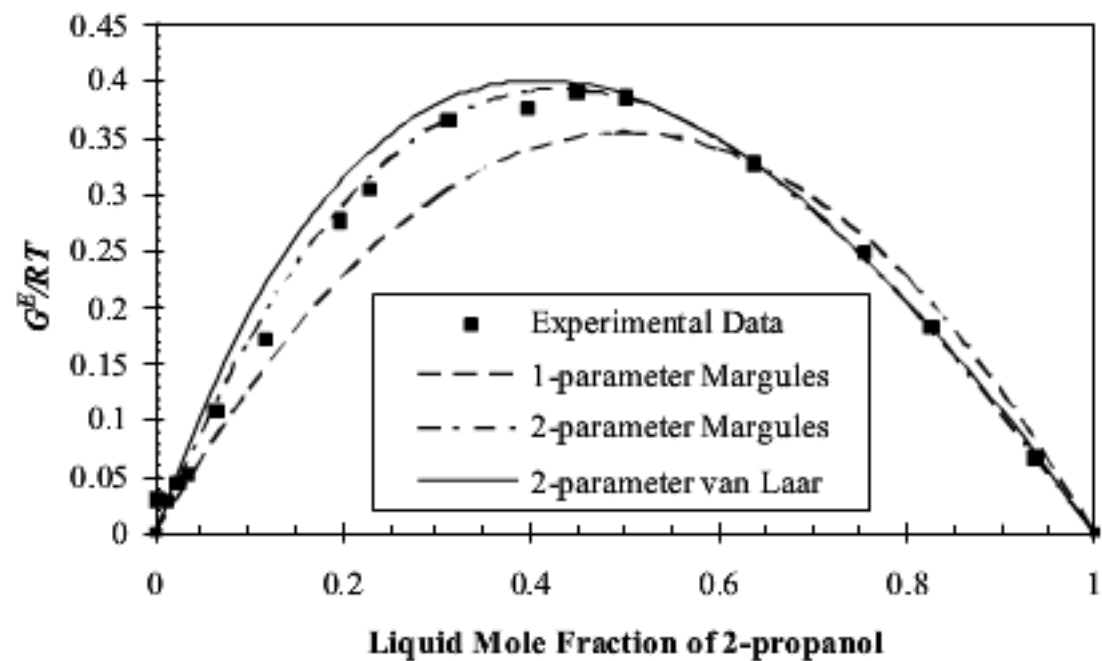


Figure 11.3 Illustration of calculation of G^E from experiment and fitting of Margules models to a single point as discussed in Examples 11.1 and 11.5, for 2-propanol + water, with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. The van Laar model fit to a single point is explained in Section 12.2.

11.2 CALCULATIONS USING ACTIVITY COEFFICIENTS

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \quad \text{“modified Raoult’s law”} \quad 11.1$$

i Margules one-parameter model for a binary mixture.

$$\ln \gamma_1 = A_{12}(1-x_1)^2 \quad 11.6$$

Table 10.1 Summary of the Types of Phase Equilibria Calculations (This Table is Independent of the VLE Model)

Type	Information known	Information computed	Criteria	Effort
BP	$T, x_i = z_i$	P, y_i	$\sum_i y_i = \sum_i K_i x_i = 1$	Easiest
DP	$T, y_i = z_i$	P, x_i	$\sum_i x_i = \sum_i (y_i / K_i) = 1$	Not bad
BT	$P, x_i = z_i$	T, y_i	$\sum_i y_i = \sum_i K_i x_i = 1$	Difficult
DT	$P, y_i = z_i$	T, x_i	$\sum_i x_i = \sum_i (y_i / K_i) = 1$	Difficult
FL	P, T^{in}, T^{out}, z_i	$x_i, y_i, V/F, Q$	$\sum_i \frac{z_i(1-K_i)}{1+(V/F)(K_i-1)} = 0$, E-bal for Q	Quite difficult
FA	$P, T^{in}, z_i, Q = 0$	$x_i, y_i, V/F, T^{out}$	$\sum_i \frac{z_i(1-K_i)}{1+(V/F)(K_i-1)} = 0$, E-bal	Most difficult

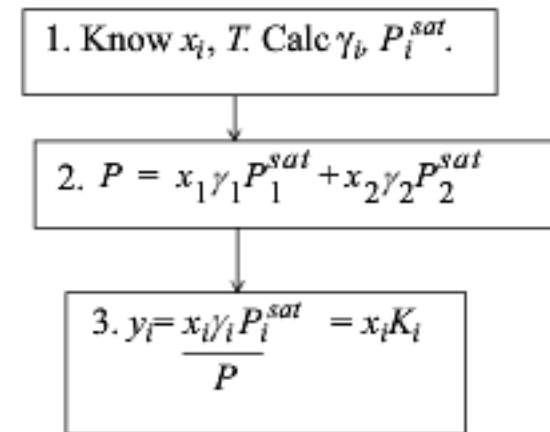


Figure 11.4 Bubble-pressure method for modified Raoult’s law.

Example 11.2 VLE predictions from the Margules equation

Use the fit of Example 11.1 to predict the P - x - y diagram for isopropanol + water at 30°C. The data used for Fig. 9.5 from Udovenko et al. for 2-propanol(1) + water(2) at 30°C show $x_1 = 0.1168$ and $y_1 = 0.5316$ at $P = 60.3$ mmHg.

Solution: This is a Stage III problem, since the first two stages have been completed earlier. Let us start by generating activity coefficients at the same composition where experimental data are provided, $x_1 = 0.1168$; we find

$$\ln \gamma_1 = A_{12} x_2^2 = 1.42(0.8832)^2 = 1.107, \Rightarrow \gamma_1 = 3.03$$

$$\ln \gamma_2 = A_{12} x_1^2 = 1.42(0.1168)^2 = 0.0194 \Rightarrow \gamma_2 = 1.02$$

Note that these activity coefficients differ substantially from those calculated in Example 11.1 because the liquid composition is different. We always recalculate the activity coefficients when new values of liquid composition are encountered.

Substituting into modified Raoult's law to perform a bubble-pressure calculation:

$$x_1 \gamma_1 P_1^{sat} = (0.1168)(3.03)(60.7) = 21.48 \text{ mmHg} = y_1 P$$

$$x_2 \gamma_2 P_2^{sat} = (0.8832)(1.02)(32.1) = 28.92 \text{ mmHg} = y_2 P$$

The total pressure is found by summing the partial pressures,

$$P = y_1 P + y_2 P = 50.4 \text{ mmHg}$$

We manipulate modified Raoult's law as shown in step 3 of Fig. 11.4:

$$y_1 = y_1 P / P = 21.48 / 50.4 = 0.426$$

Therefore, compared to the experimental data, the model underestimates the pressure and the vapor composition of y_1 is too low, but the use of one measurement and one parameter is a great improvement over Raoult's law. The estimation can be compared with the data by repeating the bubble-pressure calculation at selected x_i values across the composition range; the results are shown in Fig. 11.5. Recall that in Fig. 11.3 we noted that the excess Gibbs energy model using $A_{12} = 1.42$ fails to capture the skewness of the excess Gibbs energy curve. The deficiency is evident in the P - x - y diagram also. Fig. 11.5 includes a two-parameter fit that will be discussed later.

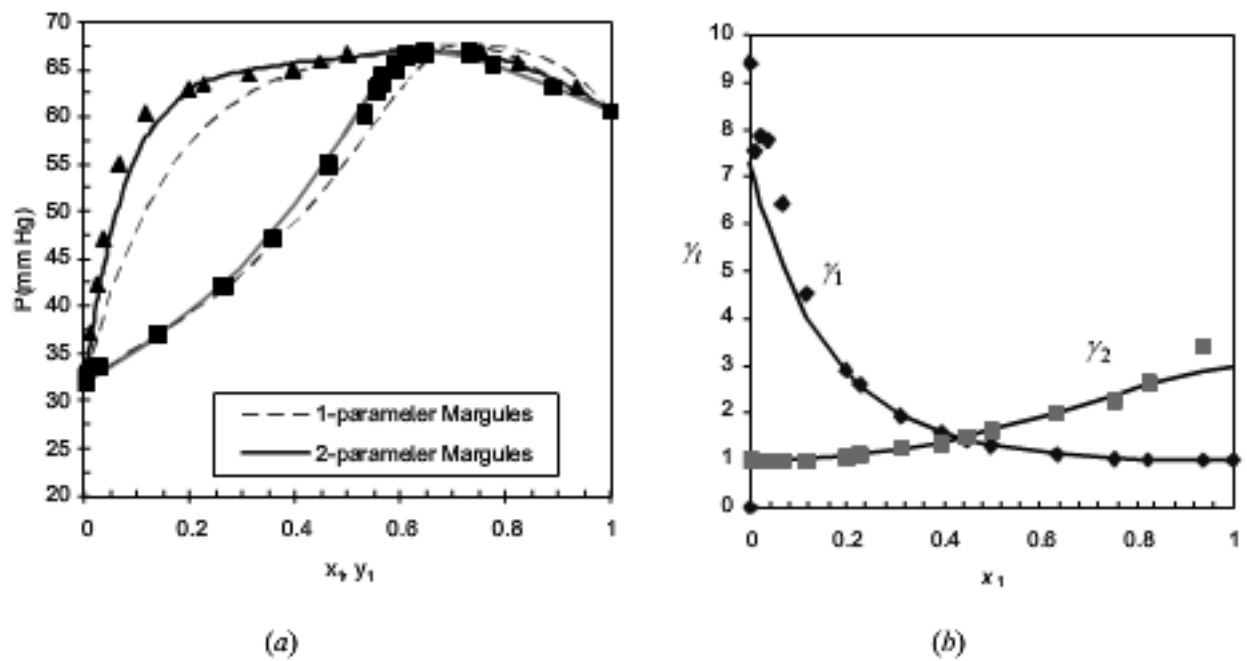


Figure 11.5 (a) One-parameter and two-parameter Margules equation fitted to a single measurement in Examples 11.2 and 11.5 compared with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. (b) Activity coefficients predicted from the parameters fitted in Example 11.5 compared with points calculated from the data.

Example 11.3 Gibbs excess characterization by matching the bubble point

The 2-propanol (1) + water (2) system is known to form an azeotrope at 760 mmHg and 80.37°C ($x_1 = 0.6854$). Estimate the Margules parameter by fitting the bubble pressure at this composition. Then compare your result to the Raoult's law approximation and to the data in Fig. 10.8(c) (at 30°C), where $P = 66.9$ mmHg at $x_1 = 0.6369$ as used in Example 11.1.

Solution: The Antoine coefficients for 2-propanol and water are given in Appendix E. At $T = 80.37^\circ\text{C}$, $P_1^{sat} = 694.0$ mmHg, and $P_2^{sat} = 359.9$ mmHg. We seek $P = 760$ mmHg. Let us use trial and error at the azeotropic composition to fit A_{12} to match the bubble pressure.

At $A_{12} = 1$, $\gamma_1 = \exp[1(1 - 0.6854)^2] = 1.104$; $\gamma_2 = \exp[1(1 - 0.3146)^2] = 1.600$; the bubble pressure is by Eqn. 11.2

$$P = 0.6854(694.)1.104 + 0.3146(359.9)1.600 = 706.3 \text{ mmHg}$$

The pressure is too low. We need larger activity coefficients, so A_{12} must be increased. Typing the bubble-pressure formula into Excel or MATLAB (see file Ex11_03.m), we can adjust A_{12} until $P = 760$ mmHg.

at $A_{12} = 1.368$, $\gamma_1 = \exp[1.368(1 - 0.6854)^2] = 1.145$; $\gamma_2 = \exp[1.368(1 - 0.3146)^2] = 1.902$; the bubble pressure is

$$P = 0.6854(694.)1.145 + 0.3146(359.9)1.902 = 760.0 \text{ mmHg}$$

Now, for the second part of the problem, to apply this at $T = 30^\circ\text{C}$, $P_1^{sat} = 58.28$ mmHg, $P_2^{sat} = 31.74$ mmHg. When $x_1 = 0.6369$ the ideal solution gives,

$$P = 0.6369(58.28) + 0.3631(31.74) = 48.64 \text{ mmHg}$$

At $A_{12} = 1.368$, $\gamma_1 = \exp[1.368(1 - 0.6369)^2] = 1.1976$;
 $\gamma_2 = \exp[1.368(1 - 0.3631)^2] = 1.7418$; the bubble pressure is

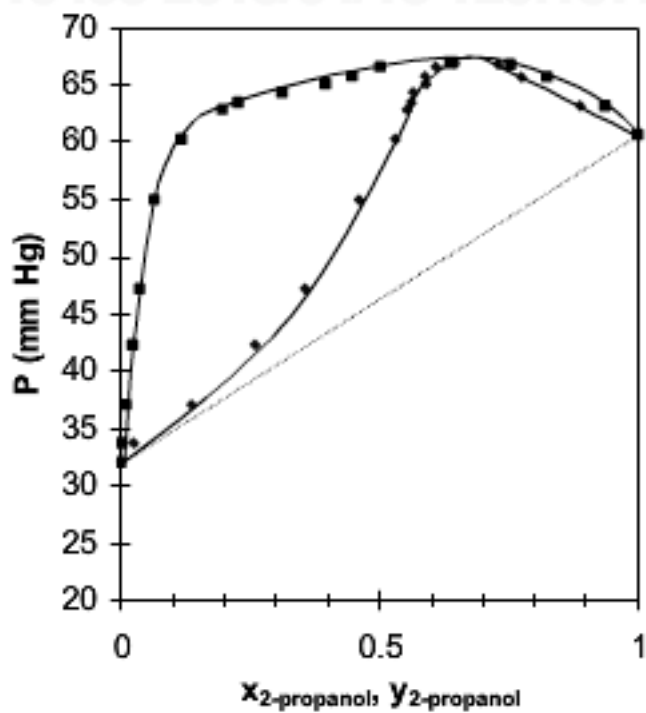
$$P = 0.6369(58.28)1.1976 + 0.3631(31.74)1.7418 = 64.53 \text{ mmHg}$$

Comparing, we see that the Raoult's Law approximation, $P = 48.6$ mmHg, deviates by 27% whereas the Margules model deviates by only 3.5%. Furthermore, the Margules model indicates an azeotrope because $64.5 > P_1^{sat} > P_2^{sat}$ means that there is a pressure maximum. Hence the Margules model "predicts" an azeotrope at this lower temperature, qualitatively consistent with Fig. 10.8(c), whereas the ideal solution model completely misses this important behavior.

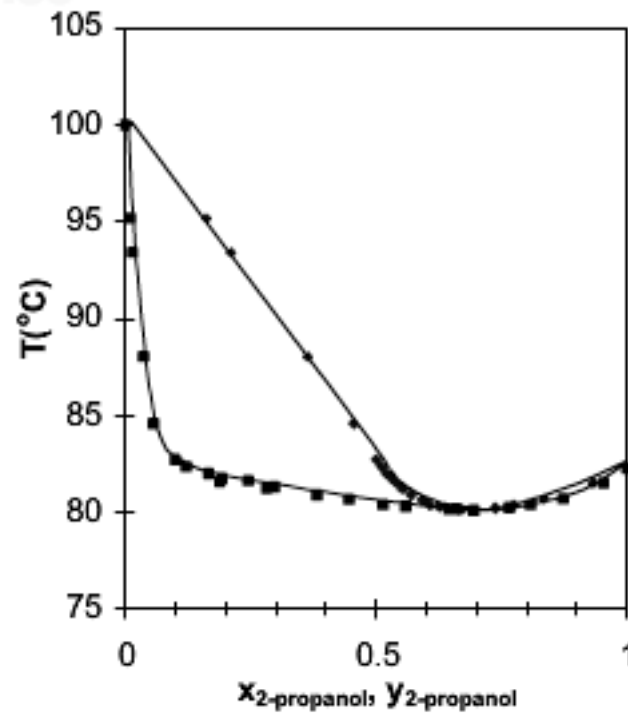
$$\ln \gamma_1 = A_{12} x_2^2$$

$$P = \gamma_1 P_1^{sat} + \gamma_2 P_2^{sat} = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

11.2  Bubble pressure calculation.



(c)



(d)

Figure 10.8 (c), (d) Phase behavior of the 2-propanol + water system. Left figure at 30°C. Right figure at 760 mm Hg. (T-x-y from Wilson, A., Simons, E.L., 1952. *Ind. Eng. Chem.* 44:2214, P-x-y from Udovenko, V.V., and Mazanko. T.F. 1967. *Zh. Fiz. Khim.* 41:1615.)

x-y Plots

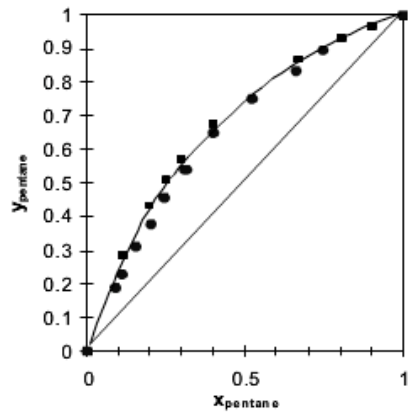


Figure 10.4 Data from Fig. 10.3 plotted with coexisting liquid and vapor values for each experimental tie line, resulting in the x - y plot. Note that the data do not superimpose exactly because one data set is isobaric and the other set is isothermal. Squares are T - x - y data. Circles are P - x - y data. The diagonal is traditionally drawn in an x - y figure, and the data never cross the diagonal for systems that follow Raoult's law.

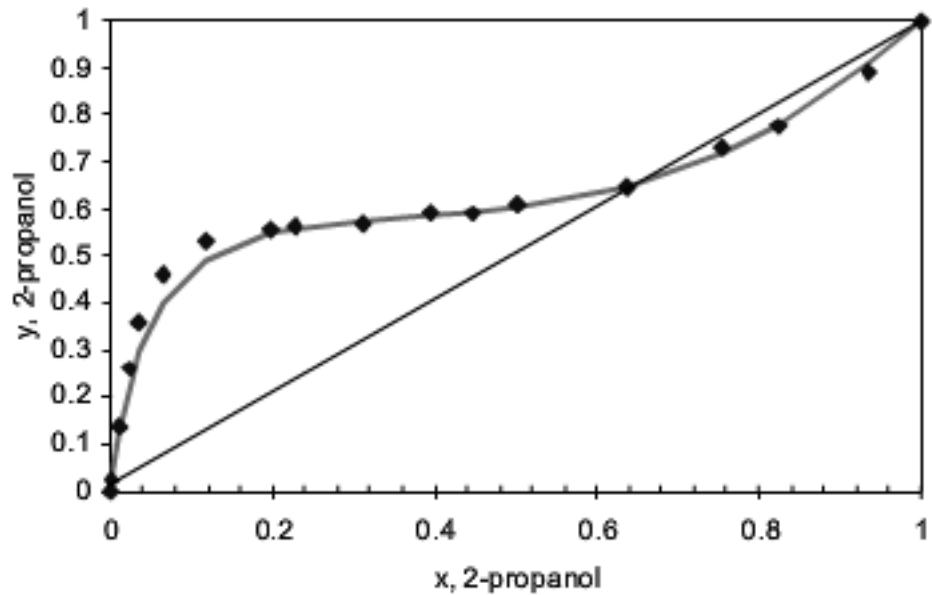
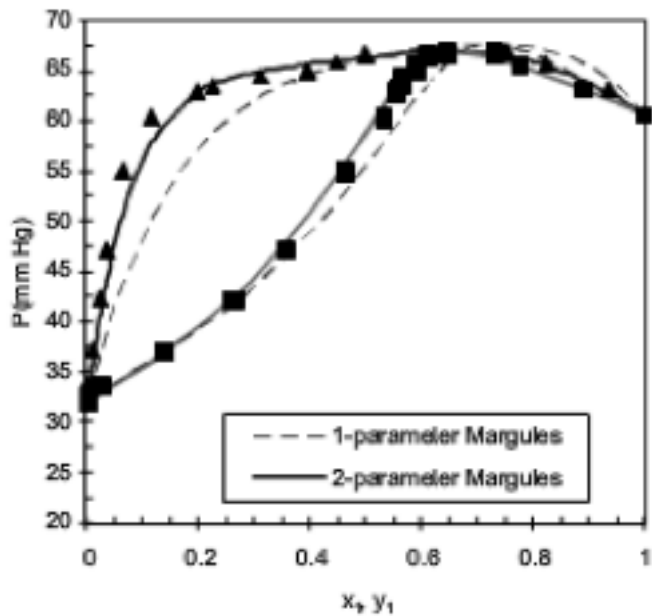


Figure 11.6 Data and the two-parameter fit of Fig. 11.5 plotted as pairs of x and y . Both T - x - y and P - x - y data can be plotted in this way.

Preliminary Predictions Based on a Molecular Perspective

You know that acids and bases interact favorably. An obvious example would be mixing baking soda and vinegar which react. You could also mix acid into water. These interactions are “favorable” because they release energy, meaning they are exothermic. They release energy because their interaction together is stronger than their self-interactions with their own species. A subtler exothermic example is hydrogen bonding, familiar perhaps from discussions of DNA, where the molecules do not react, but form exothermic hydrogen bonds. Unlike a covalent bond, the hydrogen sits in a minimum energy position between the donor and acceptor sites. The proton of a hydroxyl (-OH) group is acidic while an amide or carbonyl group acts as a base. We can extend this concept and assign qualitative numerical values characterizing the acidity and basicity of many molecules as suggested by Kamlet et al.³ These are the **acidity parameter**, α , and **basicity parameter**, β , values listed on the back flap. For example, this simple perspective suggests that chloroform ($\alpha > 0$) might make a good solvent for PMMA (a polymer with a molecular structure similar to methyl ethyl ketone, $\beta > 0$) because the α and β values should lead to favorable interactions. This is the perspective suggested by Fig. 11.7(a).

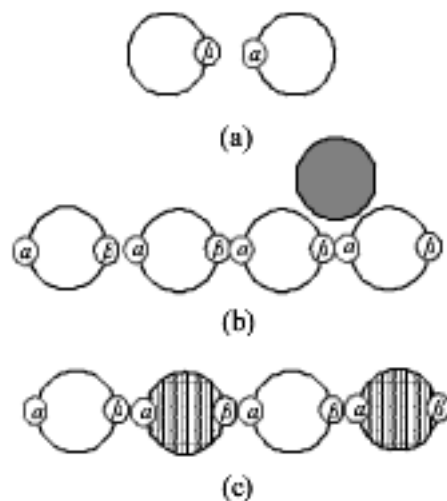


Figure 11.7 Observations about complexation. (a) A mixture of acid with base suggests favorable interactions, as in acetone + chloroform. (b) Hydrogen bonding leads to unfavorable interactions when one component associates strongly and the other is inert, as in isooctane + water. (c) Hydrogen bonding solutions can also be ideal solutions if both components have similar acidity and basicity, as in methanol + ethanol.

We can go a step further by formulating numerical predictions using what we refer to as the **Margules acid-base (MAB)** model. The model provides first-order approximations. The model is:

! Margules acid-base (MAB) model.

$$A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)/(4RT) \quad 11.9$$

where $V_i = M_{wi}/\rho_i^L$ is the liquid molar volume at 298.15K in cm^3/mol . The MAB model is introduced here for pedagogical purposes. MAB is a simplification of SSCED⁴ which is in turn a simplified adaptation of MOSCED⁵, both of which are covered in Chapter 12. Typical values of V , α , and β are presented in Table 11.1. For example, with chloroform + acetone at 60°C, this formula gives

$$A_{12} = (5.8 - 0)(0.12 - 11.14)(80.5 + 73.4)/[4(8.314)333] = -0.888 \quad 11.10$$

Table 11.1 Acidity (α) and Basicity (β) Parameters in $(\text{J}/\text{cm}^3)^{1/2}$ and Molar Volumes (cm^3/mol) for Various Substances as liquids at 298 K^a

Compound	α	β	V^L
Acetone	0	11.14	73.4
Benzene	0.63	2.24	89.7
Chloroform	5.80	0.12	80.5
Ethanol	12.58	13.29	58.2
<i>n</i> -Hexane	0	0	130.3
Isooctane	0	0	162.9
Isopropanol	9.23	11.86	76.8
Methanol	17.43	14.49	40.5
MEK	0	9.70	90.1
Water	50.13	15.06	18.0

a. Additional parameters are on the back flap.

Note how the order of subtraction results in a negative value for A_{12} when one of the components is acidic and the other is basic. If you switched the subscript assignments, then $\Delta\alpha$ would be negative and $\Delta\beta$ would be positive, but A_{12} would still be negative. This negative value makes the value of γ_i smaller, and that is basically what happens when hydrogen bonding is favorable. Something else happens when one compound forms hydrogen bonds but the other is inert. Taking isooctane(1) as representative of oil (or gasoline) and mixing it with water(2) at 25°C,

$$A_{12} = (50.13 - 0)(15.06 - 0)(18.0 + 162.9)/[4(8.314)298] = 12.33 \quad 11.11$$

This large positive value results in $\gamma_1 > 7.5$ for the isooctane. We can use $\gamma_i > 7.5$ to suggest a liquid phase split, as we should expect from the familiar guideline that oil and water do not mix. Furthermore, we can quantify the solubilities of the components in each other (aka. **mutual solubilities**) by noting that $x_i \approx 1/\gamma_i$ when $\gamma_i > 100$. Knowing the saturation limit of water contaminants can be useful in environmental applications. As a final example, note that we recover an ideal solution when both components hydrogen bond similarly, as in the case of ethanol + methanol at 70°C.

$$A_{12} = (17.43 - 12.58)(14.49 - 13.29)(40.5 + 58.2)/[4(8.314)343] = 0.05 \quad 11.12$$

In this case, we see that hydrogen bonding by itself is not the cause of solution non-ideality. A *mismatch* of hydrogen bonding is required to create non-idealities.

Example 11.4 Predicting the Margules parameter with the MAB model

Predict the A_{12} value of the 2-propanol (1) + water (2) system using the MAB model at 30°C. Then compare your result to those of Examples 11.1 and 11.3.

Solution: From Eqn. 11.9, $A_{12} = (50.13 - 9.23)(15.06 - 11.86)(76.8 + 18.0)/[4(8.314)303] = 1.08$. This compares to the value $A_{12}/RT = 1.42$ from Example 11.1 and $A_{12}/RT = 1.37$ from Example 11.3 at 30°C. The MAB model does not provide a precise prediction, but qualitatively indicates a positive deviation of the right magnitude.

11.3 DERIVING MODIFIED RAOULT'S LAW

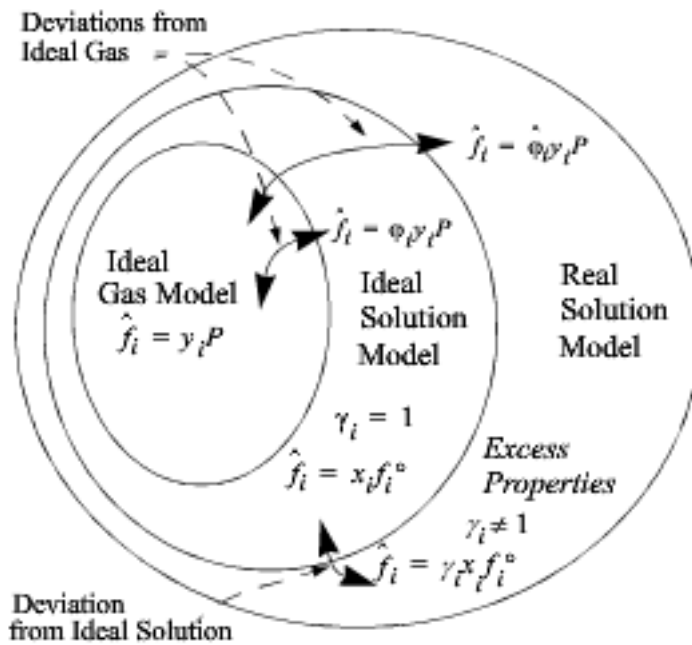



Figure 11.8 Schematic of the relations between different fluid models. Ideal gases are a subset of ideal mixtures, which in turn are a subset of real mixtures. Departure functions (fugacity coefficients) characterize deviations from ideal-gas behavior, and excess properties (activity coefficients) characterize deviations from ideal-solution behavior.

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o}$$

11.13  Activity coefficients are commonly used for highly non-ideal solutions.

A value of $\gamma_i = 1$ will denote an ideal solution; f_i^o is the value of the fugacity at **standard state**. A standard state is slightly different from a reference state. The standard state is a specified temperature, pressure, and composition. The most common standard state in solution thermodynamics is the pure component at the same temperature pressure as the system. You can see that this is clearly different

$$\hat{f}_i^L = x_i \gamma_i f_i^L \quad 11.14$$

$$f_i^L = \phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^L(P - P_i^{sat})}{RT}\right)$$

$$y_i \phi_i P = x_i \gamma_i \phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^L(P - P_i^{sat})}{RT}\right) \quad 11.15 \quad \text{the gamma-phi method}$$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \left[\frac{\phi_i^{sat} \exp[V_i^L(P - P_i^{sat})/(RT)]}{\hat{\phi}_i} \right] \quad 11.16$$

$$\hat{f}_i^L = \hat{f}_i^V$$

$$\left[K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \right]; \quad \left[\hat{f}_i^L \approx x_i \gamma_i P_i^{sat} \right]; \quad \left[\hat{f}_i^V \approx y_i P \right] \quad 11.17 \quad \text{Modified Raoult's law.}$$

 Modified Raoult's law.

$$\left[y_i P = x_i \gamma_i P_i^{sat} \right] \quad \text{or} \quad \left[K_i = \frac{\gamma_i P_i^{sat}}{P} \right] \quad 11.18$$

11.4 EXCESS PROPERTIES

The deviation of a property from its ideal-solution value is called the **excess property**.

$$V^E = V - V^{is} = V - \sum_i x_i V_i \quad 11.19$$

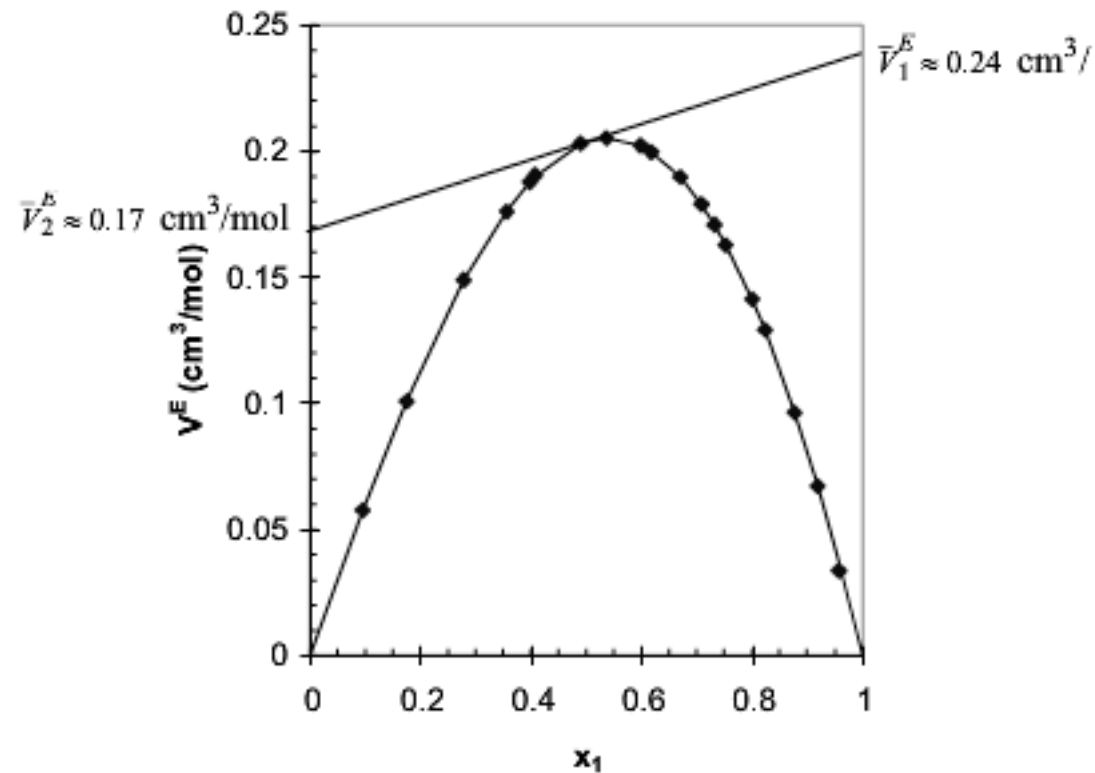


Figure 11.9 Excess volume for the 3-pentanone (1) + 1-chlorooctane (2) system at 298.15 K.

$$H^E = H - H^{is} = H - \sum_i x_i H_i \quad 11.20$$

A solution with $H^E > 0$ has an **endothermic heat of mixing**, and when $H^E < 0$, the heat of mixing is **exothermic**. In an adiabatic mixing process an endothermic mixing process will cool and an exothermic mixing process will heat.

11.5 MODIFIED RAOULT'S LAW AND EXCESS GIBBS ENERGY

$$\begin{aligned}
 G^E &= G - G^{is} \\
 &= \left(G - \sum_i x_i G_i \right) - \left(G^{is} - \sum_i x_i G_i \right) \\
 &= \Delta G_{mix} - \Delta G_{mix}^{is} = \Delta G_{mix} - RT \sum_i x_i \ln(x_i)
 \end{aligned}$$

11.21  Excess Gibbs energy.

$$G = \sum_i x_i \mu_i$$

$$\mu_i - \mu_i^o = RT \ln \frac{\hat{f}_i}{f_i^o}$$

11.22

 Activity.

$$a_i = \frac{\hat{f}_i}{f_i^o} = x_i \gamma_i$$

11.23

$$\Delta G_{mix} = G - \sum_i x_i G_i = \sum_i x_i (\mu_i - G_i) = RT \sum_i x_i \ln \left(\frac{f_i}{f_i^*} \right) \quad 11.24$$

$$\Delta G_{mix} = RT \sum_i x_i \ln(a_i) = RT \sum_i x_i \ln(x_i \gamma_i) \quad 11.25$$

$$G^E = \Delta G_{mix} - RT \sum_i x_i \ln(x_i) = RT \sum_i x_i \ln(x_i \gamma_i) - RT \sum_i x_i \ln(x_i) = RT \sum_i x_i \ln(\gamma_i) \quad 11.26$$

$$G^E = RT \sum_i x_i \ln(\gamma_i) \quad 11.27$$

ⓘ Excess Gibbs energy is zero for an ideal solution, and activity coefficients are unity.

Note that the activity coefficients and excess Gibbs energy are coupled—when the activity coefficients of all components are unity, the excess Gibbs energy goes to zero. The excess Gibbs energy is zero for an ideal solution.

Example 11.1 $\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

$$G^E = RT \sum_i x_i \ln(\gamma_i)$$

Activity Coefficients as Derivatives

$$\left(\frac{\partial G^E}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \bar{G}_i^E = \mu_i^E = RT \ln \gamma_i$$

11.28 **!** Activity coefficients are related to the partial molar excess Gibbs energy.

$$\frac{G^E}{RT} = A_{12} x_1 x_2 \qquad \frac{G^E}{RT} = n(A_{12} x_1 x_2) = (A_{12} n_2) \left(\frac{n_1}{n} \right) \qquad 11.29$$

$$\frac{1}{RT} \left(\frac{\partial G^E}{\partial n_1} \right)_{T, P, n_2} = \ln \gamma_1 = A n_2 \left[\frac{1}{n} - \frac{n_1}{n^2} \right] = A \frac{n_2}{n} \left[1 - \frac{n_1}{n} \right] = A x_2 (1 - x_1) \qquad 11.30$$

$$\ln \gamma_1 = A x_2^2 \quad ; \quad \text{similarly } \ln \gamma_2 = A x_1^2 \qquad 11.31$$

11.6 REDLICH-KISTER AND THE TWO-PARAMETER MARGULES MODELS

$$\frac{G^E}{RT} = A_{12}x_1x_2$$

$$\frac{G^E}{RT} = x_1x_2(B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \dots) \quad 11.32$$

Two-Parameter Margules Model

$$\boxed{\frac{G^E}{RT} = x_1x_2(A_{21}x_1 + A_{12}x_2)}^{10} \quad 11.33$$

where we relate the constants to the Redlich-Kister via $A_{21} = B_{12} + C_{12}$, $A_{12} = B_{12} - C_{12}$, and $D_{12} = 0$. The constants A_{21} and A_{12} are fitted to experiment as we show below. Note that if $A_{21} = A_{12}$, the expression reduces to the one-parameter model. The expression for the activity coefficient of the

$$\ln \gamma_1 = A_{12} x_2^2$$

$$\ln \gamma_2 = A_{12} x_1^2$$

$$\frac{1}{RT} \left(\frac{\partial G^E}{\partial n_1} \right)_{T,P,n_2} = \ln \gamma_1 = n_2 \left(A_{21} + \frac{n_2}{n} (A_{12} - A_{21}) \right) \left[\frac{1}{n} - \frac{n_1}{n^2} \right] + n_2 \left(\frac{n_1}{n} \right) \left(\frac{-n_2}{n} \right) (A_{12} - A_{21}) \quad 11.35$$

$$\ln \gamma_1 = x_2^2 [(A_{21} + (1-x_1)(A_{12}-A_{21})) + (A_{21}-A_{12})x_1] \quad 11.36$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1] ; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2] \quad 11.37$$

The two parameters can be fitted to a single VLE measurement using

$$A_{12} = \left(2 - \frac{1}{x_2} \right) \frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \quad A_{21} = \left(2 - \frac{1}{x_1} \right) \frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2} \quad 11.38$$

Example 11.5 Fitting one measurement with the two-parameter Margules equation

We mentioned following Example 11.2 that a single experiment could be used more effectively with the two-parameter model. Apply Eqn. 11.38 to the two activity coefficients values calculated in Example 11.1 and estimate the two parameters. This is an example of a Stage II calculation.

Solution: From Example 11.1, $x_1 = 0.6369$, $x_2 = 0.3631$, and $\gamma_1 = 1.118$, $\gamma_2 = 2.031$. From Eqn. 11.38,

$$A_{12} = \left(2 - \frac{1}{0.3631}\right) \frac{\ln 1.118}{0.3631} + \frac{2 \ln 2.031}{0.6369} = 1.99$$

$$A_{21} = \left(2 - \frac{1}{0.6369}\right) \frac{\ln 2.031}{0.6369} + \frac{2 \ln 1.118}{0.3631} = 1.09$$

$$A_{12} = \left(2 - \frac{1}{x_2}\right) \frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \quad A_{21} = \left(2 - \frac{1}{x_1}\right) \frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2}$$

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

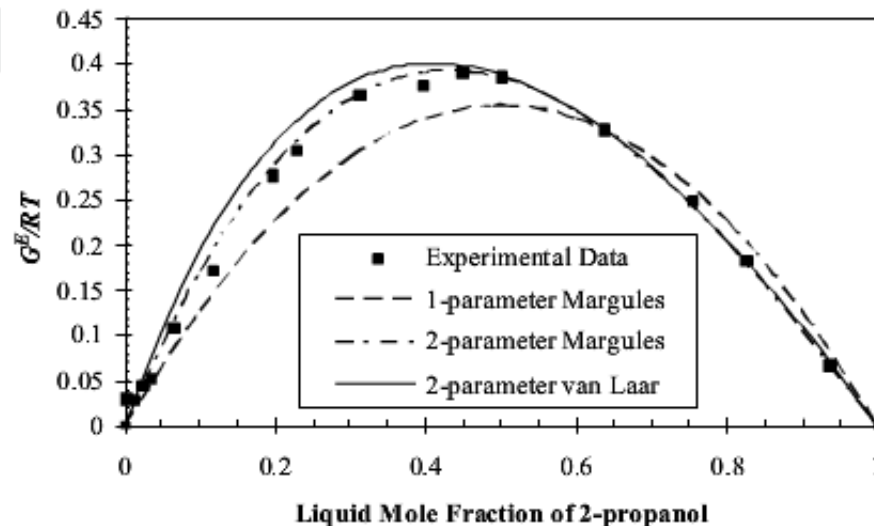
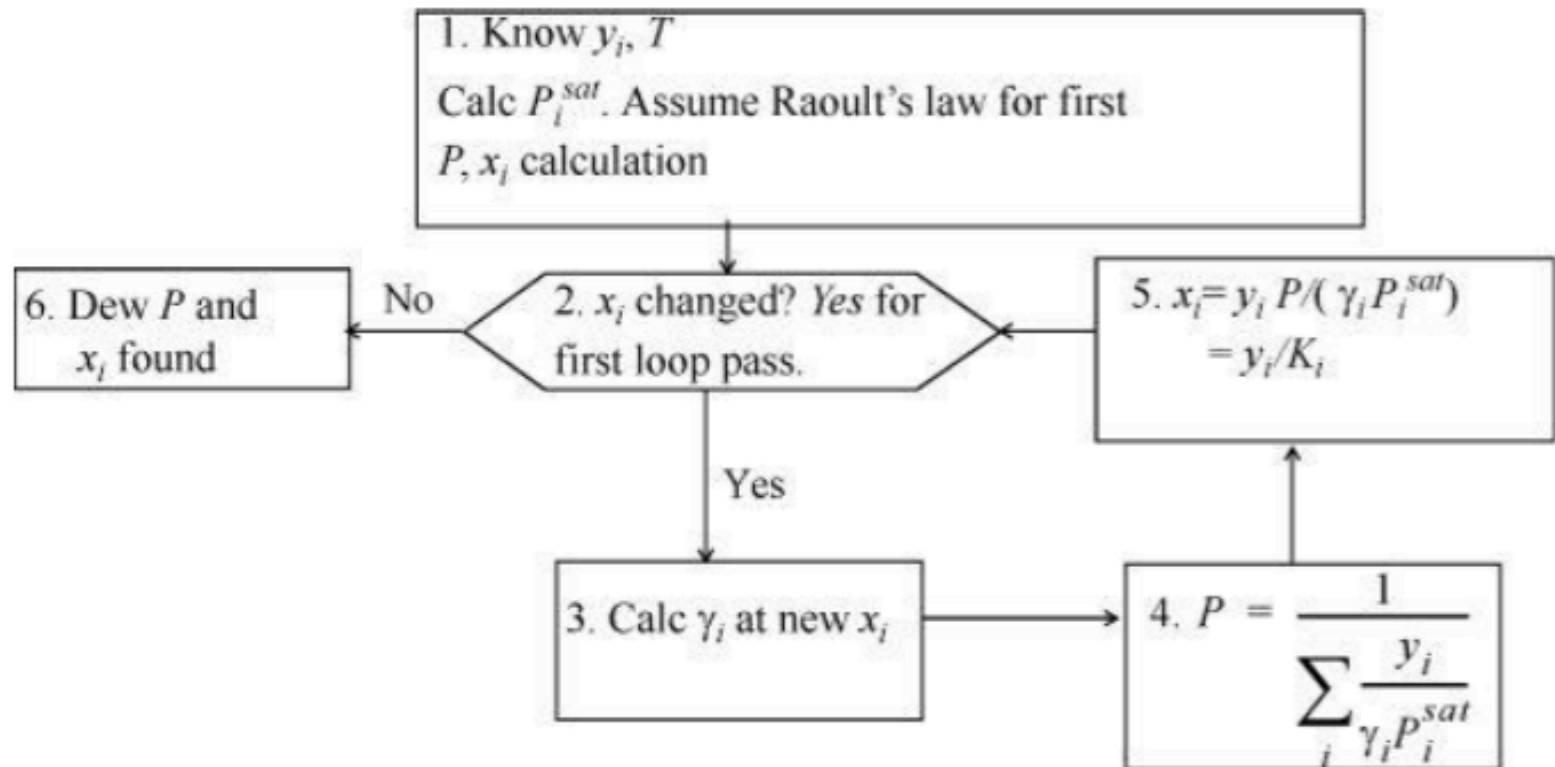


Figure 11.3 Illustration of calculation of G^E from experiment and fitting of Margules models to a single point as discussed in Examples 11.1 and 11.5, for 2-propanol + water, with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. The van Laar model fit to a single point is explained in Section 12.2.

Dew P



Example 11.6 Dew pressure using the two-parameter Margules equation

Use the parameters of Example 11.5 to predict the dew-point pressure and liquid composition for the 2-propanol(1) + water(2) system at $T = 30^\circ\text{C}$, $y_1 = 0.4$, and compare with Fig. 11.5. Use the vapor pressures, $P_1^{sat} = 60.7$ mmHg, $P_2^{sat} = 32.1$ mmHg.

Solution: We will apply the procedure in Appendix C and refer to step numbers there.

Step 1. Refer to Chapter 10, $P = 1/(0.4/60.7 + 0.6/32.1) = 39.55$ mmHg,

$x_1 = 0.4(39.55)/60.7 = 0.26$. We skip Step 2 the first time.

Step 3. Using parameters from Example 11.5 in Eqn. 11.37,

$\gamma_1 = \exp(0.74^2(1.99 - 1.8(0.26))) = 2.30$; $\gamma_2 = \exp(0.26^2(1.09 + 1.8(0.74))) = 1.18$.


Step 4. $P = 1/(0.4/(2.3 \cdot 60.7) + 0.6/(1.18 \cdot 32.1)) = 53.46$ mmHg

Note the jump in P compared to Step 1 for the first loop.

Step 5. $x_1 = 0.4(53.46)/(2.3 \cdot 60.7) = 0.153$. Continuing the loop:

γ_1	γ_2	P (mmHg)	x_1
3.421	1.063	51.26	0.0987
4.359	1.027	50.73	0.0767
4.849	1.016	50.62	0.0688

Continuing for several more iterations with four digits, $P = 50.63$ mmHg, and $x_1 = 0.0649$. The calculations agree favorably with Fig. 11.5. The dew calculations are consistent with a bubble calculation at $x_1 = 0.0649$.

 Dew-pressure calculation.

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$

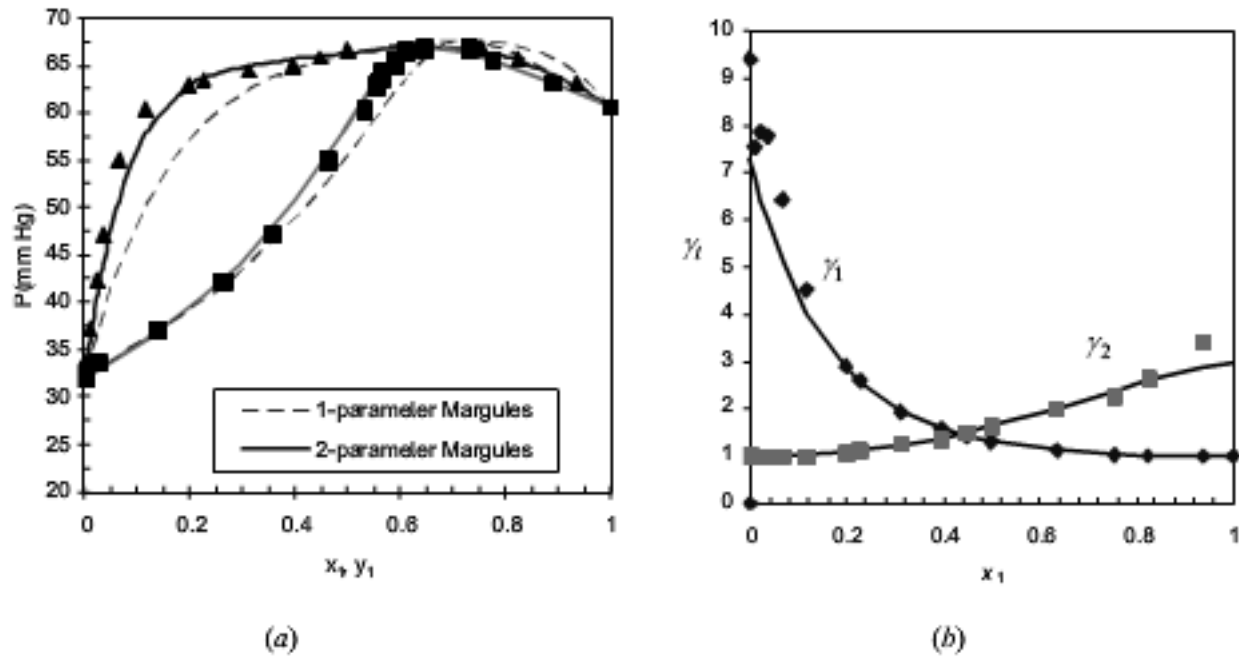


Figure 11.5 (a) One-parameter and two-parameter Margules equation fitted to a single measurement in Examples 11.2 and 11.5 compared with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. (b) Activity coefficients predicted from the parameters fitted in Example 11.5 compared with points calculated from the data.

Table 11.2 Summary of Empirical Activity Models and Simplifications Relative to the Redlich-Kister

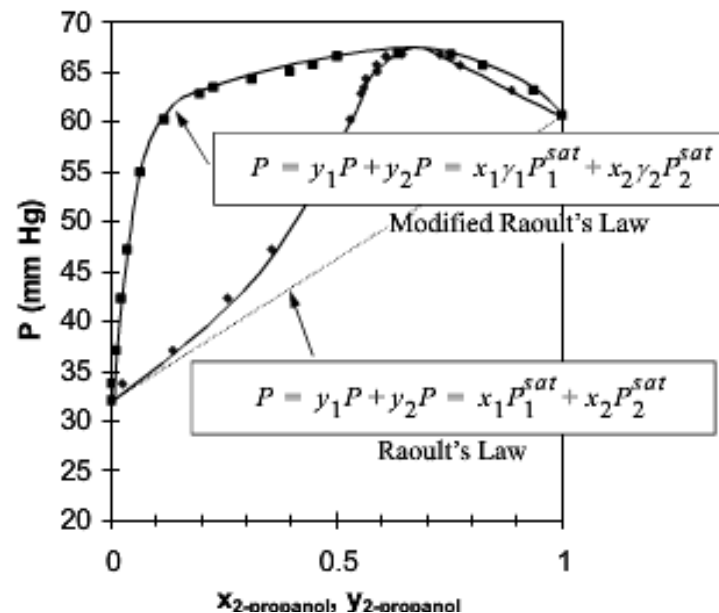
Model	G^E/RT	$\ln \gamma_1$	Simplification
Redlich-Kister	$x_1 x_2 [B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \dots]$	cf. Practice problem P11.2	--
Margules two-parameter	$x_1 x_2 (A_{21} x_1 + A_{12} x_2)$	$x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]$	$D_{12}=0; A_{21}=B_{12}+C_{12}; A_{21}=B_{12}-C_{12}$
Margules one-parameter	$x_1 x_2 A_{12}$	$x_2^2 A_{12}$	$C_{12}=D_{12}=0; A_{12}=A_{12}=B_{12}$
Ideal solution	0	0	$B_{12} = C_{12} = D_{12} = 0$

11.7 ACTIVITY COEFFICIENTS AT SPECIAL COMPOSITIONS

Azeotropes

Many tables of known azeotropes are commonly available.¹² For systems with an azeotrope, the azeotropic pressure and composition provide a useful data point for fitting activity coefficient models because $x_1 = y_1$. Then $\gamma_1 = P/P_1^{sat}$; $\gamma_2 = P/P_2^{sat}$. Then the typical single point fitting formulas are used with the azeotrope composition to find the model parameters.

! The azeotrope is a useful point to fit parameters.



The location of an azeotrope is very important for distillation design because it represents a point at which further purification in a single distillation column is impossible. Look back at Fig. 11.1 on page 412. Looking at dilute isopropanol concentrations, note $x_{2\text{-propanol}} = 0.01 < y_{2\text{-propanol}}$, but near purity, $x_{2\text{-propanol}} = 0.99 > y_{2\text{-propanol}}$. The relative magnitudes have crossed and thus we expect $y_{2\text{-propanol}} = x_{2\text{-propanol}}$ (i.e., there is an azeotrope) somewhere in between. If the relative sizes are the same at both ends of the composition range, then we expect that an azeotrope does not exist.¹¹ Certainly, the best way to identify an azeotrope is to plot T - x - y or P - x - y , but a quick calculation at each end of the diagram is usually sufficient.

! Any deviation from ideality will create an azeotrope at a Bancroft point.

We noted in Section 10.7 on page 393 that azeotropic behavior was dependent on the magnitude of deviations from ideality *and* the vapor pressure ratio. Look back at Fig. 11.1 on page 412 and recall that deviations from Raoult's law create the curve in the bubble line. When the pure component vapor pressures are nearly the same then a slight curve due to non-ideality can cause an azeotrope. The same size deviation in a system with widely different vapor pressure may not have an azeotrope. A plot of $\log P^{sat}$ versus $1/T$ with both components may show a point where the two curves cross when the heats of vaporization are different. This point is called a **Bancroft point**. Since the vapor pressures are exactly equal at the Bancroft point, any small non-ideality generates

A **Bancroft point** is the temperature where an **azeotrope** occurs in a **binary system**. Although **vapor liquid** azeotropy is impossible for binary systems which are rigorously described by **Raoult's law**, for real systems, azeotropy is inevitable at temperatures where the saturation **vapor pressure** of the components are equal. Such a temperature is called a Bancroft point. However, not all binary systems exhibit such a point. Also, a Bancroft point must lie in the valid temperature ranges of the **Antoine equation**.

Bancroft point is named after **Wilder Dwight Bancroft**.

Could find an Azeotrope by setting Antoine eqn for two components equal and solving for the temperature (must be in the range of the AE).

Born in [Middletown, Rhode Island](#), he received a [B.A.](#) from [Harvard University](#) in 1888, a [Ph.D.](#) from [University of Leipzig](#) in 1892, and honorary [SCDs](#) from [Lafayette College](#) (in 1919) and [Cambridge University](#) (in 1923). He was the grandson of historian and statesman [George Bancroft](#) and great-grandson of [Aaron Bancroft](#).

He was an assistant [chemistry](#) instructor at [Harvard University](#) from 1888–1889 and 1893–1894, then a full instructor from 1894–1895. He then became an assistant professor at [Cornell University](#) in 1895, then a full professor (at Cornell) in 1903. He was elected a Fellow of the [American Academy of Arts and Sciences](#) in 1913.^[1]

Bancroft was trained by [Wilhelm Ostwald](#) and [Jacobus Henricus van 't Hoff](#), and introduced a number of thermodynamic and colloid-chemical concepts into American physicochemistry. He is known for the [Bancroft rule](#): a predominantly hydrophilic emulsifier stabilizes an oil-in-water emulsion, whereas a predominantly hydrophobic emulsifier stabilizes a water-in oil emulsion.

The lunar crater [Bancroft](#) is named in his honor.

His daughter, Mary Warner Bancroft (1896–1967) married another Cornell chemistry professor, [Melvin Lorrel Nichols](#) (1894–1981).

Example 11.7 Azeotrope fitting with bubble-temperature calculations

Consider the benzene(1) + ethanol(2) system which exhibits an azeotrope at 760 mmHg and 68.24°C containing 44.8 mole% ethanol. Using the two-parameter Margules model, calculate the composition of the vapor in equilibrium with an equimolar liquid solution at 760 mmHg given the following Antoine constants:

$$\log P_1^{sat} = 6.87987 - 1196.76/(T + 219.161)$$

$$\log P_2^{sat} = 8.1122 - 1592.86/(T + 226.18).$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2] \quad 11.37$$

$$A_{12} = \left(2 - \frac{1}{x_2}\right) \frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \quad A_{21} = \left(2 - \frac{1}{x_1}\right) \frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2} \quad 11.38$$

Solution: At $T = 68.24^\circ\text{C}$, $P_1^{sat} = 519.7$ mmHg; $P_2^{sat} = 503.5$ mmHg, and the azeotrope composition is known, $x_1 = 0.552$; $x_2 = 0.448$. At this composition, the activity coefficients can be calculated.

$$\gamma_1 = (y_1 P) / (x_1 P_1^{sat}) = P / P^{sat} = 760 / 519.7 = 1.4624; \text{ likewise, } \gamma_2 = 760 / 503.5 = 1.5094$$

Using Eqn. 11.38 with the composition and γ 's just tabulated, $A_{12} = 1.2947$, $A_{21} = 1.8373$.

New activity coefficient values must be found at the composition, $x_1 = x_2 = 0.5$. Using Eqn. 11.37, $\gamma_1 = 1.583$; $\gamma_2 = 1.382$. The problem statement requires a bubble-temperature calculation. Using the method of Table 10.1 (a flow sheet is available in Appendix C, option (a); a MATLAB example is provided in Ex11_07.m),

Guess $T = 60^\circ\text{C} \Rightarrow P_1^{sat} = 391.63$ mmHg; $P_2^{sat} = 351.82$ mmHg. For this model, the activity coefficients do not change with temperature. The K -ratio depends on the activity coefficients:

$$y_i = x_i \gamma_i P_i^{sat} / P \Rightarrow y_1 = 0.408; y_2 = 0.320;$$

Checking the sum of y_i , $\sum_i y_i = 0.728 \Rightarrow T_{\text{guess}}$ is too low. Try a higher T .

After a few trials, at $T = 68.262^\circ\text{C}$, $P_1^{sat} = 520.13$ mmHg; $P_2^{sat} = 504.1$ mmHg

$$y_i = x_i \gamma_i P_i^{sat} / P \Rightarrow y_1 = 0.542; y_2 = 0.458; \sum_i y_i = 1 \Rightarrow T_{\text{guess}} \text{ is } T_{\text{azeotrope}}$$

⚠ Positive deviations from Raoult's law, $\gamma_i > 1$.

⚠ Bubble-temperature calculation.

📄 Ex11_07.m.

Bubble T

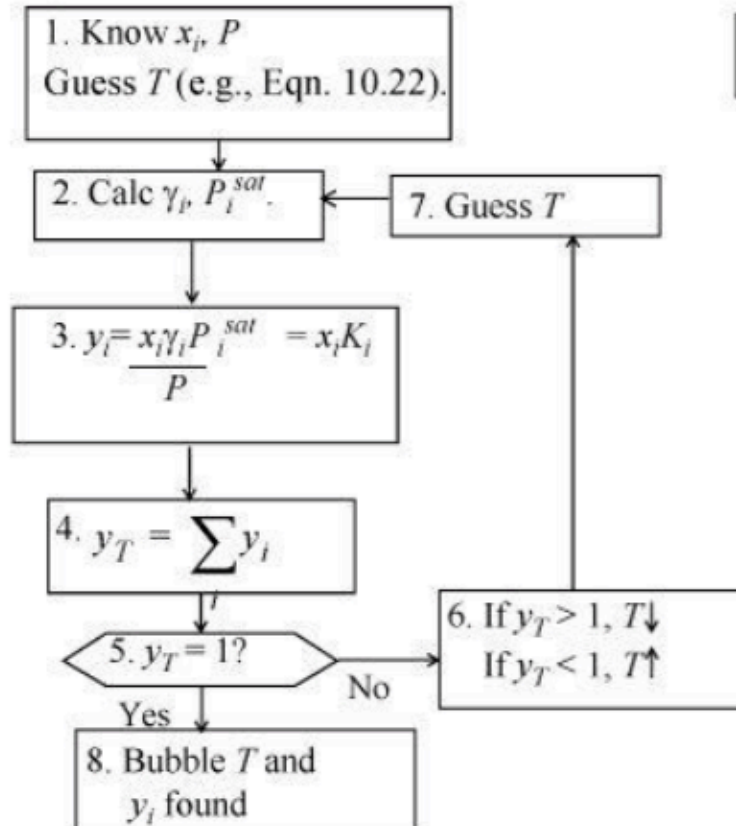
(Choose one flow sheet.)

Appendix C pp. 832

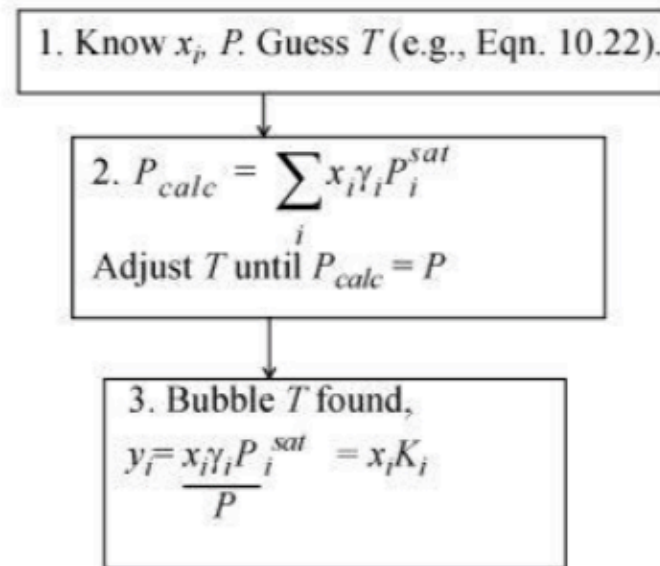
$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2] \quad 11.37$$

$$A_{12} = \left(2 - \frac{1}{x_2}\right) \frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \quad A_{21} = \left(2 - \frac{1}{x_1}\right) \frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2} \quad 11.38$$

Option (a)



Option (b)



11.7 ACTIVITY COEFFICIENTS AT SPECIAL COMPOSITIONS

Purity and Infinite Dilution

$$\lim_{x_i \rightarrow 1} \gamma_i = 1 \text{ and } \lim_{x_i \rightarrow 0} \gamma_i = \gamma_i^\infty$$

11.39

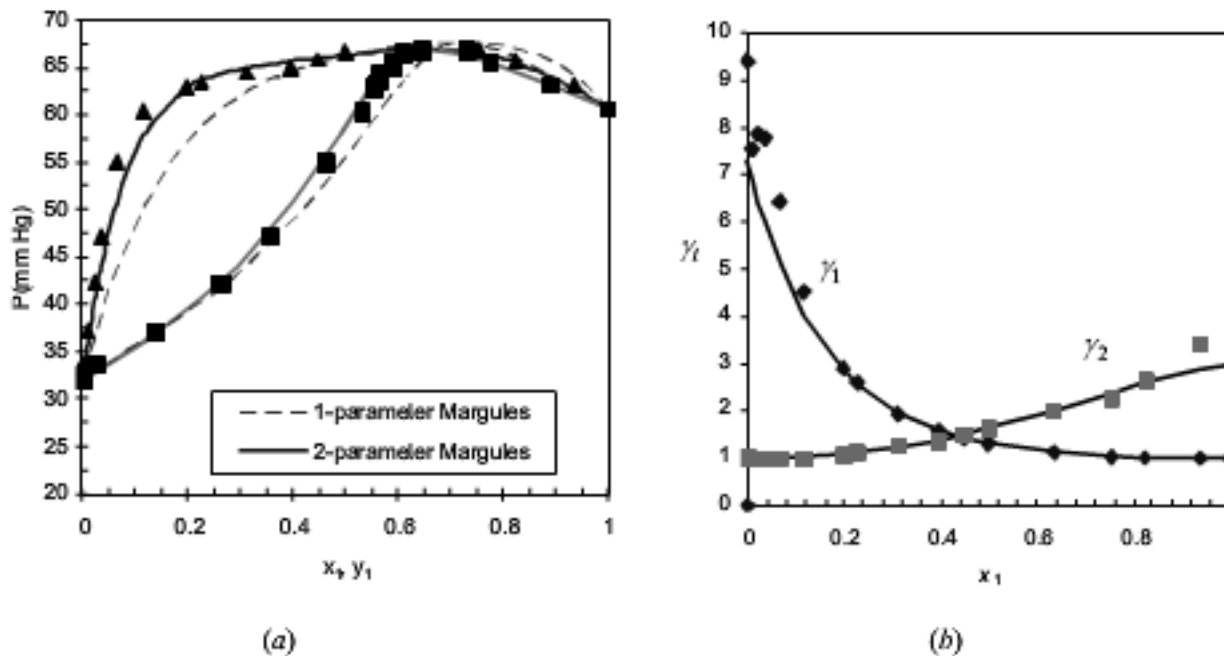


Figure 11.5 (a) One-parameter and two-parameter Margules equation fitted to a single measurement in Examples 11.2 and 11.5 compared with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. (b) Activity coefficients predicted from the parameters fitted in Example 11.5 compared with points calculated from the data.

Purity and Infinite Dilution

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1] ; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2] \quad 11.37$$

$$A_{12} = \ln \gamma_1^\infty, \quad A_{21} = \ln \gamma_2^\infty$$

11.8 PRELIMINARY INDICATIONS OF VLE

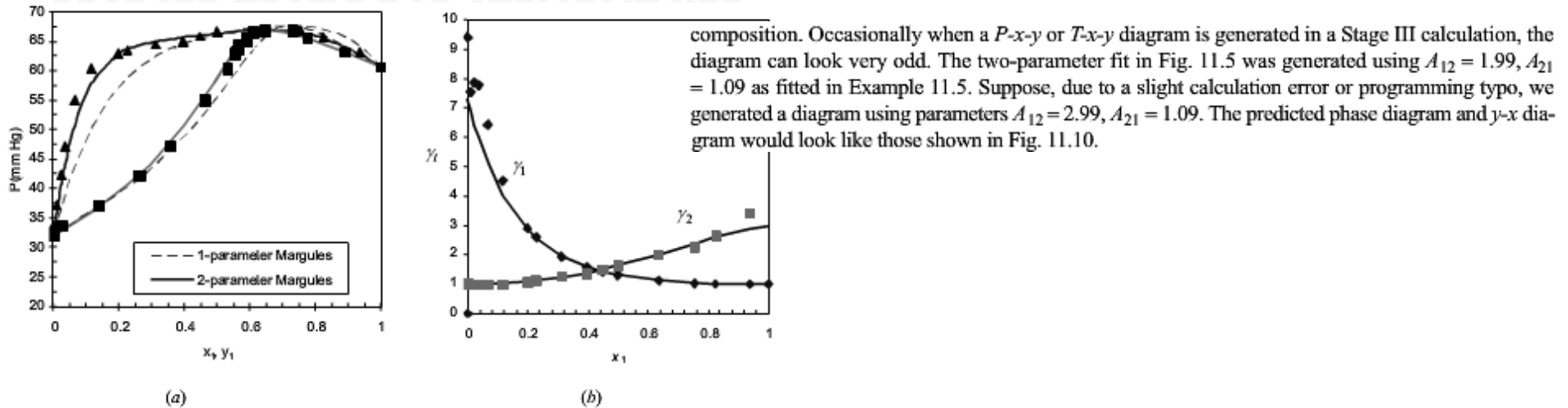


Figure 11.5 (a) One-parameter and two-parameter Margules equation fitted to a single measurement in Examples 11.2 and 11.5 compared with the experimental data points from Fig. 10.8 on page 395. Data are tabulated in Example 11.8. (b) Activity coefficient parameters fitted in Example 11.5 compared with points calculated

The behavior of the lines using these parameters actually predicts that two liquid phases exist. However, the diagram requires additional modification before coexisting compositions and the vapor-liquid-liquid equilibria (VLE) can be read from the diagram. It is important to understand that the diagram has been generated assuming that only one liquid phase exists. Though we started the discussion by assuming that a parameter calculation error resulted in predictions, all systems that exhibit VLE will have similarly odd diagrams when only one liquid phase is assumed to exist. This assumption is the default in common process simulators such as ASPEN Plus and ChemCAD because the calculations are faster when the simulator can avoid checking for two phases. When working with simulators, you should check the phase diagrams to see if liquid-liquid phase behavior exists and you should understand where to change the simulator settings to calculate liquid-liquid behavior when it exists. Within this chapter, you should be ready to recognize that such diagrams are indicative of two liquid phases. Also recall that a T - x - y diagram qualitatively resembles an inverted P - x - y , so peculiar loops appear on a T - x - y diagram if a similar situation exists. When models incorrectly predict VLE behavior that we know to be incorrect, we need to check our calculations. We learn how to rigorously characterize VLE phase diagrams and how to eliminate the loops in Chapter 14.

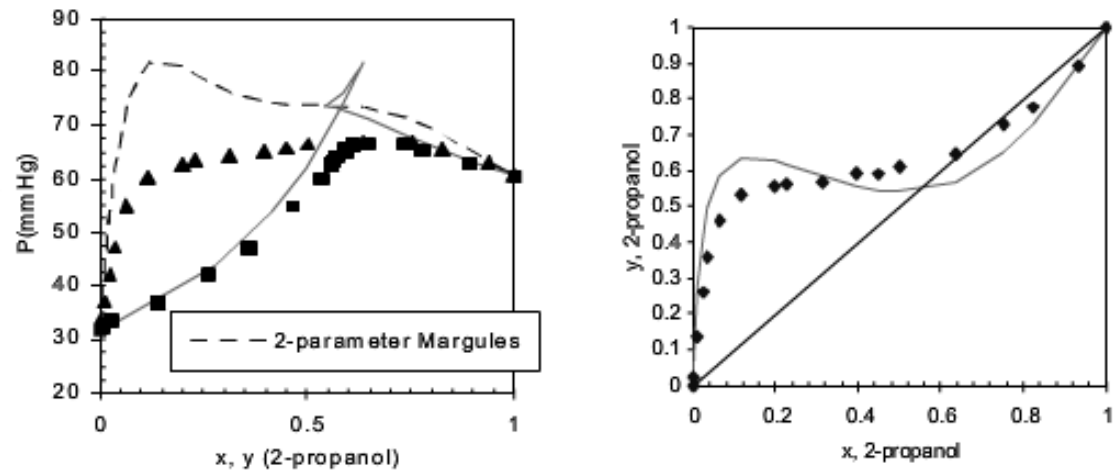


Figure 11.10 Phase diagram calculations for the 2-propanol + water system at 30°C compared with data cited in Example 11.2. The parameters were selected as described in the text to illustrate how a numerical error can result in thermodynamically unstable loops. Note the dew line has a loop and the maximum in the bubble line is not at the azeotropic condition. Note in the y - x plot that the coexistence curve has maxima and minima. These calculated conditions are indicative of LLE as discussed in the text, though the experiments do not show LLE.

11.9 FITTING ACTIVITY MODELS TO MULTIPLE DATA


Linear Fitting of the Margules Equation

Eqn. 11.33 can be linearized:

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

$$\frac{G^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \quad 10$$

11.33

 Margules models can be linearized for fitting of parameters.

11.40

Nonlinear fitting techniques

$$OBJ = \sum_{\text{all points}} (P_{\text{expt}} - P_{\text{calc}})^2$$

Solver tool or the MATLAB `fminsearch` or `lsqnonlin` can provide rapid fits. The spreadsheet `Gamfit.xlsx` or MATLAB m-file `GammaFit.m` permit nonlinear fitting of activity coefficient parameters for the Margules equation by fitting total pressure. Either can be easily modified to find

Example 11.8 Fitting parameters using nonlinear least squares

 Gammfit.xlsx,
Gammfit.m.

Measurements for the 2-propanol + water system at 30°C have been published by Udovenko, et al. (1967).^a Use the pressure and liquid composition to fit the two-parameter Margules equation to the bubble pressure. Plot the resultant P - x - y diagram.

Solution: In the experimental data, the researchers report experimental vapor pressures. It is best to use experimental values from the same publication to reduce the effect of systematic errors which may be present in the data due to impurities or calibration errors. The solution will be obtained by minimizing the sum of squares of error for the bubble pressures across the composition range.

MATLAB (condensed to show the major steps):

```
function GammaFit()
% statements omitted to load experiments into matrix 'Data'
x1 = Data(:,1); %data have been entered into columns of 'Data'
y1expt = Data(:,2); Pexpt = Data(:,3);
Ps1Calc = 60.7; Ps2Calc = 32.1; %experimental values used for Psat
x2 = 1-x1; % calculate x2
x = [x1 x2]; % create a 2 column matrix of x1 & x2
A = [0 0]; % initial guess for A12 and A21
A = lsqnonlin(@calcError,A); %optimize, calling 'calcError' as needed
function obj = calcError(A)
    A12 = A(1); %extract coeffs so eqns look like text
    A21 = A(2);
    Gamma1Calc = exp((x2.^2).*(A12 + 2*(A21 - A12).*x1));
    Gamma2Calc = exp((x1.^2).*(A21 + 2*(A12 - A21).*x2));
    Pcalc = (x1.*Gamma1Calc)*(Ps1Calc) + ...
            (x2.*Gamma2Calc)*(Ps2Calc);
    obj = Pcalc - Pexpt;
end
```

The resultant parameters are $A_{12} = 2.173$, $A_{21} = 0.9429$. The distributed file includes statements to plot the final figure similar to that shown below. Note that `fminsearch` can be used if `lsqnonlin` is not available due to the toolboxes on your MATLAB installation. See the fit in Fig. 11.11.

Example 11.8 Fitting parameters using nonlinear least squares (Continued)

Excel: The spreadsheet “P-x-y fit P” in the workbook Gammfit.xlsx is used to fit the parameters as shown below. Antoine coefficients are entered in the table for the components shown at the top of the spreadsheet. The flag in the box in the center right determines whether experimental vapor pressures are used in the calculations or values calculated from the Antoine equation.

System Components		Parameters to adjust			Antoine Coefficients			Calculated P^{calc} (mm Hg)	Expt P^{expt} (mm Hg)	Selected P^{sel} (mm Hg)	
					A	B	C				
(1) 2-propanol		A_{12}	A_{21}	T(C)	1	8.87829	2010.33	252.636	58.277822	60.7	60.7
(2) water		2.173055	0.942929	30	2	8.07131	1730.63	233.426	31.740167	32.1	32.1
← optional →											
x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$\gamma_{1,expt}$	$\gamma_{2,expt}$	$\gamma_{1,calc}$	$\gamma_{2,calc}$	P_{expt}	P_{calc}	$(P_{error})^2$	Enter 1 to use Calculated P^{calc} Enter 0 to use Expt P^{expt}
0	1	8.785079	1	0	1	0	1	32.1	32.1	0	0
0.0015	0.9985	8.695982	1.000008	0.0254	0.9746	0.024107	0.975893	33.8	32.84386	0.9141954	0
0.0111	0.9889	8.152908	1.000418	0.1374	0.8626	0.147468	0.852532	37.1	37.25008	0.0225244	0
0.0231	0.9769	7.535179	1.001787	0.2803	0.7397	0.251681	0.748319	42.3	41.98014	0.102312	0
0.0357	0.9643	6.95177	1.004234	0.3577	0.6423	0.326426	0.673574	47.2	46.14952	1.1035166	0
0.0649	0.9351	5.815504	1.013755	0.4804	0.5398	0.42951	0.57049	55	53.33938	2.7576741	0
0.1188	0.8832	4.353254	1.043423	0.5316	0.4694	0.510802	0.489398	60.3	60.44532	0.0211192	0
0.197	0.803	2.970369	1.119928	0.5547	0.4453	0.551655	0.448345	62.9	64.38897	2.2110888	0
0.2271	0.7729	2.62311	1.158008	0.5811	0.4389	0.557245	0.442755	63.6	64.88977	1.9314539	0
0.312	0.688	1.945005	1.292474	0.5859	0.4341	0.563409	0.436591	64.4	65.3793	0.9590351	0
0.3958	0.6042	1.549309	1.483142	0.5907	0.4093	0.567416	0.432584	65.1	65.59962	0.2496163	0
0.4477	0.5523	1.386629	1.586209	0.589	0.411	0.572644	0.427356	65.8	65.80383	1.468E-05	0
0.5009	0.4991	1.264065	1.724032	0.6096	0.3902	0.581846	0.418154	66.6	66.05434	0.2977452	0
0.6389	0.3631	1.083192	2.106142	0.6462	0.3538	0.630433	0.389587	66.9	66.42417	0.2264146	0
0.7542	0.2458	1.01937	2.411709	0.7296	0.2704	0.710348	0.289652	66.8	65.69551	1.2198966	0
0.8245	0.1755	1.004463	2.546001	0.7752	0.2248	0.778018	0.221982	65.7	64.61353	1.1804165	0
0.9383	0.0637	0.999471	2.822202	0.8892	0.1108	0.913749	0.086251	63.2	62.16513	1.0709806	0
1	0	1	2.587492	1	0	1	0	60.7	60.7	0	0

Objective Function
 14.28798435

Experimental data for x_1 and P_{expt} are entered in columns A and I. Initial guesses for the constants A_{12} and A_{21} are entered in the labeled cells in the top table. Solver is then called to minimize the error in the objective function by adjusting the two parameters. Calculated pressures are determined by bubble-pressure calculations.

The results of the fit are shown by the plot on spreadsheet “P-x-y Plot.” See the fit in Fig. 11.11.

Note that the system is the same used in Example 11.2 on page 417 and Example 11.5 on page 430. The fit in this example using all data is superior. The parameters are also slightly different from the linear fit discussed above because the objective function is different.

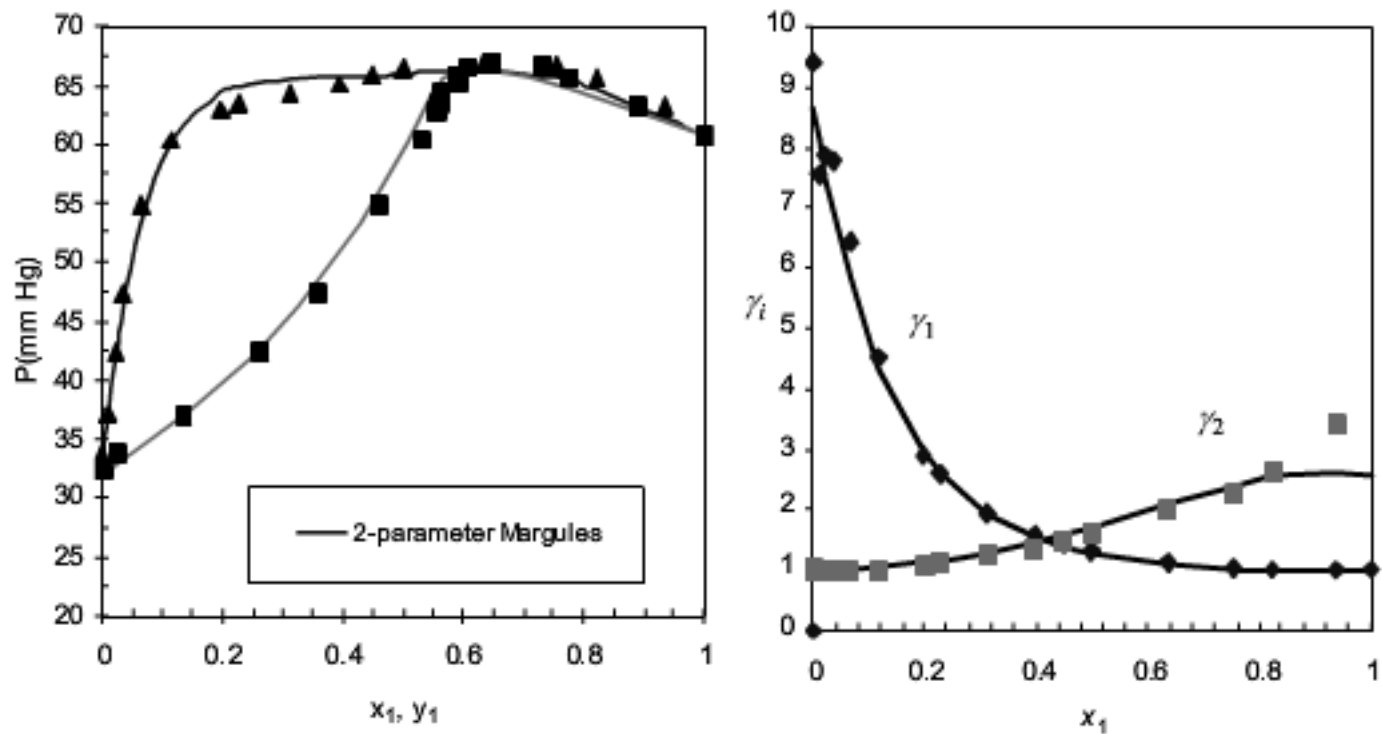


Figure 11.11 Comparison of experimental data with regressed model as explained in Example 11.8.

Alternative Objective Functions

$$\sum_{\text{points}} \left\{ \frac{(P_{\text{true}} - P_{\text{expt}})_i^2}{\sigma_P^2} + \frac{(T_{\text{true}} - T_{\text{expt}})_i^2}{\sigma_T^2} + \frac{(x_{1\text{true}} - x_{1\text{expt}})_i^2}{\sigma_x^2} + \frac{(y_{1\text{true}} - y_{1\text{expt}})_i^2}{\sigma_y^2} \right\} \quad 11.41$$

$$\sigma_P = 2 \text{ mmHg}, \sigma_T = 0.2 \text{ K}, \sigma_x = 0.005, \sigma_y = 0.01,$$

11.10 RELATIONS FOR PARTIAL MOLAR PROPERTIES

Gibbs-Duhem Equation

$$\boxed{d\underline{G} = \underline{V}dP - \underline{S}dT + \sum_i \mu_i dn_i} \quad 10.40$$

$$\underline{G} = \sum_i n_i \bar{G}_i = \sum_i n_i \mu_i \text{ or } G = \sum_i x_i \bar{G}_i = \sum_i x_i \mu_i \quad 10.42$$

$$d\underline{G} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad 11.42$$

$$\sum_i \mu_i dn_i + \sum_i n_i d\mu_i = -\underline{S}dT + \underline{V}dP + \sum_i \mu_i dn_i \quad 11.43$$

Simplifying, we obtain the Gibbs-Duhem equation,

$$\boxed{0 = -\underline{S}dT + \underline{V}dP - \sum_i n_i d\mu_i} \quad 11.44$$

Therefore, we conclude at constant T and P :

$$\sum_i n_i d\mu_i = 0 \text{ at constant } T \text{ and } P \quad 11.45$$

Gibbs-Duhem Relation for Activity Coefficients

To extend the Gibbs-Duhem equation to excess properties, the excess Gibbs energy can be manipulated in a manner analogous to the derivation above. Therefore,

$$0 = -\underline{S}^E dT + \underline{V}^E dP - \sum_i n_i d\mu_i^E \quad 11.46$$

resulting in

$$\sum_i n_i d\mu_i^E = 0 \text{ at constant } T \text{ and } P \quad 11.47$$

Inserting the relation between excess chemical potential and activity coefficients gives

$$\boxed{\sum_i n_i d\mu_i^E = RT \sum_i n_i d\ln \gamma_i = 0} \quad 11.48$$

$$\boxed{x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} = 0} \quad \text{binary at fixed } T \text{ and } P \quad 11.49$$

This equation means that the activity coefficients for a binary system, when plotted versus composition, must have slopes with opposite signs, and the slopes are related in magnitude by Eqn. 11.49. A further deduction is that if one of the activity coefficients in a binary system exhibits a maximum, the other must exhibit a minimum at the same composition. We find this relation useful in: 1) testing data for experimental errors (grossly inconsistent data); 2) generating the activity coefficients in a binary for a second component based on the behavior of the first component in experimental techniques where only one activity coefficient is measured; 3) for development of theories for the Gibbs energy of a mixture, since our model must follow this relation. The Gibbs-Duhem equation is also useful for checking thermodynamic consistency of data; however, the

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_i} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_i} \right)_{T,P} = 0 \quad \text{binary at fixed } T \text{ and } P \quad 11.49$$

Relations between Various Excess Properties

excess functions follow the same relations as the total functions, $H^E = U^E + PV^E$, $G^E = H^E - TS^E$, and $A^E = U^E - TS^E$. The derivative relations are also followed,

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E; \quad \left(\frac{\partial \bar{G}_i^E}{\partial T}\right)_{P,x} = -\bar{S}_i^E \quad 11.50$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E; \quad \left(\frac{\partial \bar{G}_i^E}{\partial P}\right)_{T,x} = \bar{V}_i^E \quad \text{for } P^\circ = P_{\text{system}} \quad 11.51$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{V}_i^E}{RT} \quad \text{for } P^\circ = P_{\text{system}} \quad 11.52$$

The **Gibbs-Helmholtz** relation applies:

$$\left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = \frac{-H^E}{T^2}; \quad \left(\frac{\partial \bar{G}_i^E/T}{\partial T}\right)_{P,x} = \frac{-\bar{H}_i^E}{T^2} \quad 11.53$$

Particularly useful is Eqn. 11.53 using the relation with activity coefficients:

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x} = \frac{-\bar{H}_i^E}{RT^2} \quad 11.54$$

Therefore, excess enthalpy data from calorimetry may be used to check the temperature dependence of the activity coefficient models for thermodynamic consistency. Typically, activity coeffi-

Example 11.9 Heats of mixing with the Margules two-parameter model

Fitting the VLE of methanol + benzene^a in the range of 308–328 K with the Margules two-parameter model and then fitting the parameters to $A_{ij} = a_{ij} + b_{ij}/T$ gives $A_{12} = 0.1671 + 714/T$ and $A_{21} = 2.3360 - 247/T$. Estimate the heat of mixing at 318 K and 50 mol% benzene.

Solution: The Margules two-parameter model is,

$$\frac{G^E}{RT} = x_1x_2(A_{21}x_1 + A_{12}x_2) \quad \left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = \frac{-H^E}{T^2}; \quad \left(\frac{\partial \bar{G}_i^E/T}{\partial T}\right)_{P,x} = \frac{-\bar{H}_i^E}{T^2} \quad 11.53$$

The relation between G^E and H^E is given by Eqn. 11.53. Noting the right side Margules parameters for the problem statement are simple functions of $(1/T)$, we can manipulate the derivative for this function. Since $d(1/T) = -T^{-2}dT$,

$$\left(\frac{\partial G^E/(RT)}{\partial T}\right) = -T^{-2}\left(\frac{\partial G^E/(RT)}{\partial(1/T)}\right) = -H^E/(RT^2) \quad 11.55$$

Thus,

$$\frac{H^E}{RT} = \frac{x_1x_2}{T} \left(\frac{x_1 dA_{21}}{d(1/T)} + \frac{x_2 dA_{12}}{d(1/T)} \right) = x_1x_2 \left(x_1 \frac{714}{T} - x_2 \frac{247}{T} \right)$$

At 318 K and $x_1 = x_2 = 0.5$, $H^E = 8.314(0.5)(0.5(0.5 \cdot 714 - 0.5 \cdot 247)) = 485$ J/mol. Note that direct measurement of excess enthalpy is recommended when possible. Phase equilibria data must be very precise to provide an accurate enthalpy of mixing.

$$\frac{H}{RT} = \frac{x_1 H_1}{RT} + \frac{x_2 H_2}{RT} + x_1x_2 \left(x_1 \frac{714}{T} - x_2 \frac{247}{T} \right) \quad 11.56$$

11.11 DISTILLATION AND RELATIVE VOLATILITY OF NONIDEAL SOLUTIONS

discussion of distillation. The relative volatility of the light to heavy key, α_{LH} is important to distillation, as discussed in Section 10.6. Since α_{LH} may not be constant over an entire distillation column, it is common to estimate the average value by the geometric mean of the bottom and top.

$$\alpha_{LH}^m = (\alpha_{LH}^{top} \alpha_{LH}^{bot})^{1/2} \quad 11.57$$

Recalling the definition of α_{LH} from Eqn. 10.32, substituting Eqn. 11.18, and canceling pressures,

$$\alpha_{LH} = K_{LK}/K_{HK} = (\gamma_{LK} P_{LK}^{sat})/(\gamma_{HK} P_{HK}^{sat}) \quad 11.58$$

Suppose in a binary mixture that we specify splits so that the top is $x_{LK}^{top} = 0.99$, and $x_{LK}^{bot} = 0.01$. Then recognizing that the activity coefficients go to unity near purity,

$$\alpha_{LH}^{top} = [(P_{LK}^{sat})/(\gamma_{HK}^{\infty} P_{HK}^{sat})]^{top} \quad \alpha_{LH}^{bot} = [(\gamma_{LK}^{\infty} P_{LK}^{sat})/(P_{HK}^{sat})]^{bot} \quad 11.59$$

Example 11.10 Suspecting an azeotrope

Make a preliminary estimate of whether we should suspect an azeotrope in the system benzene (*B*) + 2-propanol (*I*) at 80°C. Assume the MAB model. A convenient feature of Margules one-parameter models (including the MAB model) is that the infinite dilution activity coefficients are equal. (Note that “convenient” may not equate to “accurate.”)

Solution: Note that this problem is isothermal rather than a distillation column design, but we can evaluate the relative volatility at either end of the composition range. Antoine.xlsx gives vapor pressures of $P_B^{sat} = 757$ mmHg and $P_I^{sat} = 683$ mmHg at 80°C, so benzene is the *LK*. For the MAB model,

$$A_{12} = (9.23 - 0.63)(11.86 - 2.24)(89.8 + 76.8)/[4(8.314)353] = 1.174;$$

$$\gamma_i^\infty = \exp(1.174) = 3.235$$

Using the component key assignments, $P_{LK}^{sat}/P_{HK}^{sat} = 757/683 = 1.108$. Therefore, at the end rich in *LK*, $\alpha_{LH} = (P_{LK}^{sat})/(\gamma_{HK}^\infty P_{HK}^{sat}) = 1.108/3.235 = 0.343$, and the end rich in *HK*, $\alpha_{LH} = (\gamma_{LK}^\infty P_{LK}^{sat})/(P_{HK}^{sat}) = 3.235 \cdot 1.108 = 3.58$. MAB predicts an azeotrope since $(\alpha_{LH} - 1)$ changes sign. The prediction should be validated with experimental data and/or more accurate models because of the approximations in the MAB model.

$$A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)/(4RT)$$

11.9

Henry's Law and Raoult's Law (Wikipedia)

Comparison to Raoult's law [\[edit \]](#)

Henry's law is a limiting law that only applies for "sufficiently dilute" solutions. The range of concentrations in which it applies becomes narrower the more the system diverges from ideal behavior. Roughly speaking, that is the more chemically "different" the solute is from the solvent.

For a dilute solution, the concentration of the solute is approximately proportional to its [mole fraction](#) x , and Henry's law can be written as

$$p = K_{\text{H}}x.$$

This can be compared with [Raoult's law](#):

$$p = p^*x,$$

where p^* is the vapor pressure of the pure component.

At first sight, Raoult's law appears to be a special case of Henry's law, where $K_{\text{H}} = p^*$. This is true for pairs of closely related substances, such as [benzene](#) and [toluene](#), which obey Raoult's law over the entire composition range: such mixtures are called "ideal mixtures".

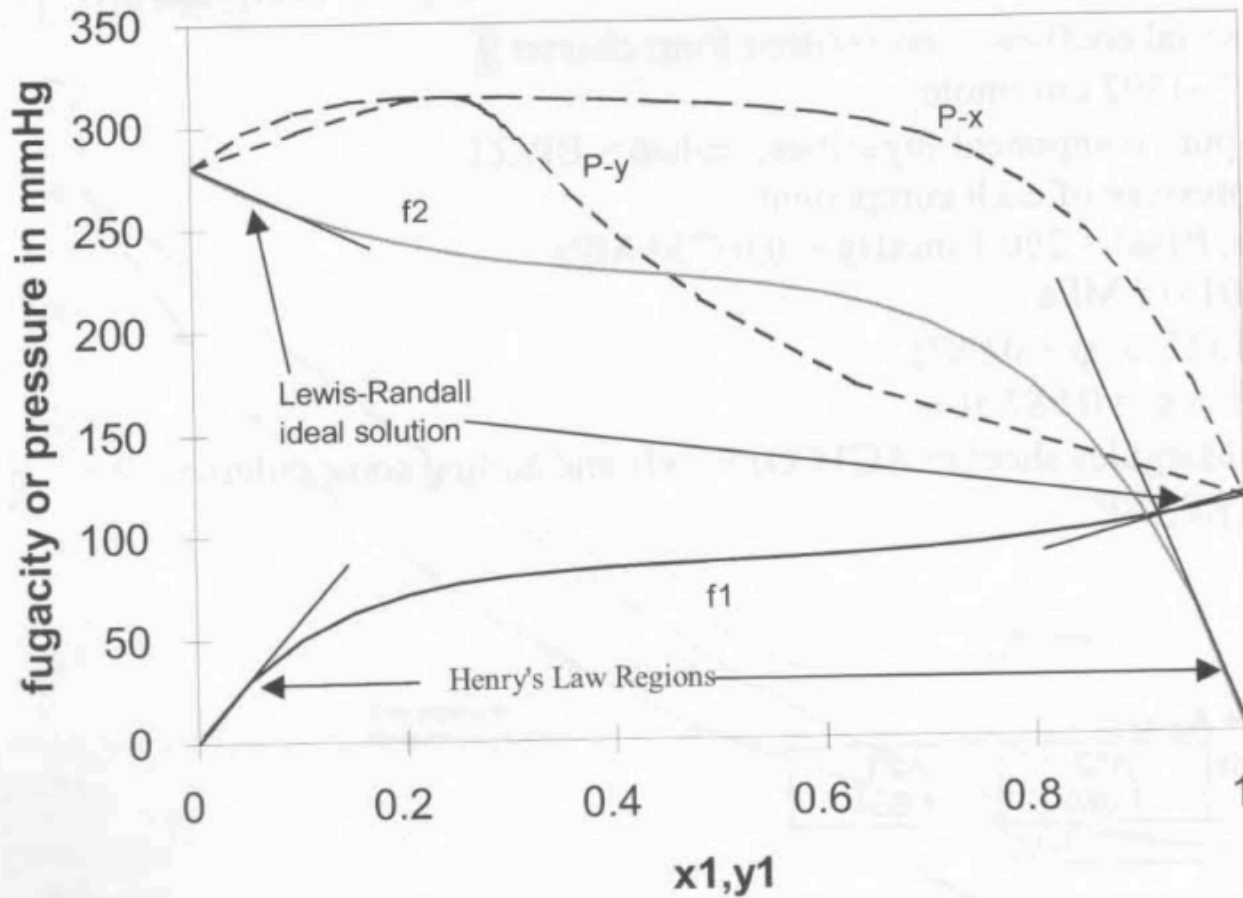
The general case is that both laws are [limit laws](#), and they apply at opposite ends of the composition range. The vapor pressure of the component in large excess, such as the solvent for a dilute solution, is proportional to its mole fraction, and the constant of proportionality is the vapor pressure of the pure substance (Raoult's law). The vapor pressure of the solute is also proportional to the solute's mole fraction, but the constant of proportionality is different and must be determined experimentally (Henry's law). In mathematical terms:

$$\text{Raoult's law: } \lim_{x \rightarrow 1} \left(\frac{p}{x} \right) = p^*.$$

$$\text{Henry's law: } \lim_{x \rightarrow 0} \left(\frac{p}{x} \right) = K_{\text{H}}.$$

Raoult's law can also be related to non-gas solutes.

Henry's Law and Raoult's Law HW Problem 10.8



Lewis-Randall and Henry's law valid at some compositions near purity, but for opposite components.

11.12 LEWIS-RANDALL RULE AND HENRY'S LAW

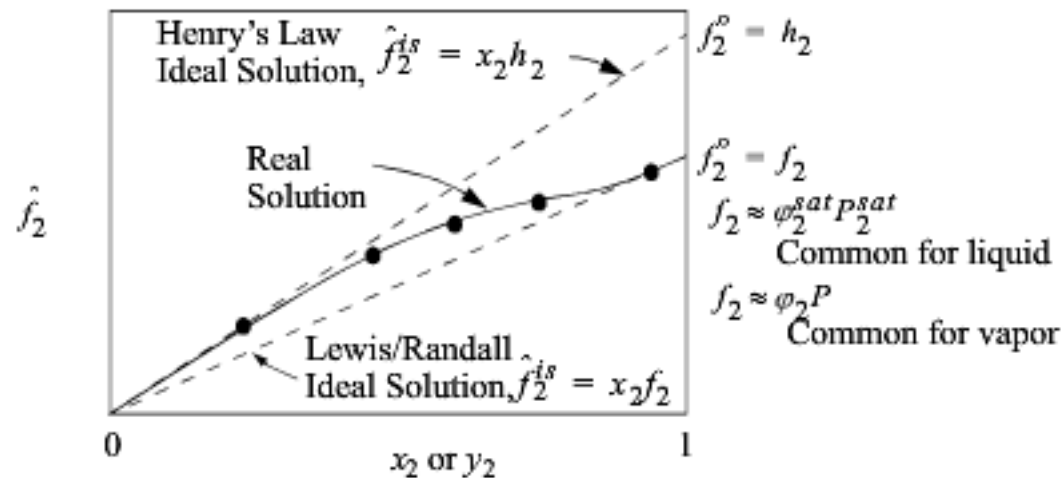


Figure 11.12 Schematic representation of the fugacity of component 2 in a binary mixture.

The Henry's Law Standard State

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o}$$

11.13 Activity coefficients are commonly used for highly non-ideal solutions.

1 Lewis-Randall rule for component fugacity in an ideal solution.

$$\hat{f}_i^{is}/f_i = x_i \Rightarrow \hat{f}_i^{is} = x_i f_i$$

10.68

Consider that the fugacity curve in Fig. 11.12 is nearly linear at low concentrations. Thus, we could express the component fugacity as proportional to concentration using a tangent line near infinite dilution,

1 Ideal Henry's law component.

$$\hat{f}_i^{is} = x_i h_i \quad 11.60$$

which is the behavior of an ideal solution given by Henry's law.

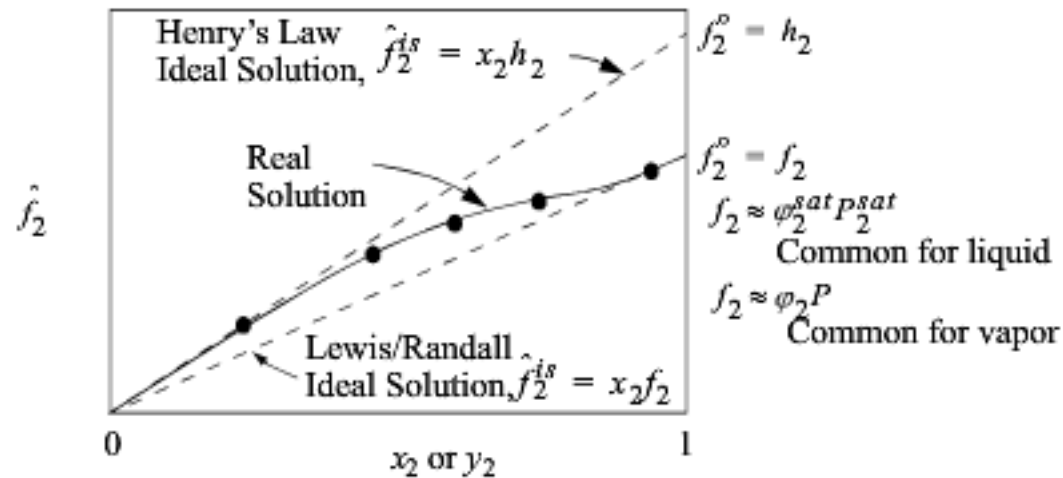


Figure 11.12 Schematic representation of the fugacity of component 2 in a binary mixture.

I Ideal Henry's law component.

$$\hat{f}_i^{is} = x_i h_i \quad 11.60$$

which is the behavior of an ideal solution given by Henry's law.

The **Henry's law constant**, h_b is usually determined experimentally, and depends on temperature, pressure, and solvent. The fact that it depends on solvent makes it very different from a pseudo-vapor pressure because a vapor pressure would be independent of solvent.

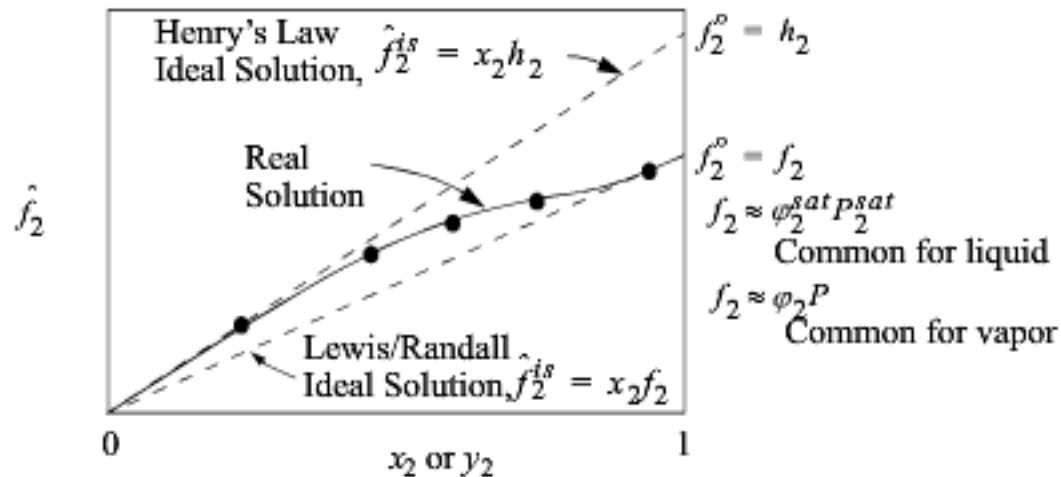


Figure 11.12 Schematic representation of the fugacity of component 2 in a binary mixture.

! Henry's law for non-ideal solution.

$$\hat{f}_i = x_i \gamma_i^* h_i$$

11.61

Gamma i star is at infinite dilution

activity, Eqn. 11.23, we see that $a_i = x_i \gamma_i^* = \hat{f}_i / f_i^o$. Comparing with Eqn. 11.61, we see that the standard state is $f_i^o = h_i$. So the important activity coefficient value is at infinite dilution, but the standard state composition is a hypothetical pure state. This perspective is especially useful for electrolyte solutions.

$$a_i = \frac{\hat{f}_i}{f_i^o} = x_i \gamma_i^*$$

11.23

Relating γ_i for Henry's Law and Lewis-Randall Rule

Note in Fig. 11.12 that both Henry's approach and the Lewis-Randall approach must represent the same fugacity. Equating the two approaches,


$$\hat{f}_i = x_i \gamma_i^* h_i = x_i \gamma_i f_i \quad 11.62$$

Taking the limit at infinite dilution where γ_i^* approaches one, and we see

$$\hat{f}_i = x_i h_i = x_i \gamma_i^\infty f_i \text{ at infinite dilution} \quad 11.63$$

resulting in the relation between the Henry's and the Lewis-Randall fugacity and activity coefficient,

$$h_i = \gamma_i^\infty f_i$$

11.64  Relation between Henry's Law constant and Lewis-Randall fugacity.

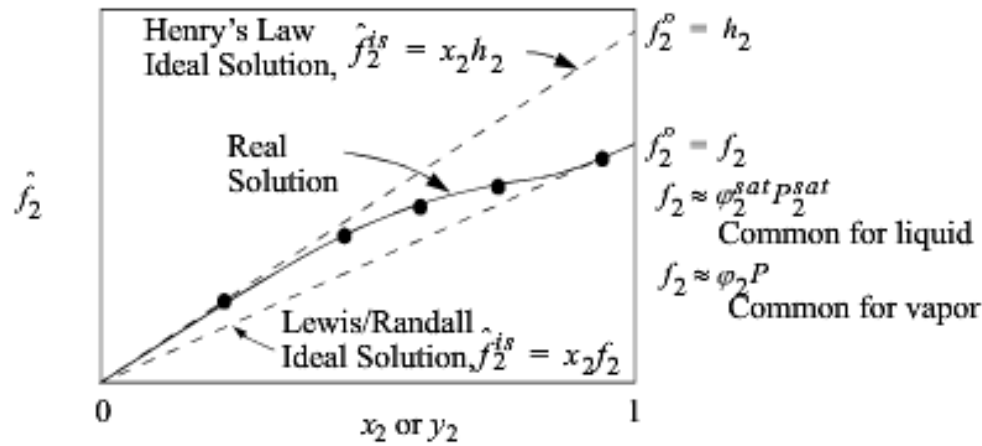


Figure 11.12 Schematic representation of the fugacity of component 2 in a binary mixture.

In Fig. 11.13, look at the right side where $\ln \gamma_2$ approaches $\ln \gamma_2^\infty$ and $\ln \gamma_2^*$ approaches zero. The difference in the intercept at $x_2 = 0$ is $\ln(h_2/f_2)$. To model the Henry's law activity coefficient, the restriction that the activity coefficients must follow the Gibbs-Duhem Eqn. 11.49 remains; thus, the slope of the logarithm of the Henry's law activity coefficient must be the same as the slope of the logarithm of the Lewis-Randall activity coefficient—the shift is independent of composition. The shift is illustrated in Fig. 11.13. We may adapt any activity model developed for the Lewis-Randall rule to Henry's law by shifting the intercept values for the components modeled by Henry's law. Thus,

$$\ln \gamma_i^* = \ln \gamma_i - \ln \gamma_i^\infty$$

11.65

! Formula to shift a Lewis-Randall activity model to a Henry's law activity model.

where any Lewis/Randall model can be used for γ_i and the same model is used for γ_i^∞ . Usually the activity coefficient model is manipulated to obtain the infinite dilution activity coefficient

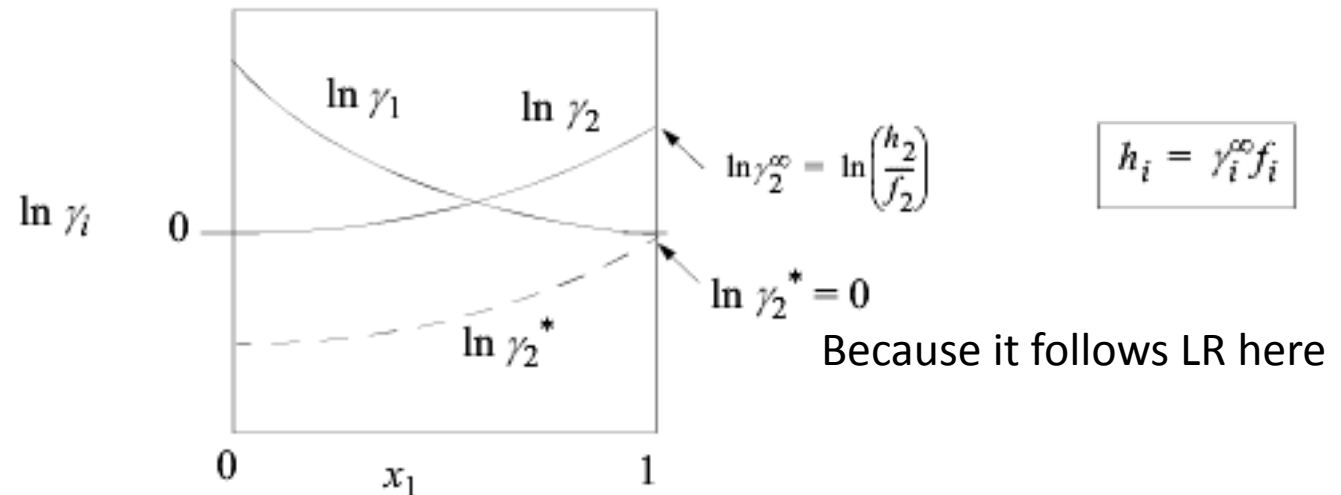


Figure 11.13 Schematic illustration of the relation of the Henry's law activity coefficient compared to the Lewis-Randall rule activity coefficient.

! Unsymmetric activity coefficients for Henry's law based on the one-parameter Margules equation.

$$\ln \gamma_2^* = \ln \gamma_2 - \ln \gamma_2^\infty = A_{12}x_1^2 - A_{12} = A_{12}(x_1^2 - 1) \quad \ln \gamma_1 = A_{12}(x_2^2) \quad 11.66$$

Henry's Law on Molal Activity Scale

Henry's law
for non-ideal
solution.

$$\hat{f}_i = x_i \gamma_i^* h_i$$

11.61

Eqn. 11.61 suggests that the units for the Henry's law constant should be pressure, but other conventions also exist. For example, a common way of presenting Henry's constants for gases is to express the liquid phase concentration in **molality** and provide a constant inverted relative to h_i . The result is

Molal activity
coefficients and
Henry's law.

$$\hat{f}_i = x_i \gamma_i^* h_i = m_i \gamma_i^\square / (K_H)$$

11.67

Example 11.11 Solubility of CO₂ by Henry's Law

Carbon dioxide solubility in water plays a critical role in biological physiology and environmental ocean chemistry, affects the accuracy of acid-base titrations in analytical chemistry, and makes many beverages fizzy. The Henry's law constant for CO₂ in water is listed on the NIST Chemistry WebBook^a as $K_H = 0.035$ mol/kg-bar at 298.15 K. Estimate the mole fraction of CO₂ in water at 0.7 MPa total pressure and 298.15 K. Treat the vapor phase as an ideal gas and the liquid as an ideal solution with the Henry's law standard state. Neglect formation of ionic carbonate species.

Solution: $K_H y_{\text{CO}_2} P = m_{\text{CO}_2}$ where m_{CO_2} is mol/(kgH₂O). First find y_{CO_2} by using Raoult's law for water. Taking P_w^{sat} from the steam tables, Raoult's law for water gives

$$y_w = P_w^{\text{sat}}/P = 0.00317/0.7 = 0.0045 \Rightarrow y_{\text{CO}_2} = 0.9955.$$

The solubility of CO₂ is thus,

$$K_H y_{\text{CO}_2} P = 0.035(\text{mol/kg-bar})(0.9955)(7 \text{ bar}) = 0.244 \text{ molal}$$

$$x_{\text{CO}_2} = m_{\text{CO}_2} x_w 0.001 M_{w,w} = m_{\text{CO}_2} 0.001 M_{w,w} (1 - x_{\text{CO}_2}) \Rightarrow$$

$$x_{\text{CO}_2} = \frac{m_{\text{CO}_2} 0.001 M_{w,w}}{1 + m_{\text{CO}_2} 0.001 M_{w,w}} = \frac{0.244(0.018)}{1 + 0.244(0.018)} = 0.0044$$

The ionic species ignored here in this binary system are sufficient to lower the pH, and though essential for comprehensive understanding, the concentrations are small relative to the molecular CO₂ modeled here. In physiology or ocean chemistry, many other salts are involved which make the equilibrium more complicated. Chapter 18 addresses several issues of ionization.

Dilute Solution Calculations Using Hypothetical Lewis-Randall Fugacities

$$\hat{f}_i = x_i h_i = x_i \gamma_i^\infty f_i \text{ at infinite dilution} \quad 11.63$$

Dissolved gas solubilities can be modeled by treating the liquid phase and vapor phase both with direct use of an equation of state (to be discussed in Chapter 15). However, Eqn. 11.63 suggests that we can model dilute solutions relative to the Lewis-Randall rule. Looking at Eqn. 11.63, you can appreciate why the Henry's law constant depends on solvent—the Lewis-Randall γ_i^∞ will be different for every solvent. The activity coefficient models we have developed can take γ_i^∞ into account. What we need is a manner to correlate the fugacity of hypothetical liquids above the critical point. A prevalent model for light gases in petrochemicals is the Grayson-Streed model (and the closely related Chao-Seader and Prausnitz-Shair models).¹⁹

Fig. 11.14 shows several generalized estimates for f^L as a function of reduced temperature. The Grayson-Streed estimates vary substantially depending on whether the general correlation is applied (GS-0) or specific correlations as for methane (CH₄) or hydrogen (H₂). The Grayson-Streed estimates have limits in their range of temperature that are reflected by their ranges in Fig. 11.14. The Prausnitz-Shair correlation gives a single curve for all compounds regardless of their acentric

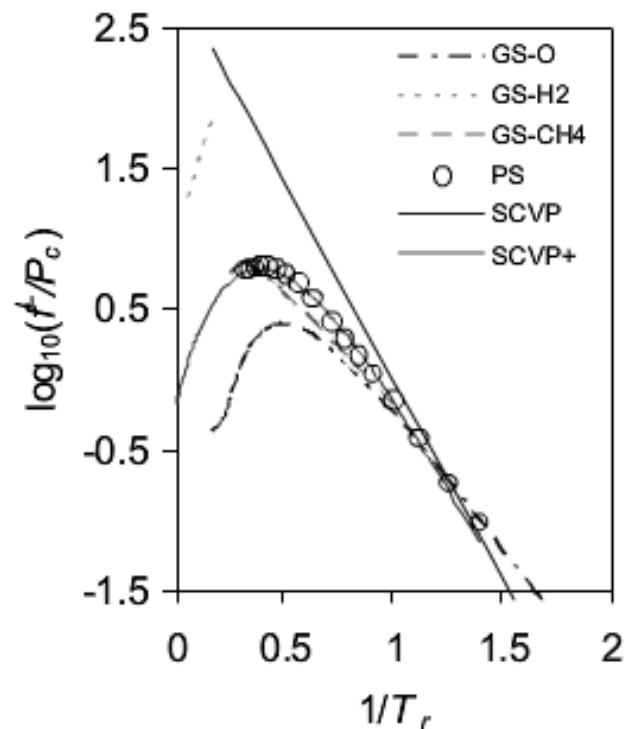


Figure 11.14 Comparison of correlations for liquid fugacity at high temperature as described in the text. GS = Grayson/Streed, PS = Prausnitz/Shair, SCVP = shortcut vapor pressure equation., SCVP+ = extended shortcut vapor pressure equation. ($\omega = 0.21$ for SCVP and SCVP+)

$$\log_{10}(f^L / P_c) = 7(1 + \omega)(1 - T_c/T)/3 - 3\exp(-3T_c/T) \quad \text{SCVP+ equation} \quad 11.68$$

This correlation is designed to match the shortcut vapor pressure (SCVP) equation at $T < T_c$. It provides a reasonable match of the Grayson-Streed estimates for CH₄ at $T > T_c$ and a fairly accurate match to the Prausnitz-Shair correlation when a value of $\omega = 0.21$ is applied to Eqn. 11.68. It also provides reasonable results for all temperatures. We refer to this as the SCVP+ equation.

! SCVP+ model for extrapolating Lewis-Randall fugacity above T_c .

Example 11.12 Henry's constant for CO₂ with the MAB/SCVP+ model

The solubility for CO₂ in water at 298 K and 7 bar can be estimated as $x_{\text{CO}_2} = 0.0044$. Treating the gas phase as an ideal gas and neglecting any aqueous ionic species, (a) fit γ_i^∞ using the Lewis-Randall rule and the SCVP+ equation for pure CO₂ and determine the one-parameter Margules parameter; (b) estimate A_{12} of the MAB model for CO₂ in water and γ_i^∞ and compare to part (a); (c) predict Henry's constant at 311 K using the MAB and the SCVP+ equation.

Solution:

(a) First use the SCVP+ equation to predict the hypothetical liquid fugacity,

$$\log_{10}(f^L / 73.82) = 7(1 + 0.228)(1 - 304.2/298)/3 - 3\exp(-3 \cdot 304.2/298)$$

$$\Rightarrow f_{\text{CO}_2}^L = 73.82 \cdot 10^{-0.200} = 47 \text{ bar.}$$

(FYI: The Lewis-Randall standard state by the SCVP model would be 64 bar instead of 47 bar.) Referring to Example 11.11, the ideal gas vapor fugacity has been calculated there, and we can equate it with Henry's law and use the fugacity just calculated with the experimental x_{CO_2} ,

$$y_{\text{CO}_2}P = 7 \cdot 0.9955 = x_{\text{CO}_2} \gamma_{\text{CO}_2}^\infty f_{\text{CO}_2}^L \Rightarrow \gamma_i^\infty = 7 \cdot 0.9955 / (0.0044 \cdot 47) = 34.$$

$$\ln \gamma_{\text{CO}_2}^\infty = A_{12} = \ln(34) = 3.52$$

(b) For MAB the default estimate is $A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)/(4RT)$

$$A_{12} = (1.87 - 50.13)(0 - 15.06)(44/1.18 + 18/1)/(4(8.314)298) = 4.05$$

$$\gamma_i^\infty = \exp(4.05) = 57.4$$

The MAB prediction for A_{12} is approximately $(100\%)(4.05 - 3.52)/3.52 = 15\%$ too high.

(c) At 311 K, the fitted MAB model suggests that $A_{12} = 3.52(298/311) = 3.37 = \ln \gamma_{\text{CO}_2}^\infty$.

So, $\gamma_{\text{CO}_2}^\infty = 29$.

By Eqn. 11.68, $\log_{10}(f^L/73.82) = 7(1 + 0.228)(1 - 304.2/311)/3 - 3\exp(-3 \cdot 304.2/311) = -0.0968$

By Eqn. 11.64, $h_{\text{CO}_2} = \gamma_{\text{CO}_2}^\infty f_{\text{CO}_2}^L = 29(10^{-0.0968}) = 23 \text{ bar}$

11.13 OSMOTIC PRESSURE

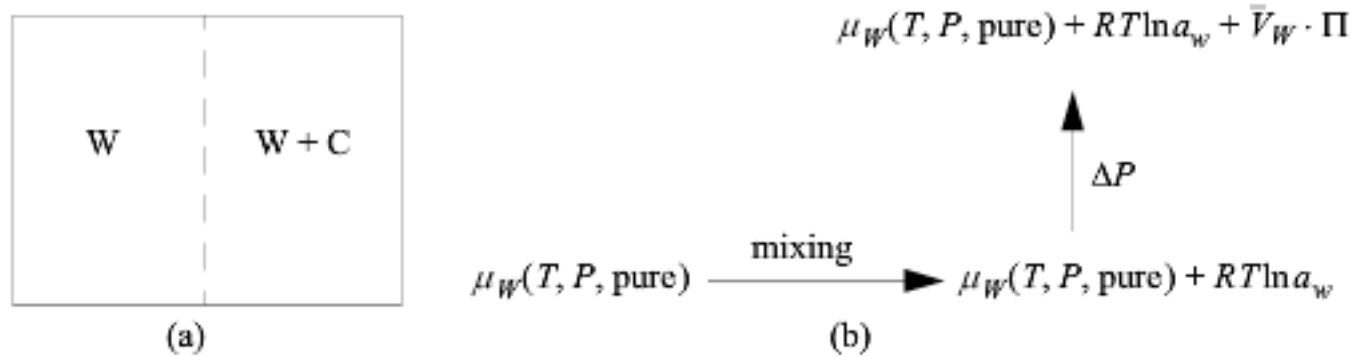


Figure 11.15 (a) Illustration of a semipermeable membrane. The membrane is permeable to component W , but not component C . The label of W is convenient because water is a typical solvent. (b) Illustration of the path used in calculation of the chemical potential in the mixture at the osmotic pressure.

brane is permeable to W but not to C . If the solutions are at the same pressure, P , then component W spontaneously flows from the left chamber (higher chemical potential because higher mole fraction) to the right chamber (lower chemical potential because lower mole fraction) in the condition of **osmosis**. If the pressure on the right side is increased, the degree of flow can be decreased. When the pressure has been increased by the **osmotic pressure**, Π , the sides achieve phase equilibrium and flow stops. If the pressure on the right side is increased by more than the osmotic pressure, a condition of **reverse osmosis** exists and component W flows from the right to the left. Reverse

At the pressure $(P + \Pi)$ on the right side, inward flow of W stops and the chemical potential is balanced. Let us create a convenient pathway to relate the chemical potential for the pure fluid at P to the mixture at $P + \Pi$. We can consider pressurizing the pure fluid and then mixing, or we can consider mixing the fluid and then pressurizing at fixed composition. Following historical derivation, it is common to use P as the standard state pressure for the mixing. The mixing process can be represented by the activity, $a_W = x_W \gamma_W$ (cf. Eqn. 11.23)

$$\mu_W(T, P, x_W) - \mu_W(T, P, \text{pure}) = RT \ln a_W \quad 11.69$$

For W in a mixture, the pressure effect on chemical potential at constant T is $d\mu_W = \bar{V}_W dP$. Because the liquid is nearly incompressible, for the pressure step $\Delta\mu_W = \bar{V}_W \cdot ((P + \Pi) - P)$ and overall,

$$\mu_W(T, P + \Pi, x_W) = \mu_W(T, P, x_W) + \bar{V}_W \cdot ((P + \Pi) - P) = \mu_W(T, P, x_W) + \bar{V}_W \cdot \Pi \quad 11.70$$

The calculation path is illustrated in Fig. 11.16(b). The initial state represents the left side of the membrane and the final state represents the right side. Equating the chemical potential expressions for the two sides of the membrane results in

$$\mu_W(T, P, \text{pure}) = \mu_W(T, P, \text{pure}) + RT \ln a_W + \bar{V}_W \cdot \Pi$$

Leading to the relation between osmotic pressure and activity of the permeable species,

$$\Pi = -\frac{RT}{\bar{V}_W} \ln a_W \quad 11.71$$

i Relation between osmotic pressure and activity of the permeable species.

The activity can be calculated from any activity coefficient model. Note that because the solution is very nearly pure W on a molar basis, we calculate activity relative to the Lewis-Randall rule

[C]. Using the molar volume of W to normalize the expression per mole of W , the McMillan-Mayer framework results in

$$RT \ln a_W = -RTV_W([C] + B_2(T)[C]^2 + B_3(T)[C]^3 + \dots) \quad 11.72$$

where $B_2(T)$ and $B_3(T)$ are functions of temperature known as the **osmotic virial coefficients**. Combining the two expressions, eliminating the molar volume, and rewriting the expression using solute generic subscript i , C_i **the solute mass density (in units of grams/(volume of solution))**, and $M_{w,i}$ molecular weight, results in the form which is common in presenting data:

$$\frac{\Pi}{RT} = \frac{C_i}{M_{w,i}}(1 + B_2(T)C_i + B_3(T)C_i^2 + \dots) \quad 11.73$$

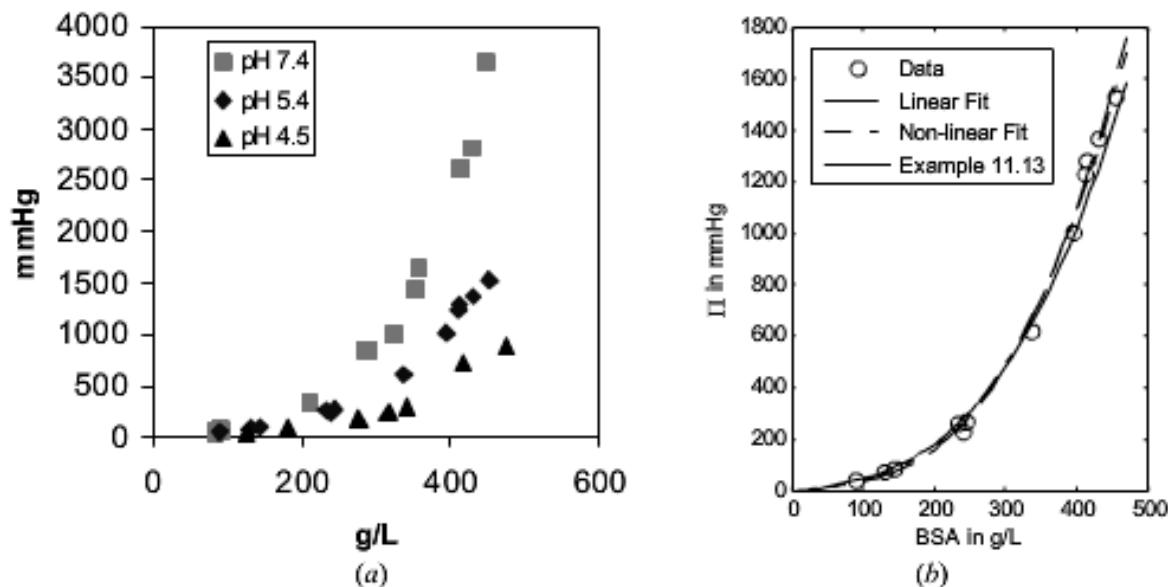


Figure 11.16 (a) Osmotic pressure in mmHg for solutions of bovine serum albumin (BSA) in water at 25°C at different pH values. Data from Vilker, V.L.; Colton, C.K.; Smith, K.A. *J. Colloid Int. Sci.* 1981. 79:548. (b) Fits of osmotic pressure at pH 5.4 as explained in Example 11.13.

Example 11.13 Osmotic pressure of BSA

Bovine serum albumin (BSA) has a molecular weight of 66399 g/mol. The osmotic pressure of an aqueous solution at 25°C and pH 5.4 is 74 mmHg when the concentration is 130 g/L and 260 mmHg at 234 g/L.^a Using only these data, determine the second and third osmotic virial coefficients and estimate the pressure needed to concentrate a solution to 450 g/L across a membrane with pure water on the other side.

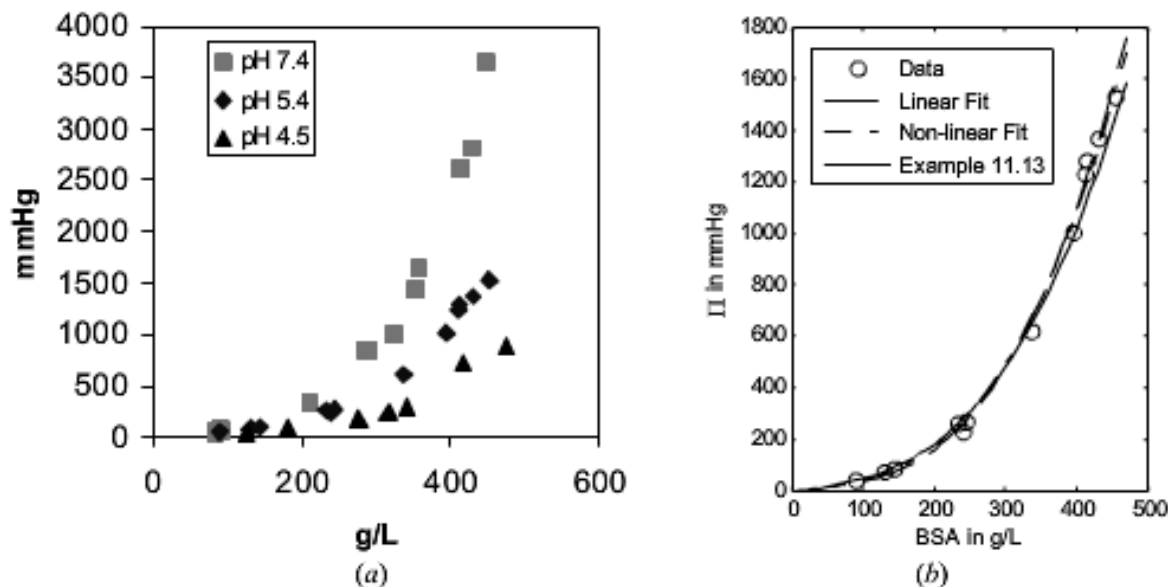


Figure 11.16 (a) Osmotic pressure in mmHg for solutions of bovine serum albumin (BSA) in water at 25°C at different pH values. Data from Vilker, V.L.; Colton, C.K.; Smith, K.A. *J. Colloid Int. Sci.* 1981, 79:548. (b) Fits of osmotic pressure at pH 5.4 as explained in Example 11.13.

Example 11.13 Osmotic pressure of BSA (Continued)

Solution: Since two points are given, let us linearize the equation for osmotic pressure to relate the coefficients to the slope and intercept. Defining a variable s to hold the rearranged variables,

$$\left(\frac{\Pi M_i}{RT C_i} - 1\right) / C_i = s_i = B_2(T) + B_3(T) C_i \quad 11.74$$

Converting the osmotic pressure to MPa, $\left(\frac{\Pi M_i}{RT C_i} - 1\right) / C_i$ is

$$s_i = \frac{\left(\frac{74\text{mmHg} | 0.1\text{MPa} | \text{mol} \cdot \text{K}}{750\text{mmHg} | 8.314\text{MPa}\cdot\text{cm}^3} | \frac{66399\text{ g/mol} | 1000\text{cm}^3/\text{L}}{298.15\text{K} | 130\text{ g/L}} - 1\right)}{130\text{g/L}} = 7.946 \times 10^{-3} \text{L/g}$$

Then at 234 g/L, $s_i = 1.269 \times 10^{-2} \text{L/g}$. The third coefficient is given by the slope of s_i versus C_i

$$B_3(T) = \frac{(s_i)_{234} - (s_i)_{130}}{(C_i)_{234} - (C_i)_{130}} = \frac{1.269 \times 10^{-2} - 7.946 \times 10^{-3}}{234 - 130} = 4.562 \times 10^{-5} (\text{L/g})^2$$

The second coefficient is found using the third coefficient with either of the original data points. From the point at 130 g/L:

$$B_2(T) = s_i - B_3(T) C_i = 7.946 \times 10^{-3} - 4.562 \times 10^{-5} (130) = 2.015 \times 10^{-3} \text{L/g} \quad 11.75$$

Now at 450 g/L,

$$\begin{aligned} \frac{\Pi}{RT} &= \frac{C_i}{M_i} (1 + 2.015 \times 10^{-3} C_i + 4.562 \times 10^{-5} C_i^2) \\ &= \frac{450}{66399} (1 + 2.015 \times 10^{-3} (450) + 4.562 \times 10^{-5} (450)^2) = 0.07548 \text{mol/L} \end{aligned}$$

$$\Pi = (0.07548 \text{mol/L})(8.314)(298.15)(\text{L}/1000\text{cm}^3)(750\text{mmHg}/0.1\text{MPa}) = 1403 \text{mmHg}$$

Therefore, we must apply a minimum estimated pressure of 1400 mmHg to concentrate the BSA to 450 g/L. The original paper cited gives a value of approximately 1500 mmHg. The estimate is within 10%. The prediction is sensitive to noise in the data points selected. A better method is to collect a few more data and regress a best fit.

Fig. 11.16(b) shows three fits of the data. For the "Linear Fit", the data are linearized following the procedure in this example, and then linear regression is used over all points. For the "Non-Linear Fit", the error in the osmotic pressure prediction of Eqn. 11.73 is minimized using nonlinear regression. The "Example 11.13" curve uses the coefficients fitted in this example. The second osmotic coefficient for this data set is sensitive to the regression method. For the linear fit $[B_2 \ B_3] = [1.93\text{E-}4 \ 5.352\text{E-}5]$, for the nonlinear fit, $[-3.57\text{E-}3 \ 6.360\text{E-}5]$. Careful analysis of the regression statistics shows that the uncertainty in the value of B_2 is larger than the value—the uncertainties for the 95% confidence limit of the nonlinear fit are $\pm[5.25\text{E-}3 \ 1.25\text{E-}5]$.

drops is to make the solution **isotonic**, meaning that the osmotic pressure of water in the solution is the same as that of the reference cellular material, the eyes in this case.²¹

stituents can simply be added up until the isotonic concentration is achieved. A property that follows this rule of adding up the constituents regardless of chemical nature is called a **colligative property**, of which osmotic pressure is an example (as long as the concentration is sufficiently low that B_2 and B_3 may be neglected).²² As a point of reference, human blood is in the concentration range where colligative properties can be assumed and isotonic with any solution of 0.308 mol/L solute.

Example 11.14 Osmotic pressure and electroporation of *E. coli*

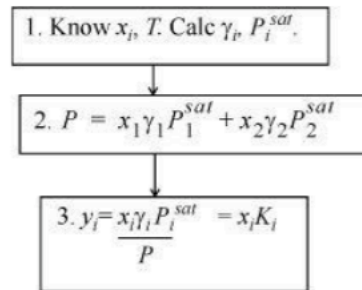
E. coli are bacteria commonly used to express desired proteins through genetic modification because they replicate and express whatever intracellular DNA they find. Introducing foreign DNA requires weakening the cell membrane by washing twice briefly (~10 min.) with pure water at 4°C, followed by a wash with 10wt% glycerol solution, centrifuging to isolate the cell pellet from the medium before washes. After the cells are rendered “electro-competent” through washing, all but 1 ml of the glycerol solution is removed and the aliquots are frozen for storage until the “electroporation” step (electrically shocking the cells) is conducted. What concentration of glycerol (wt%) is necessary to make a solution that is isotonic with human blood? Describe what happens to the water in the cells and the glycerol outside the cells when the medium is replaced with 10 wt% glycerol.

Solution: The molecular weight of glycerol can be found from the NIST Chemistry WebBook as 92.1. This means that a 0.308 mol/L solution has 0.308·92.1 g/L of glycerol. Assuming 1000g/L as the density (the same as water since the concentration is low), this gives a weight fraction of $0.308 \cdot 92.1 / 1000 = 0.0284 = 2.84$ wt%. Therefore, the 10 wt% is **hypertonic**. The activity of water is too low to be isotonic. The driving force is for water to come out of the cells, diluting the glycerol outside the cells. The cells will shrink and shrivel.

C.1. Modified Raoult's Law Methods

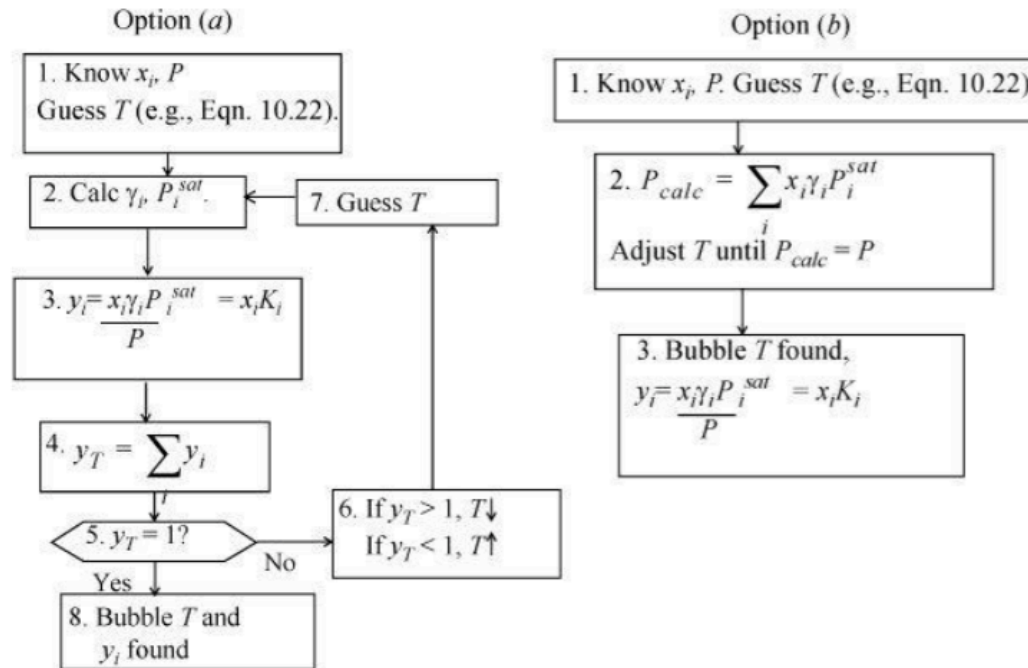
The equation that must be solved is: $y_i P = x_i \gamma_i P_i^{sat}$

Bubble P

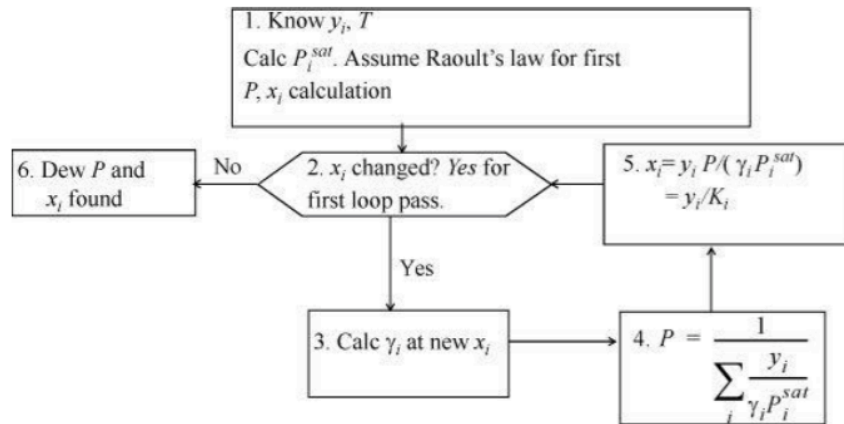


Bubble T

(Choose one flow sheet.)



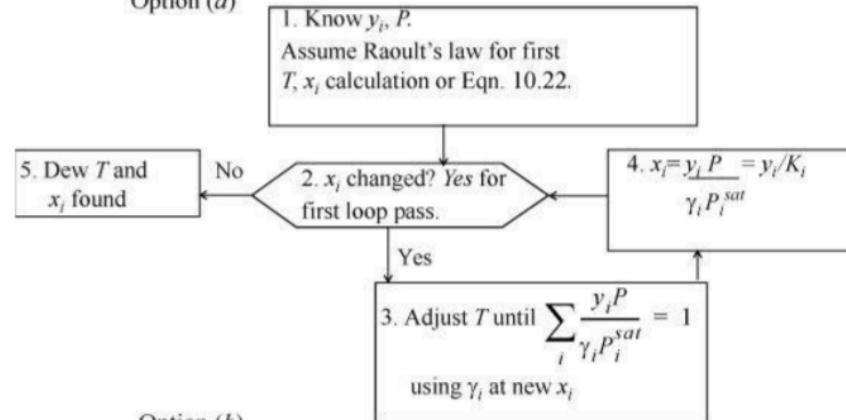
Dew P



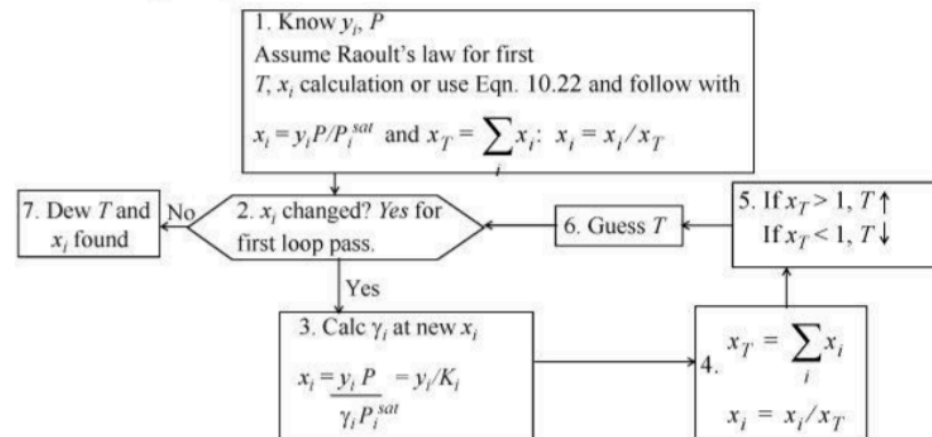
Dew T

(Choose one flow sheet.)

Option (a)



Option (b)



Isothermal Flash

