Assignment #7 - Solutions

1. M&S #10.2 –10.4:

10.2: Euler’s theorem says that if \( f(z_1, z_2, \ldots, z_N) \) is homogeneous then

\[
f(z_1, z_2, \ldots, z_N) = z_1 \frac{\partial f}{\partial z_1} + z_2 \frac{\partial f}{\partial z_2} + \cdots + z_N \frac{\partial f}{\partial z_N}.
\]

Prove Euler’s theorem by differentiating the equation in Problem 10-1 with respect to \( \lambda \) and then setting \( \lambda = 1 \). Apply Euler’s theorem to \( G = G(T, P, n_1, n_2) \) to derive Eq. 10.6.

10.3: Use Euler’s theorem to prove that \( Y(T, P, n_1, n_2, \ldots, n_c) = \sum_{i=1}^{c} n_i \bar{Y}_i \) for any extensive quantity \( Y \).

10.4: Apply Euler’s theorem to \( U = U(S, V, n) \). Do you recognize the resulting equation?

10.2: Begin with the definition of a (1st order) homogeneous function provided in problem 10-1:

\[
f(\lambda z_1, \lambda z_2, \ldots, \lambda z_N) = \lambda f(z_1, z_2, \ldots, z_N)
\]

Differentiate both sides of this expression with respect to \( \lambda \) as instructed. Differentiation of the r.h.s. is easy. The result is \( f(z_1, z_2, \ldots, z_N) \). Differentiation of the l.h.s. is accomplished as follows:

\[
\frac{\partial}{\partial \lambda} f(\lambda z_1, \lambda z_2, \ldots, \lambda z_N) = \frac{\partial (\lambda z_1)}{\partial \lambda} \frac{\partial f}{\partial (\lambda z_1)} + \frac{\partial (\lambda z_2)}{\partial \lambda} \frac{\partial f}{\partial (\lambda z_2)} + \cdots + \frac{\partial (\lambda z_N)}{\partial \lambda} \frac{\partial f}{\partial (\lambda z_N)}
\]

\[
= \lambda \frac{\partial f}{\partial (\lambda z_1)} + \lambda \frac{\partial f}{\partial (\lambda z_2)} + \cdots + \lambda \frac{\partial f}{\partial (\lambda z_N)}
\]

(I haven’t explicitly stated what is being held constant in these partial derivatives. What’s constant are all of the products \( \lambda z_i \) other than the particular \( \lambda z_i \) being differentiated in a given term. If this differentiation seems suspect to you, just think of defining a new set of independent variables, \( y_i \equiv \lambda z_i \) and differentiating \( f(y_1, y_2, \ldots, y_N) \) with respect to \( \lambda \).)

Given that \( \lambda \) can be any constant, set it equal to unity to find:

\[
f(z_1, z_2, \ldots, z_N) = z_1 \left( \frac{\partial f}{\partial z_1} \right)_{z_{j=1}} + z_2 \left( \frac{\partial f}{\partial z_2} \right)_{z_{j=2}} + \cdots + z_N \left( \frac{\partial f}{\partial z_N} \right)_{z_{j=N}}.
\]

One can apply this theorem to the Gibbs energy \( G = G(T, P, n_1, n_2) \), which is a homogeneous 1st order function of the mole numbers \( n_1 \) and \( n_2 \), but not of \( T \) and \( P \), simply requiring that \( T, P \) be held constant during the differentiation:
\[ G(T, P, n_1, n_2) = n_1 \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2} + n_2 \left( \frac{\partial G}{\partial n_2} \right)_{T,P,n_1} \]

\[ = n_1 \vec{G}_1 (T, P, \vec{x}) + n_2 \vec{G}_2 (T, P, \vec{x}) \]

\[ = n_1 \mu_1 (T, P, \vec{x}) + n_2 \mu_2 (T, P, \vec{x}) \]

### 10.3: The formal definition of an extensive quantity is one that is a 1\textsuperscript{st} order homogeneous function of all of the mole numbers (which specify the overall size of the system). The mathematical statement of this definition is: \( Y(T, P, \lambda n_1, \lambda n_2, ..., \lambda n_c) = \lambda Y(T, P, n_1, n_2, ..., n_c) \). As with \( G \) above, Euler's theorem can be applied to \( Y \) if we consider \( T \) and \( P \) to be constants during the differentiations wrt mole numbers:

\[ Y(T, P, n_1, n_2, ..., n_c) = \sum_{i=1}^{c} n_i \left( \frac{\partial Y}{\partial n_i} \right)_{T,P,n_{\text{rest}}} = \sum_{i=1}^{c} n_i \vec{y}_i (T, P, \vec{x}) . \]

### 10.4: All of the independent variables in the relation \( U = U(S, V, n) \) are extensive, i.e.

\[ U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n) \]

so that application of Euler’s theorem provides:

\[ U(S, V, n) = S \left( \frac{\partial U}{\partial S} \right)_{V,n} + V \left( \frac{\partial U}{\partial V} \right)_{S,n} + n \left( \frac{\partial U}{\partial n} \right)_{S,V} \]

Identifying the derivatives in this expression with basic thermodynamic derivatives one can rewrite it in the form:

\[ U = S(T) + V(-P) + n(\mu) = TS - PV + \mu n \]

Note the resemblance to the differential relation \( dU = TdS - PdV + \mu dn \). This resemblance makes it look as if one simply integrated \( dU \). This similarity holds only because all of the natural variables of \( U(S, V, n) \) are extensive quantities. It is important to recognize that similar relationships exist for the other thermodynamic potentials (like the Gibbs energy of 10.2) but only the extensive quantities get “integrated”: Thus, although \( dA = -SdT - PdV + \mu dn \), one doesn’t have \( A = -TS - PV + \mu n \) but rather \( A = -PV + \mu n = -PV + G \), etc.

2. In Topic Summary 10 the fugacity of a pure condensed phase “C” was written as:

\[ f^C (T, P) = f^V (T, P^{\text{vap}}) \exp \left\{ \frac{1}{RT} \int_{P^{\text{vap}}}^{P} V^C dP' \right\} \]

(2.1)

where \( f^V (T, P^{\text{vap}}) \) is the fugacity of the vapor phase (“V”) that coexists with the condensed phase at temperature \( T \) and pressure \( P^{\text{vap}} \), i.e.
\[ f^V(T, P_{vap}) = P_{vap} \exp \left\{ \frac{1}{RT} \int_{0}^{p_{vap}} \left( \bar{V}^V - \frac{RT}{P'} \right) dP' \right\} \] (2.2)

(a) Use the general expression for the fugacity of a single-component system,

\[ f(T, P) \equiv P \exp \left\{ \frac{(\mu - \mu^\text{IG})_{T, P}}{RT} \right\} = P \exp \left\{ \frac{1}{RT} \int_{0}^{P} \left( \bar{V} - \frac{RT}{P'} \right) dP' \right\} \] (2.2)

to derive Eq. 2.1. [Hint: Break up the original integral in Eq. 2.1 into two parts, one over pressures 0 to \( P_{vap} \) and the other over pressures \( P_{vap} \) to \( P \) and remember that phase coexistence implies equality of either chemical potentials or fugacities.]

Throughout Chapter 10, M&S employ the approximation \( f^C(T, P) \approx P_{vap} \) (or its equivalent for mixtures). This approximation assumes (i) that the fugacity coefficient of the vapor, \( f^V / P \), is unity, thereby neglecting any vapor non-idealities and (ii) that the “Poynting correction”, \( \exp \left\{ \frac{1}{RT} \int_{P_{vap}}^{P} \bar{V}^C dP' \right\} \), is also unity. Examine both of these approximations for the case of liquid benzene at a pressure of 1 bar and temperatures of 30, 70, and 110 °C using the coexistence data provided in M&S Fig 9.3. Proceed as follows:

(b) Estimate the fugacities of benzene vapor at these three temperatures using the expression for \( \ln(f / P) \) of a van der Waals fluid in Topic Summary 8.

(c) Calculate the magnitude of the Poynting correction at 30 °C. At this temperature the density of liquid benzene is 0.8683 g cm\(^{-1}\) and for the pressures relevant here liquid benzene can be considered incompressible.

(d) At what pressures would the magnitude of the Poynting correction of part (c) differ from unity by 1%, 5%, and 10%? (Again assume that benzene can be treated as an incompressible liquid.)

(a) Begin by writing the general expression for the fugacity of the condensed phase in terms of an integral over \( P \) and then break the integral into two pieces as suggested:

\[ f^C(T, P) = P \exp \left\{ \frac{1}{RT} \int_{0}^{P} \left( \bar{V}^C - \frac{RT}{P'} \right) dP' \right\} \]

\[ = P \exp \left\{ \frac{1}{RT} \int_{0}^{P_{vap}} \left( \bar{V}^C - \frac{RT}{P'} \right) dP' + \frac{1}{RT} \int_{P_{vap}}^{P} \left( \bar{V}^C - \frac{RT}{P'} \right) dP' \right\} \]

\[ = \frac{P}{P_{vap}} \left[ P_{vap} \exp \left\{ \frac{1}{RT} \int_{0}^{P_{vap}} \left( \bar{V}^C - \frac{RT}{P'} \right) dP' \right\} \right] \exp \left\{ \frac{1}{RT} \int_{P_{vap}}^{P} \left( \bar{V}^C - \frac{RT}{P'} \right) dP' \right\} \]

The first term in brackets here is simply the fugacity of the condensed phase at the temperature \( T \) and pressure \( P_{vap} \), \( f^C(T, P_{vap}) \). If \( P_{vap} \) is the equilibrium vapor pressure of the condensed phase for the temperature \( T \), the chemical potentials of the condensed and vapor phases must be equal and so too must
their fugacities, i.e. \( f^C(T,V) = f^V(T,P) \). Making this substitution and breaking up the remaining integral one has:

\[
\frac{P}{P^\text{vap}} f^V(T,P^\text{vap}) \exp \left\{ \frac{1}{RT} \int_{P^\text{vap}}^P \left( \frac{V^C}{P} - \frac{RT}{P'} \right) dP' \right\} - \frac{P^\text{vap}}{P} f^V(T,P^\text{vap}) \exp \left\{ \frac{1}{RT} \int_{P^\text{vap}}^P V^C dP' - \int_{P^\text{vap}}^P dP' \right\} = \frac{P}{P^\text{vap}} f^V(T,P^\text{vap}) \exp \left\{ \frac{1}{RT} \int_{P^\text{vap}}^P V^C dP' - \ln(P/P^\text{vap}) \right\}
\]

as desired.

(b) The pressures I read from Fig. 9.3 for temperatures of 30, 70, and 110°C are: 113, 562, and 1813 torr, respectively. (Since I was working in Mathcad anyway, I also computed these pressures from the vapor pressure equation provided in M&S problem 9.9. The results, tabulated below, are close to those read directly from the graph.)

Given a sufficiently simple equation of state, the integral relating \( f^V(T,P^\text{vap}) \) to volumetric data can be performed analytically. Using the van der Waals e.o.s.,

\[
P = \frac{RT}{V - b} - \frac{a}{V^2}
\]

to represent a non-ideal vapor phase, Topic Summary 8 provided the fugacity in the form

\[
\ln(f/P) = (Z - 1) - \ln(Z - B) - A/Z.
\]

The fugacity coefficient (“\( \gamma \)” in M&S or “\( \varphi \)” in most texts) which describes the deviation from ideality is thus:

\[
\varphi \equiv f^V(T,P)/P = \exp\{Z - 1 - \ln(Z - B) - A/Z\}
\]

where

\[
Z = P V / RT, \quad A = aP / (RT)^2, \quad \text{and} \quad B = bP / RT.
\]

To evaluate fugacity coefficients I used a Mathcad worksheet (below) and obtained the results:

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( P^\text{vap}/\text{torr} )</th>
<th>( P^\text{vap}/\text{bar} )</th>
<th>( Z )</th>
<th>( \varphi )</th>
<th>( \varphi(Z=1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>119</td>
<td>0.159</td>
<td>0.996</td>
<td>0.996</td>
<td>0.996</td>
</tr>
<tr>
<td>70</td>
<td>551</td>
<td>0.735</td>
<td>0.986</td>
<td>0.986</td>
<td>0.986</td>
</tr>
<tr>
<td>110</td>
<td>1756</td>
<td>2.341</td>
<td>0.964</td>
<td>0.965</td>
<td>0.966</td>
</tr>
</tbody>
</table>

The column labeled “\( \varphi \)” is the result obtained from an exact calculation of \( Z \) using the “find” function of Mathcad and the column labeled \( \varphi(Z=1) \) is what is obtained making the approximation \( Z \approx 1 \). As shown above this approximation is quite accurate in the present case.
Note that even at pressures above 2 bar, the error in assuming that the vapor is ideal is only about 4%. These estimates are typical of the small effect that vapor-phase non-idealities have at pressures of less than a few bar. Similar values of \( \phi \) are found for most gases, even polar and hydrogen bonding gases like water and methanol. (I estimated fugacity coefficients of ~0.94-0.98 for water and methanol at their boiling points.) The only cases in which this non-ideal vapor correction is important at low pressures are ones that involve molecules which associate strongly in the vapor phase due to specific interactions. One example of such a case is acetic acid, whose vapor is nonideal even at low pressures because of extensive dimerization. At its boiling point (118°C) acetic acid vapor has a fugacity coefficient of 0.42.

**Mathcad worksheet:**

Fundamental Constants & Conversion Factors:

\[
R := 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad dm := 0.1 \text{ m} \quad \text{bar} := 10^5 \text{ Pa} \quad \text{torr} = 133.322 \text{ Pa}
\]

Vapor Pressure Eq. (M&S prob. 9-9):

\[
ap := -10.655375 \quad bp := 23.941912 \quad cp := -22.388714 \quad dp := 20.2085593 \quad ep := -7.219556 \quad fp := 4.84728
\]

\[
T_c := 561.7 \text{ K} \quad t := 110 \quad T := K(t + 273.15)
\]

\[
P_v(x) := \text{bar} \cdot \exp \left[ \frac{ap}{x} + bp \cdot x + cp \cdot x^2 + dp \cdot x^3 + fp \cdot (1 - x)^{1.70} \right] \frac{P_v \left( \frac{T}{T_c} \right)}{\text{torr}} = 1.756 \times 10^3
\]

Fugacities coefficients from van der Waals EOS:

\[vdW \text{ constants (M&STable 2.3):} \quad a := 18.876 \text{ dm}^6 \text{bar} \cdot \text{mol}^{-2} \quad b := 0.11974 \text{ dm}^3 \text{mol}^{-1}\]

\[P := P_v \left( \frac{T}{T_c} \right) \quad A := \frac{a \cdot P}{(R \cdot T)^2} \quad B := \frac{b \cdot P}{R \cdot T} \quad V := \frac{R \cdot T}{P}
\]

Mathcad "Solve" Block to find \( V(P) \):

\[
\begin{align*}
P &= \frac{R \cdot T}{V - b} - \frac{a}{V^2} \\
V &= \text{Find}(V)
\end{align*}
\]

\[Z := \frac{P \cdot V}{R \cdot T} \quad Z = 0.964 \quad \phi := \exp \left( Z - 1 - \ln(Z - B) - \frac{A}{Z} \right) \quad \phi = 0.965
\]

(c) For an incompressible substance the Poynting correction can be approximated:

\[
PCorr = \exp \left\{ \frac{1}{RT} \int_{P_{vap}}^{P} \bar{P} \bar{C} dP' \right\}
\]

\[
\approx \exp \left\{ \frac{\bar{P} \bar{C}}{RT} \int_{P_{vap}}^{P} dP' \right\} = \exp \left\{ \frac{\bar{P} \bar{C} (P - P_{vap})}{RT} \right\}
\]

For the conditions: \( P_{vap} = 119 \text{ torr} \), \( T = 30^\circ \text{C} \), and \( P = 1 \text{ bar} \), and a molar volume of liquid benzene of \( \bar{V} = 90.0 \text{ cm}^3/\text{mol} \) (see below), I estimate this Poynting correction to be a factor of \( 1.003 \).

Fundamental Constants & Conversion Factors:

\[
R := 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad dm := 0.1 \text{ m} \quad \text{bar} := 10^5 \text{ Pa} \quad \text{torr} = 133.322 \text{ Pa}
\]

Vapor Pressure Eq. (M&S prob. 9-9):

\[
ap := -10.655375 \quad bp := 23.941912 \quad cp := -22.388714 \quad dp := 20.2085593 \quad ep := -7.219556 \quad fp := 4.84728
\]

\[
T_c := 561.7 \text{ K} \quad t := 110 \quad T := K(t + 273.15)
\]

\[
P_v(x) := \text{bar} \cdot \exp \left[ \frac{ap}{x} + bp \cdot x + cp \cdot x^2 + dp \cdot x^3 + fp \cdot (1 - x)^{1.70} \right] \frac{P_v \left( \frac{T}{T_c} \right)}{\text{torr}} = 1.756 \times 10^3
\]

Fugacities coefficients from van der Waals EOS:

\[vdW \text{ constants (M&STable 2.3):} \quad a := 18.876 \text{ dm}^6 \text{bar} \cdot \text{mol}^{-2} \quad b := 0.11974 \text{ dm}^3 \text{mol}^{-1}\]

\[P := P_v \left( \frac{T}{T_c} \right) \quad A := \frac{a \cdot P}{(R \cdot T)^2} \quad B := \frac{b \cdot P}{R \cdot T} \quad V := \frac{R \cdot T}{P}
\]

Mathcad "Solve" Block to find \( V(P) \):

\[
\begin{align*}
P &= \frac{R \cdot T}{V - b} - \frac{a}{V^2} \\
V &= \text{Find}(V)
\end{align*}
\]

\[Z := \frac{P \cdot V}{R \cdot T} \quad Z = 0.964 \quad \phi := \exp \left( Z - 1 - \ln(Z - B) - \frac{A}{Z} \right) \quad \phi = 0.965
\]

(c) For an incompressible substance the Poynting correction can be approximated:

\[
PCorr = \exp \left\{ \frac{1}{RT} \int_{P_{vap}}^{P} \bar{P} \bar{C} dP' \right\}
\]

\[
\approx \exp \left\{ \frac{\bar{P} \bar{C}}{RT} \int_{P_{vap}}^{P} dP' \right\} = \exp \left\{ \frac{\bar{P} \bar{C} (P - P_{vap})}{RT} \right\}
\]

For the conditions: \( P_{vap} = 119 \text{ torr} \), \( T = 30^\circ \text{C} \), and \( P = 1 \text{ bar} \), and a molar volume of liquid benzene of \( \bar{V} = 90.0 \text{ cm}^3/\text{mol} \) (see below), I estimate this Poynting correction to be a factor of \( 1.003 \).
(d) Solving the above equation for $P$, $P(\text{PCorr}) = P_{vap} + RT \ln(\text{PCorr}) / \bar{v}_c$, the total pressures at which the Poynting correction reaches 1, 5, and 10% are 2.9, 14, and 27 bar, respectively. The Mathcad sheet I used for these calculations is shown below.

\[
T := 303.15 \text{K} \quad d := 0.868 \text{kg dm}^{-3} \quad MW := 0.078113 \text{kg mol}^{-1} \quad V_L := \frac{MW}{d} \quad V_L = 8.999 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}
\]

\[
P_{vap} := 119 \text{ torr} \quad P := 1 \text{ bar} \quad \text{PCorr} := \exp \left[ \frac{V_L \cdot (P - P_{vap})}{R \cdot T} \right] \quad \text{PCorr} = 1.003
\]

\[
P(\text{PCorr}) := \frac{P_{vap} + \frac{R \cdot T \cdot \ln(\text{PCorr})}{V_L}}{P(1.01) \text{ bar}} = 2.945 \quad P(1.05) \text{ bar} = 13.823 \quad P(1.10) \text{ bar} = 26.852
\]

3. (a) M&S 10-22: The vapor pressures of benzene and toluene between 80°C and 110°C as a function of Kelvin temperature are given by the empirical formulas:

\[
\ln(P_{\text{benz}}^* / \text{torr}) = 17.551 - 3856.6(K / T) \quad \text{and} \quad \ln(P_{\text{tol}}^* / \text{torr}) = 18.397 - 4514.6(K / T)
\]

Assuming that benzene and toluene form an ideal solution, use these formulas to construct a temperature-composition diagram of this system at an ambient pressure of 760 torr.

(b) On the plot you make, illustrate the use of the lever rule for determining the % of the mixture that is liquid versus vapor when the system consists of 40 mole % toluene and the temperature is 365 K.

[Hint: It is not necessary to solve equations for $T(x_2)$ and $T(y_2)$. Simply solve the equations provided in problem 10-17 for $x_2(T)$ and $y_2(T)$ as functions of $P_1^*(T)$ and $P_2^*(T)$ for a fixed total pressure and plot $\{T, x_2(T)\}$ and $\{T, y_2(T)\}$ points.]

I will label benzene as component 1 and toluene as component 2. The relations needed for this problem are then:

\[
x_2(T) = \frac{760 \text{ torr} - P_{\text{benz}}^*(T)}{P_{\text{tot}}^*(T) - P_{\text{benz}}^*(T)} \quad y_2(T) = \frac{x_2(T)P_{\text{tot}}^*(T)}{760 \text{ torr}} \quad F_L = \frac{L_1}{L_1 + L_2}
\]

with all pressures expressed in torr.

(a) Calculations were performed using an Excel spreadsheet and the results plotted below.

(b) The fraction of the system in the liquid is $F_L$, where the lengths $L_1$ and $L_2$ are defined in the plot. I find:

$F_L = 0.65, F_V = 0.35$
4. At 60 °C the vapor pressure of methyl acetate is 1.126 bar and the vapor pressure of methanol is 0.847 bar. Their excess Gibbs energy of mixing can be described by the Margules equation: \( \overline{G}^e / RT = 1.06x_1x_2 \).

(a) Estimate the fugacities of the two components in the mixture and the mixture’s vapor pressure as functions of composition at 60 °C and make a plot of your results. Clearly state any approximations you make in your analysis.

(b) What is the Henry’s law constant for each component?

(a) The fugacities of the two components in the liquid mixture can be written in terms of their activity coefficients by:

\[
f_i^{L}(\bar{x}) = f_i^{L*}a_i(\bar{x}) = f_i^{L*}x_i\gamma_i(\bar{x})
\]

(I haven’t explicitly displayed the dependence of these quantities on \( T \) and \( P \) but it is to be understood that these equations apply to a specific \( T \) and \( P \), as does the expression for \( \overline{G}^e \)). The activity coefficients are related to the Margules constant \( A = 1.06 \) by:

\[
\gamma_1(\bar{x}) = \exp(Ax_2^2) \quad \text{and} \quad \gamma_2(\bar{x}) = \exp(Ax_1^2)
\]

Using \( x_2 \) as the composition variable, the fugacities in solution are:

\[
f_i^{L}(x_2) = f_i^{L*}(1-x_2)\exp(Ax_2^2) \quad \text{and} \quad f_i^{L}(x_2) = f_i^{L*}x_2\exp(A(1-x_2)^2)
\]

If one ignores the Poynting correction and vapor non-ideality, the liquid-state fugacities can be equated to the partial pressures of vapor-phase components as:

\[
f_i^{L*}(T, P) \cong f_i^{L*}(T, P_{vap}(T)) \cong P_{vap}(T)
\]

and the total vapor pressure above the solution can be approximated by:
\[ P = P_1 + P_2 \cong P_1^* x_1 \gamma_1 + P_2^* x_2 \gamma_2 \]

I did the calculations in the Excel spreadsheet shown below and used the results to make the plot at the right.

<table>
<thead>
<tr>
<th>x2</th>
<th>(\gamma_1)</th>
<th>(\gamma_2)</th>
<th>(f_1/\text{bar})</th>
<th>(f_2/\text{bar})</th>
<th>P/\text{bar}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.000</td>
<td>2.886</td>
<td>0.000</td>
<td>1.126</td>
<td>1.126</td>
</tr>
<tr>
<td>0.05</td>
<td>1.003</td>
<td>2.603</td>
<td>0.110</td>
<td>1.183</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>1.011</td>
<td>2.360</td>
<td>0.200</td>
<td>1.224</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>1.024</td>
<td>2.151</td>
<td>0.273</td>
<td>1.253</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>1.043</td>
<td>1.971</td>
<td>0.334</td>
<td>1.274</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>1.068</td>
<td>1.815</td>
<td>0.384</td>
<td>1.287</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>1.100</td>
<td>1.681</td>
<td>0.427</td>
<td>1.294</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>1.139</td>
<td>1.565</td>
<td>0.464</td>
<td>1.297</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>1.185</td>
<td>1.465</td>
<td>0.496</td>
<td>1.297</td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>1.239</td>
<td>1.378</td>
<td>0.525</td>
<td>1.293</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.303</td>
<td>1.303</td>
<td>0.552</td>
<td>1.286</td>
<td></td>
</tr>
<tr>
<td>0.55</td>
<td>1.378</td>
<td>1.239</td>
<td>0.577</td>
<td>1.276</td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>1.465</td>
<td>1.185</td>
<td>0.602</td>
<td>1.262</td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>1.565</td>
<td>1.139</td>
<td>0.627</td>
<td>1.244</td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>1.681</td>
<td>1.100</td>
<td>0.652</td>
<td>1.220</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>1.815</td>
<td>1.068</td>
<td>0.679</td>
<td>1.190</td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td>1.971</td>
<td>1.043</td>
<td>0.707</td>
<td>1.151</td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>2.151</td>
<td>1.024</td>
<td>0.737</td>
<td>1.101</td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.360</td>
<td>1.011</td>
<td>0.770</td>
<td>1.036</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>2.603</td>
<td>1.003</td>
<td>0.807</td>
<td>0.953</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>2.886</td>
<td>1.000</td>
<td>0.000</td>
<td>0.847</td>
<td>0.847</td>
</tr>
</tbody>
</table>

Fig. 6

(b) The Henry’s law constants for component 2 dilute in 1 (which I’ll denote \(H_{2(1)}\)) and for 1 dilute in 2 (\(H_{1(2)}\)) are defined by the initial slopes:

\[
H_{2(1)} = \lim_{x_2 \to 0} \frac{f_2}{x_2} = \exp(A) f_2^L \cong \exp(A) P_2^* \quad \text{and} \quad H_{1(2)} = \lim_{x_1 \to 0} \frac{f_1}{x_1} \cong \exp(A) P_1^*
\]

Here \(H_{\text{OH(Ac)}} \cong 2.44 \text{ bar}\) (methanol solute) and \(H_{\text{Ac(OH)}} \cong 3.25 \text{ bar}\) (methyl acetate solute).

5. Analysis of the partitioning of a species between two immiscible liquids phases involves the same logic as the partitioning of a solution component between mixed liquid and vapor phases.

(a) Show that the distribution coefficient, defined as the ratio of the concentrations of the species in the two phases is determined by:

\[
K = \frac{x_i^I}{x_i^II} = \frac{\gamma_i(T, P, x^I)}{\gamma_i(T, P, x^II)}
\]

(b) Carbon tetrachloride and water are almost completely immiscible (meaning the 2-phase coexistence of \(\text{CCl}_4/\text{H}_2\text{O}\) mixtures is such that there is little carbon-tetrachloride in the water-rich phase and vice-versa, for any composition of the mixture). When enough \(\text{Br}_2\) is added to a 2-phase \(\text{CCl}_4/\text{H}_2\text{O}\) system to make the concentration of \(\text{Br}_2\) in carbon tetrachloride 1.0 mol/L, the \(\text{Br}_2\) concentration in water is found to be 0.0329 mol/L. What is the distribution coefficient in this case and what is the ratio \(\gamma_{\text{Br}_2}^{\text{H}_2\text{O}} / \gamma_{\text{Br}_2}^{\text{CCl}_4}\)?
(c) Without using other sources of data (other than your brain) would you guess for the values of the individual activity coefficients $\gamma_{Br_2}^{H_2O}$ and $\gamma_{Br_2}^{CCl_4}$? Explain your reasoning.

(d) Estimate the activity coefficients $\gamma_{Br_2}^{H_2O}$ and $\gamma_{Br_2}^{CCl_4}$ using the regular solution model.

(a) The requirement for two phases (I and II) to be in equilibrium is that the chemical potentials or the fugacities of each component be the same in the two phases:

$$f_i^I(T,P,\bar{x}^I) = f_i^II(T,P,\bar{x}^II)$$

The fugacities are related to activity coefficients by:

$$f_i^I(T,P,\bar{x}^I) = f_i^o(T)\gamma_i(T,P,\bar{x}^I) = f_i^o(T)x_i^I\gamma_i(T,P,\bar{x}^I)$$

where $f_i^o(T)$ is the fugacity of $i$ in some pre-defined standard state, for example the pure species in whatever form is most stable at the specified $T$ and $P=1$ bar. (The choice of standard state is irrelevant here as long as the activities in the two phases employ this same state for reference.) The ratio of concentrations of species $i$ in the two phases is then:

$$\frac{x_i^I}{x_i^II} = \frac{f_i^I(T)\gamma_i(T,P,\bar{x}^II)}{f_i^o(T)\gamma_i(T,P,\bar{x}^I)} = \frac{\gamma_i^II}{\gamma_i^I} = K(T,P)$$

(b) The data provided is insufficient to calculate the mole fractions of Br$_2$ in the two solutions exactly. However, the mole fractions should be well approximated by making the assumption that the excess volume of mixing is zero. ($\Delta V^ex/\Delta V$ is at most a few percent for all liquid mixtures.) This assumption leads to the results shown on the Mathcad worksheet shown on the following page. (Here “C”=CCl$_4$, “W”=water, $x_{BC}^I=x_{Br_2}^{CCl_4}$ and $x_{BW}^I=x_{Br_2}^{water}$):

CCl$_4$ Solution: $n_B := 1$mol

$$V_C := 1L - n_B \frac{MW_B}{d_B} \quad n_C := \frac{V_C d_C}{MW_C} \quad n_C = 9.84$mol \quad x_{BC}^I := \frac{n_B}{n_B + n_C} \quad n_{BC} = 0.092$$

Water Solution: $n_B := 0.0329$mol

$$V_W := 1L - n_B \frac{MW_B}{d_B} \quad n_W := \frac{V_W d_W}{MW_W} \quad n_W = 55.462$mol \quad x_{BW}^I := \frac{n_B}{n_B + n_W} \quad n_{BW} = 5.928 \times 10^{-4}$$

So the distribution coefficient is:

$$K = \frac{x_{Br_2}^{CCl_4}}{x_{Br_2}^{water}} \frac{\gamma_{Br_2}^{water}}{\gamma_{Br_2}^{CCl_4}} = 155.6$$
(If you simply ignored the volume of Br₂, a relatively inaccurate approach, the results would have been, \( x_{Br_2} = 0.088 \), and \( K = 148.6 \).)

(c) Based on the fact that the intermolecular interactions in Br₂(l) are similar to those in CCl₄(l) (the interactions in both liquids are dominated by dispersion interactions) I would guess that \( \gamma_{Br_2}^{CCl_4} \) should be close to unity. Liquid water, on the other hand, is dominated by hydrogen-bonding interactions. Since the interactions are very different from those in Br₂(l), I would anticipate that \( \gamma_{Br_2}^{water} \gg 1 \). So, as a first guess I would say \( \gamma_{Br_2}^{CCl_4} \approx 1 \), \( \gamma_{Br_2}^{water} \approx 156 \).

(d) The regular solution model would predict:

\[
\ln \gamma_{Br_2}^{CCl_4} = \frac{V_{Br_2} \phi_{CCl_4}^2}{RT} \left( \delta_{Br_2} - \delta_{CCl_4} \right)^2 \quad \text{and} \quad \ln \gamma_{Br_2}^{water} = \frac{V_{Br_2} \phi_{water}^2}{RT} \left( \delta_{Br_2} - \delta_{water} \right)^2 \quad \text{with} \quad \delta_i \equiv \left( \frac{\Delta vap \bar{U}_i^*}{\bar{V}_i^*} \right)
\]

Approximating the vapors as ideal gases, \( \Delta vap \bar{U}_i^* \approx \Delta vap \bar{H}_i^* - RT \), and using the data supplied, I worked in Mathcad (sheet below) to find: \( \gamma_{Br_2}^{CCl_4} = 2.0 \) and \( \gamma_{Br_2}^{water} = 3 \times 10^5 \).

From this exercise we see that the regular solution equations predict a value of \( \gamma_{Br_2}^{water} / \gamma_{Br_2}^{CCl_4} = 10^5 \), which is several orders of magnitude larger than the actual value. This discrepancy is not surprising. Regular solution theory is only expected to be of quantitative value when dealing with two liquids having similar (and nonpolar) interactions. Although this restriction is fulfilled in the case of Br₂ / CCl₄, it is clearly not the case for Br₂ / water. Nevertheless, the theory does predict the correct qualitative behavior, \( \gamma_{Br_2}^{water} \gg 1 \) (indicating that Br₂ should be sparingly soluble in water.)

\[
\Delta H_B := 29.45 \times 10^3 \text{J} \cdot \text{mol}^{-1} \quad \Delta H_C := 30.0 \times 10^3 \text{J} \cdot \text{mol}^{-1} \quad \Delta H_W := 43.99 \times 10^3 \text{J} \cdot \text{mol}^{-1} \quad T := 298.15 \text{K}
\]

\[
V_{mB} := \frac{MW_B}{d_B} \quad V_{mC} := \frac{MW_C}{d_C} \quad V_{mw} := \frac{MW_w}{d_w} \quad \delta_B := \frac{\Delta H_B - R \cdot T}{V_{mB}} \quad \delta_C := \frac{\Delta H_C - R \cdot T}{V_{mC}}
\]

\[
\delta_W := \sqrt{\frac{\Delta H_W - R \cdot T}{V_{mw}}} \quad \delta_B := 23.014 \quad \delta_W := 47.931 \quad \delta_C := 16.892
\]

\[
\gamma_C := \exp \left[ V_{mB} \frac{V_C}{R \cdot T \cdot (1 \text{L})} \left( \delta_B - \delta_C \right)^2 \right] \quad \gamma_W := \exp \left[ V_{mB} \frac{V_W}{R \cdot T \cdot (1 \text{L})} \left( \delta_B - \delta_W \right)^2 \right] \quad \gamma_C = 2.001 \quad \gamma_W = 3.315 \times 10^5
\]

6. Using the data on mixtures of ethanol and water provided in M&S question 10-50:
   (a) Compute the activities, activity coefficients of both components, and the Gibbs excess and plot them as functions of \( x_2 \).
(b) Fit the activity coefficient data to the van Laar equations to determine the constants $\alpha$ and $\beta$. Also predict $\bar{G}^{\text{ex}} / RT$ from your fit and compare it to the experimental data.

(c) Fit $\bar{G}^{\text{ex}} / RT$ versus $x_2$ to Redlich-Kister expression using as many terms as are needed for good fit. Also compute the individual activity coefficients from this fit and compare them to the experimental data.

(d) Comment on the relative quality of the results obtained with these two empirical fitting methods.

(e) If the van Laar equations are interpreted in terms of regular solution theory, one finds

$$\alpha = \frac{\bar{V}_1^*}{RT} \left( \delta_1 - \delta_2 \right)^2 \quad \text{and} \quad \beta = \frac{\bar{V}_2^*}{RT} \left( \delta_1 - \delta_2 \right)^2$$

According to these expressions, the ratio of the $\alpha$ and $\beta$ constants should be equal to the ratio of the molar volumes of the components. Is this borne out in the present case?

---

(a) Assuming ideal vapors and neglecting the Poynting correction, the solution-phase activities and activity coefficients can be estimated from the observed vapor pressures via:

$$a_i \equiv f_i / f_i^* \approx P_i / P_i^* \quad \text{and} \quad \gamma_i \equiv a_i / x_i$$

The excess Gibbs energy is given by:

$$\bar{G}^{\text{ex}} = x_1 \mu_{1}^{\text{ex}} + x_2 \mu_{2}^{\text{ex}} = RT \left\{ x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right\}.$$ 

I computed these various quantities in Excel, and the results are tabulated and plotted (Figs. 6-2 and 6-3) on the following page. Note that in this table and throughout the analysis I’ve labeled component #1 = water and component #2 = ethanol.

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$P_2$ /torr</th>
<th>$P_1$ /torr</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\bar{G}^{\text{ex}} / RT$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0</td>
<td>23.8</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>4.3</td>
<td>23.3</td>
<td>0.980</td>
<td>0.072</td>
<td>1.000</td>
<td>3.615</td>
<td>0.026</td>
<td>2.915</td>
<td>1.309</td>
</tr>
<tr>
<td>0.05</td>
<td>10.0</td>
<td>22.7</td>
<td>0.953</td>
<td>0.168</td>
<td>1.003</td>
<td>3.365</td>
<td>0.064</td>
<td>1.300</td>
<td>1.350</td>
</tr>
<tr>
<td>0.08</td>
<td>14.8</td>
<td>22.1</td>
<td>0.928</td>
<td>0.251</td>
<td>1.009</td>
<td>3.133</td>
<td>0.099</td>
<td>1.334</td>
<td>1.352</td>
</tr>
<tr>
<td>0.10</td>
<td>17.7</td>
<td>21.7</td>
<td>0.913</td>
<td>0.298</td>
<td>1.014</td>
<td>2.981</td>
<td>0.122</td>
<td>1.322</td>
<td>1.355</td>
</tr>
<tr>
<td>0.20</td>
<td>27.0</td>
<td>20.3</td>
<td>0.852</td>
<td>0.456</td>
<td>1.064</td>
<td>2.282</td>
<td>0.215</td>
<td>1.156</td>
<td>1.400</td>
</tr>
<tr>
<td>0.30</td>
<td>31.2</td>
<td>19.3</td>
<td>0.813</td>
<td>0.528</td>
<td>1.162</td>
<td>1.758</td>
<td>0.274</td>
<td>1.024</td>
<td>1.482</td>
</tr>
<tr>
<td>0.40</td>
<td>33.9</td>
<td>18.5</td>
<td>0.778</td>
<td>0.573</td>
<td>1.297</td>
<td>1.433</td>
<td>0.300</td>
<td>0.961</td>
<td>1.561</td>
</tr>
<tr>
<td>0.50</td>
<td>36.9</td>
<td>17.3</td>
<td>0.727</td>
<td>0.623</td>
<td>1.454</td>
<td>1.245</td>
<td>0.297</td>
<td>0.942</td>
<td>1.607</td>
</tr>
<tr>
<td>0.60</td>
<td>40.23</td>
<td>15.53</td>
<td>0.653</td>
<td>0.680</td>
<td>1.633</td>
<td>1.133</td>
<td>0.271</td>
<td>0.935</td>
<td>1.636</td>
</tr>
<tr>
<td>0.70</td>
<td>43.94</td>
<td>13.16</td>
<td>0.553</td>
<td>0.742</td>
<td>1.845</td>
<td>1.060</td>
<td>0.225</td>
<td>0.916</td>
<td>1.759</td>
</tr>
<tr>
<td>0.80</td>
<td>48.24</td>
<td>9.89</td>
<td>0.416</td>
<td>0.815</td>
<td>2.079</td>
<td>1.019</td>
<td>0.161</td>
<td>0.887</td>
<td>2.204</td>
</tr>
<tr>
<td>0.90</td>
<td>53.45</td>
<td>5.38</td>
<td>0.226</td>
<td>0.903</td>
<td>2.262</td>
<td>1.003</td>
<td>0.085</td>
<td>0.875</td>
<td>2.768</td>
</tr>
<tr>
<td>0.93</td>
<td>55.14</td>
<td>3.83</td>
<td>0.161</td>
<td>0.931</td>
<td>2.301</td>
<td>1.002</td>
<td>0.060</td>
<td>0.874</td>
<td>2.707</td>
</tr>
<tr>
<td>0.96</td>
<td>56.87</td>
<td>2.23</td>
<td>0.094</td>
<td>0.961</td>
<td>2.344</td>
<td>1.001</td>
<td>0.035</td>
<td>0.884</td>
<td>1.957</td>
</tr>
<tr>
<td>0.98</td>
<td>58.02</td>
<td>1.13</td>
<td>0.048</td>
<td>0.980</td>
<td>2.376</td>
<td>1.000</td>
<td>0.017</td>
<td>0.872</td>
<td>4.560</td>
</tr>
<tr>
<td>1</td>
<td>59.2</td>
<td>0</td>
<td>0.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6-1

Mole Fraction Ethanol $x_2$

Activity $a_i$

Activity Coefficient $\gamma_i$

Fig. 6-2

Mole Fraction Ethanol $x_2$

Gibbs Excess $G^{\text{ex}}/RT$

(b) The values of $\alpha$ and $\beta$ computed using the expressions,

$$\alpha = \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 \ln \gamma_1 \quad \text{and} \quad \beta = \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 \ln \gamma_2$$

and the experimental activity coefficient data are listed in the last two columns in the table on the previous page. Note that the values of $\alpha$ and $\beta$ are not constant, which reflects the fact that the van Laar equations do not fit these data exactly. Some average sort of average values of $\alpha$ and $\beta$ must be chosen in order to provide an overall representation of the data. In considering best values for these constants one should note that the nature of the above relations is such that large uncertainties in values of $\alpha$ are expected when $x_2$ is near zero ($\gamma_1 \cong 1$) and large uncertainties in $\beta$ when $x_1$ is near zero ($\gamma_2 \cong 1$). For this reason I did not use the extremes of the data set for determining $\alpha$ and $\beta$. I examined the results obtained by averaging the individual values of $\alpha$ and $\beta$ over two ranges of the data:

<table>
<thead>
<tr>
<th>#</th>
<th>$x_2$ range</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\beta/\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2-0.8</td>
<td>0.974</td>
<td>1.664</td>
<td>1.71</td>
</tr>
<tr>
<td>2</td>
<td>0.05-0.96</td>
<td>1.031</td>
<td>1.780</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The activity coefficients and Gibbs excesses calculated using both sets are shown in Figs. 6-3 and 6-4. The solid curves are the results obtained using parameter set #1 and the dashed lines with set #2.
(c) I used SigmaPlot to fit the Gibbs excess data directly to the function:
\[
\frac{G^{ex}}{RT} = x_2(1-x_2)\left\{A + B(1-2x_2) + ...\right\}
\]
The results of this fit are displayed in Fig. 6-4. The best fit parameters were \( A = 1.182 \), \( B = 0.273 \). I found no improvement in the fit upon adding a further term, \( C(1-2x_2)^2 \), to the expansion. An alternative method of analyzing the data would have been to fit \( \frac{G^{ex}}{RT}x_2 \) to a line \( a + bx_2 \). The RK parameters would have been related to this linear fit by: 
\[
2/BA + = \quad \text{and} \quad 2/BB - = .
\]
Activity coefficients are obtained from the RK fit using the expressions:
\[
\gamma_1 = \exp\{A + 3B)x_2^2 - 4Bx_2^3\} \quad \text{and} \quad \gamma_2 = \exp\{A - 3B)x_1^2 + 4Bx_1^3\}
\]
A comparison of the observed and calculated activity coefficients is provided in Fig. 6-3.

(d) First, it should be noted that neither function reproduces the data perfectly over the entire composition range. Of these two 2-parameter equations, the Redlich-Kister function appears to provide superior fits to the present set of data.

(e) The molar volumes of ethanol and water are \( V_{\text{EtOH}} = 58.7 \text{ cm}^3 \text{ mol}^{-1} \) and \( V_{\text{H,O}} = 18.1 \text{ cm}^3 \text{ mol}^{-1} \). According to regular solution theory the ratio \( \beta / \alpha = V_{\text{EtOH}} / V_{\text{H,O}} \). The ratio of the estimates of \( \alpha \) and \( \beta \) yield a ratio of 1.7 whereas the volume ratio is 3.2. The regular solution model predicts the right direction for the difference between \( \alpha \) and \( \beta \) but is slightly off on the magnitude.