In this solution set, an underline is used to show the last significant digit of numbers. For instance in

\[ x = 2.51693 \]

the 2, 5, 1, and 6 are all significant. Digits to the right of the underlined digit, the 9 & 3 in the example, are not significant and would be rounded off at the end of calculations. Carrying these extra digits for intermediate values in calculations reduces rounding errors and ensures we get the same answer regardless of the order of arithmetic steps. Numbers without underlines (including final answers) are shown with the proper number of sig figs.

1 Exercise 5.5b pg 201

Given

The vapour pressure of 2-propanol \((M_{w,p} = 60.1 \text{ g/mol})\) is 50.00 kPa at 338.8°C, but it fell to 49.62 kPa when \(m_u = 8.69 \text{ g}\) of an involatile organic compound was dissolved in \(m_p = 250 \text{ g}\) of 2-propanol.

In terms of given variables, this is written:

\[ M_{w,p} = 60.1 \text{ g/mol} \]

\[ T = 338.8^\circ C \]

\[ p^*_p = 50.0 \text{ kPa} \quad \text{Pressure of pure 2-propanol solvent} \]

\[ p_p = 49.62 \text{ kPa} \quad \text{Pressure of solution containing unknown} \]

\[ m_u = 8.69 \text{ g} \]

\[ m_p = 250 \text{ g} \]

Find

Calculate the molar mass \(M_{w,u}\) of this unknown compound.

Strategy

We’ll start with Raoult’s Law (eq 5.21 on pg 164) which relates the partial pressure \(p_a\) of a liquid in a solution to its pure vapour pressure \(p^*_a\) by its mole fraction in solution \(\chi_a\).

\[ p_a = \chi_a p^*_a \]

This allows us to calculate the mole fraction of 2-propanol \(\chi_p\) (in the solution with the dissolved unknown) to the solutions vapour pressure \(p_p\) and the vapour pressure of pure 2-propanol \(p^*_p\).

\[ \chi_p = \frac{p_p}{p^*_p} \]
Additionally, we know the solution only contains 2-propanol and the unknown with moles fraction of \( \chi_p \) and \( \chi_u \) respectively, and therefore \( \chi_p + \chi_u = 1 \). Combining this with our expression for \( \chi_p \) gives an expression for \( \chi_u \) in terms of measured pressures.

\[
\chi_u = 1 - \frac{p_p}{p_u^*}
\]

Next, we’ll use the definition of mole fraction to relate \( \chi_u \) to the moles of unknown by

\[
\chi_u = \frac{n_u}{n_u + n_p}
\]

where \( n_u \) and \( n_p \) are the moles of unknown and 2-propanol respectively. This equation can be solved for \( n_u \)

\[
n_u = \frac{\chi_u n_p}{1 - \chi_u}
\]

We also know moles is equal to mass over molecule weight.

\[
n_u = \frac{m_u}{M_{w,u}} \quad \quad \quad n_p = \frac{m_p}{M_{w,p}}
\]

Equating these two expressions for \( n_u \), inserting the expression for \( n_p \), and rearranging for \( M_{w,u} \) gives

\[
M_{w,u} = m_u \frac{1 - \chi_u}{\chi_u \frac{m_p}{M_{w,p}}}
\]

Lastly, we can insert our earlier expression for \( \chi_u \) and simplify the resulting equation to

\[
M_{w,u} = m_u \frac{M_{w,p}}{m_p} \left( \frac{1}{1 - \frac{p_u^*}{p_p}} - 1 \right)
\]

\[
= 8.69 \text{ g/ mol} \times \frac{250 \text{ g}}{50.00 \text{ kPa}} \times \left( \frac{1}{1 - \frac{49.62 \text{ kPa}}{50.00 \text{ kPa}}} - 1 \right)
\]

\[
= 272.79 \text{ g/ mol}
\]

**Solution**

\[
M_{w,u} = 273 \text{ g/ mol}
\]
2 Exercise 5.7b pg 201

Given

The osmotic pressure of an aqueous solution at \( T = 288 \text{ K} \) is \( \Pi = 99.0 \text{ kPa} \).

In terms of given variables, this is written:

\[
T = 288 \text{ K} \\
\Pi = 99.0 \text{ kPa}
\]

Find

Calculate the freezing point \( T_f \) of the solution.

Strategy

In solving this exercise, we’ll use two important equation: the van’t Hoff equation to calculate the concentration of solute from the solutions osmotic pressure, and the equation for freezing point depression in terms of the solute concentration.

The van’t Hoff equation (eq 5.38 on pg 173) gives the osmotic pressure \( \Pi \) in terms of solute concentration \( n_b/V \)

\[
\Pi = \frac{n_b}{V} RT
\]

where \( n_b \) is the moles of solute and \( V \) is the solution volume.

The solution of volume can be found from the moles of water solution \( n_{H_2O} \).

\[
V = n_{H_2O} V_{m,H_2O}
\]

where \( V_{m,H_2O} \) is the molar volume of water which is related to the density of water and its molecular weight

\[
V_{m,H_2O} = \frac{M_{w,H_2O}}{\rho_{H_2O}}
\]

and this can be substituted into our expression for \( V \).

\[
V = n_{H_2O} \frac{M_{w,H_2O}}{\rho_{H_2O}}
\]

Substituting this expression for \( V \) in the van’t Hoff equation and solving for moles of solute \( n_b \) gives

\[
n_b = \frac{\Pi n_{H_2O} M_{w,H_2O}}{RT \rho_{H_2O}}
\]

Next, will use the equation for freezing point depression (eq 5.35 on pg 172)

\[
\Delta T = K_f b
\]
where \( \Delta T \) is the quantity by which the freezing point is decreased, \( b \) is the molality of solute, and \( K_f \) is an empirical constant (\( K_f = 1.86 \text{ K kg mol}^{-1} \) for water as found in Table 5.2).

We know molality is given by moles of solute over mass of solvent.

\[
b = \frac{n_b}{M_{\text{H}_2\text{O}}} = \frac{n_b}{n_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}}} = \frac{\Pi n_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}}}{RT_{\text{H}_2\text{O}}} = \frac{\Pi}{RT_{\text{H}_2\text{O}}}
\]

where in the second equation we’ve calculated the mass of water from the moles of water solvent and in the third expression we’ve used the expression for \( n_b \) calculated earlier.

Inserting this expression for \( b \) into the freezing point depression equation gives

\[
\Delta T = \frac{K_f \Pi}{RT_{\text{H}_2\text{O}}} = \frac{1.86 \text{ K kg mol}^{-1} \times 99.0 \times 10^3 \text{ Pa}}{8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 288 \times 1.000 \times 10^3 \text{ kg m}^3} = 0.076899 \text{ K} = 0.076899 \text{ } ^\circ \text{C} \quad \text{(as we’re only looking at a change, Kelvin and Celsius are the same)}
\]

With \( \Delta T \) we know the the freezing point is given by \( T_f = T_f^* - \Delta T \) where \( T_f^* \) is the original freezing point, which for water is \( T_f^* = 0.000^\circ \text{C} \).

\[
T_f = T_f^* - \Delta T = 0.000^\circ \text{C} - 0.076899 \text{ } ^\circ \text{C} = -0.076899 \text{ } ^\circ \text{C}
\]

**Solution**

\[
T_f = -0.0769^\circ \text{C}
\]
3 Exercise 5.13b pg 201

Given

Predict the ideal solubility of lead \((M_{w,Pb} = 207.2 \text{ g/mol})\) in bismuth \((M_{w,Bi} = 208.98 \text{ g/mol})\) at \(T = 280^\circ C\) given that its melting point is \(T_f = 327^\circ C\) and its enthalpy of fusion is \(5.2 \text{ kJ mol}^{-1}\).

In terms of given variables, this is written:

\[ M_{w,Pb} = 207.2 \text{ g/mol} \]

\[ M_{w,Bi} = 208.98 \text{ g/mol} \]

\[ T = 280^\circ C \]

\[ T_f = 327^\circ C \]

\[ \Delta_{fus}H = 5.2 \text{ kJ mol}^{-1} \]

Find

The ideal solubility of lead.

Strategy

For this problem we’ll use the equation for ideal solubility (eq 5.37 on pg 172)

\[ \ln \chi_B = \frac{\Delta_{fus}H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right) \]

Solving for \(\chi_B\), the solubility of the solute, which is \(\chi_{Pb}\) in this case gives

\[ \chi_{Pb} = \exp \left[ \frac{\Delta_{fus}H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right) \right] \]

We can simply substitute the given values into the expression for \(\chi_{Pb}\) after temperatures have been converted from Celsius to Kelvin.

\[ T = 280^\circ C = 553 \text{ K} \]

\[ T_f = 327^\circ C = 600 \text{ K} \]

\[ \chi_{Pb} = \exp \left[ \frac{5.2 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{600 \text{ K}} - \frac{1}{553 \text{ K}} \right) \right] \]

\[ \chi_{Pb} = 0.9152 \]
This gives the molar fraction solubility of lead in bismuth. Solubility can also be calculated in terms moles of lead \( n_{\text{Bi}} \) that can be dissolved in a kilogram of bismuth. The moles of bismuth in a sample of mass \( m_{\text{Bi}} = 1.000 \times 10^3 \text{ g} \) is given by

\[
 n_{\text{Bi}} = m_{\text{Bi}}/M_{w,\text{Bi}}
\]

The mole fraction of lead \( \chi_{\text{Pb}} \) is related to moles by

\[
 \chi_{\text{Pb}} = \frac{n_{\text{Pb}}}{n_{\text{Pb}} + n_{\text{Bi}}}
\]

and this can be solved for \( n_{\text{Pb}} \) to gets moles of lead in terms of mole fraction of lead and moles of bismuth.

\[
 n_{\text{Pb}} = \frac{\chi_{\text{Pb}} n_{\text{Bi}}}{1 - \chi_{\text{Pb}}}
 = \frac{\chi_{\text{Pb}} m_{\text{Bi}}/M_{w,\text{Bi}}}{1 - \chi_{\text{Pb}}}
 = \frac{0.9152 \times 1.000 \times 10^3 \text{ g}/208.98 \text{ g/mol}}{1 - 0.9152}
 = 51.64 \text{ mol}
\]

We can also calculate the mass of lead that can be dissolved in a kilogram of bismuth.

\[
 m_{\text{Pb}} = n_{\text{Pb}} \times M_{w,\text{Pb}}
 = 51.64 \text{ mol} \times 207.2 \text{ g/mol}
 = 10700 \text{ g}
 = 10.70 \text{ kg}
\]

Lastly, we can calculate the composition in terms of lead mass fraction \( w_a = \frac{m_a}{\sum_i m_i} \).

\[
 w_{\text{Pb}} = \frac{m_{\text{Pb}}}{m_{\text{Bi}} + m_{\text{Pb}}}
 = \frac{10.70 \text{ kg}}{1.000 \text{ kg} + 10.70 \text{ kg}}
 = 0.9145
\]

As you can see, the mass fraction of lead \( w_{\text{Pb}} \) and the mole fraction of lead \( \chi_{\text{Pb}} \) are quite similar in this problem. This is because the components have very similar molecules weights; \( M_{w,\text{Pb}} = 207.2 \text{ g/mol} \) and \( M_{w,\text{Bi}} = 208.98 \text{ g/mol} \).

**Solution**

\[
 \chi_{\text{Pb}} = 0.92
\]

\[
 n_{\text{Pb}} = 52 \text{ mol}
\]
\[ m_{\text{Pb}} = 11 \text{ kg} \]

\[ w_{\text{Pb}} = 0.91 \]
4 Exercise 5.19b pg 202

Given

Calculate the masses of (a) KNO\textsubscript{3} \((M_{w,\text{KNO}\textsubscript{3}} = 101.11 \text{ g/mol})\) and, separately, (b) Ba(NO\textsubscript{3})\textsubscript{2} \((M_{w,\text{Ba(NO}_3)_2} = 261.32 \text{ g/mol})\) to add to a \(b_0 = 0.110 \text{ mol kg}^{-1}\) solution of KNO\textsubscript{3}(aq) containing \(M_{\text{solv}} = 500 \text{ g}\) of solvent to raise its ionic strength to \(I = 1.00\).

In terms of given variables, this is written:

\[
M_{w,\text{KNO}_3} = 101.11 \text{ g/mol}
\]

\[
M_{w,\text{Ba(NO}_3)_2} = 261.32 \text{ g/mol}
\]

\[
b_0 = 0.110 \text{ mol kg}^{-1}
\]

\[
M_{\text{solv}} = 500 = 500 \text{ g} = 0.500 \text{ kg}
\]

\[
I = 1.00
\]

Find

Calculate the masses of . . .

- (a) KNO\textsubscript{3} and
- (b) Ba(NO\textsubscript{3})\textsubscript{2}

to add.

Strategy

We’ll start with the definition of ionic strength (eq 5.76 on pg 196)

\[
I = \frac{1}{2} \sum_i z_i^2 \left( \frac{b}{b^{\oplus}} \right)
\]

For part (a) we have two ions, K\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-}, with charges of \(z = +1\) and \(z = -1\) respectively.

\[
I = \frac{1}{2} \sum_i z_i^2 \left( \frac{b}{b^{\oplus}} \right)
\]

\[
= \frac{1}{2} \left[ (+1)^2 \frac{b_{K^+}}{b^{\oplus}} + (-1)^2 \frac{b_{NO_3^-}}{b^{\oplus}} \right]
\]

\[
= \frac{b}{b^{\oplus}}
\]

with \(b\) as the concentration of KNO\textsubscript{3}; \(b = b_{K^+} = b_{NO_3^-}\).
We can construct an expression for $b$ in terms of the initial concentration $b_0$ and the moles $n$ of KNO$_3$ added to the solution volume $M_{\text{solv}}$.

$$b = b_0 + \frac{n}{M_{\text{solv}}}$$

Additionally, as we’re interested in mass of KNO$_3$ we can replace moles $n$ with mass $m$ using molecular weight $M_{w,KNO_3}$.

$$b = b_0 + \frac{m}{M_{\text{solv}}M_{w,KNO_3}}$$

This can be substituted back into our expression for ionic strength $I$ and the resulting equation can be solved for $m$ (mass of KNO$_3$ to add).

For part (b) we’ll once again begin with the definition of ionic strength and this time we’ll include the ion Ba$^{+2}$ with $z = +2$.

$$I = \frac{1}{2} \left[ (+1)^2 \frac{b_{KNO_3}}{b^{+2}} + (-1)^2 \frac{b_{KNO_3}}{b^{-2}} + (+2)^2 \frac{b_{Ba(NO_3)_2}}{b^{+2}} + (-1)^2 \frac{b_{Ba(NO_3)_2}}{b^{-2}} + \right]$$

where in this equation $b_{KNO_3}$ is the initial (and constant) concentration of potassium nitrate and $b_{Ba(NO_3)_2}$ is the concentration of barium dinitrate created by adding Ba(NO$_3$)$_2$ to the solution.

Similarly to part (a) we’ll construct an expression for $b_{Ba(NO_3)_2}$ in terms of mass of Ba(NO$_3$)$_2$ added $m$.

$$b_{Ba(NO_3)_2} = \frac{m}{M_{\text{solv}}M_{w,Ba(NO_3)_2}}$$

Substituting this into our expression for $I$ and solving for $m$ gives

$$m = \frac{(Ib^{+2} - b_{KNO_3}) M_{\text{solv}}M_{w,KNO_3}}{3}$$

$$= \left( 1.00 \text{mol kg}^{-1} - 0.110 \text{mol kg}^{-1} \right) \times 0.500 \text{kg} \times 261.32 \text{g mol}^{-1}$$

$$= 38.762 \text{g}$$

Solution

- (a) $m = 45.0 \text{g}$
- (b) $m = 38.8 \text{g}$
5  Exercise 5.25b pg 202

Given

Benzene and toluene form nearly ideal solutions. Consider an equimolar solution of benzene and toluene. At 20°C the vapour pressure of pure benzene and pure toluene are 9.9 kPa and 2.9 kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure.

In terms of given variables, this is written:

\[ T = 20^\circ C \]

\[ p_b^* = 9.9 \text{ kPa} \]

\[ p_t^* = 2.9 \text{ kPa} \]

\[ \chi_b = \chi_t = 0.5000 \quad \text{(Equimolar solution)} \]

Find

Calculate . . .

- (a) the pressure when boiling begins
- (b) the composition of each component in the vapour
- (c) the vapour pressure when only a few drops of liquid remain.

Assume that the rate of vaporization is low enough for the temperature to remain constant at 20°C.

Strategy

For part (a) we’ll start with Raoult’s Law (Equation 5.21 pg 164) that relates the partial pressure of the vapour of a liquid in a solution \( p_a \) to the partial pressure of the pure liquid \( p_a^* \) by the mole fraction of the liquid in solution \( \chi_a \).

\[ p_a = \chi_a p_a^* \]

The partial pressures of each component are thereby given as

\[ p_b = \chi_b p_b^* = 0.5000 \times 9.9 \text{ kPa} = 4.950 \text{ kPa} \]

\[ p_t = \chi_t p_t^* = 0.5000 \times 2.9 \text{ kPa} = 1.450 \text{ kPa} \]
The sum of the partial pressures gives the total vapour pressure of the solution \( p \).

\[
p = p_b + p_t = 4.250 \text{kPa} + 1.450 \text{kPa} = 6.700 \text{kPa}
\]

This solution will boil once the external pressure has been lowered to vapour pressure of the solution; i.e. it will boil at 6.4 kPa. This is the answer to part (a).

For part (b) we can calculate the molar composition of the vapour from the partial pressures using equation 5.43 (pg 176) from our text book.

\[
y_a = \frac{p_a}{p}
\]

This gives the mole fraction \( y_a \) of compound \( a \) in the vapour from its partial pressure \( p_a \) and the total solution pressure \( p \). Therefore the mole fractions of vapour are given as

\[
y_b = \frac{p_b}{p} = \frac{4.250 \text{kPa}}{6.700 \text{kPa}} = 0.6334
\]

\[
y_t = \frac{p_t}{p} = \frac{1.450 \text{kPa}}{6.700 \text{kPa}} = 0.2200
\]

As a quick check, the sum of the mole fractions is equal to 1 within the precision of the measurements; 0.6334 + 0.2200 = 0.9999 = 1.00. Also, you could use equation 5.44 (pg 176) from the text book to calculate these quantities as this equation just includes the calculation of the solution pressure that we calculated in part (a).

Lastly, for part (c) we’re asked to calculate the vapour pressure of the solution when only a few drops of solution remain. At this point the majority of both benzene and toluene are in the vapour phase and we can therefore assume the vapour is now equimolar as the solution was originally equimolar.

\[
y_b = y_t = 0.5000
\]

Using equation 5.43 again \( (y_a = p_a/p) \) this implies

\[
p_b/p = p_t/p = 0.5000
\]

and further

\[
2p_b = 2p_t = p
\]

\[
2\chi_b p_b^* = 2\chi_t p_t^* = p
\]

If we combine the last equation \( 2\chi_b p_b^* = 2\chi_t p_t^* \) with \( \chi_b + \chi_t = 1 \) we can create an expression for the mole fraction of benzene remaining in solution.
\[
\chi_b = \frac{1}{\frac{p_b^*}{p_b^*} + 1}
\]

As in part (a) we can use the mole fractions of each liquid to calculate the solution pressure as the sum of partial pressures.

\[
p = p_b + p_t
= \chi_b p_b^* + \chi_t p_t^*
= \chi_b p_b^* + (1 - \chi_b) p_t^*
= p_t^* + (p_b^* - p_t^*) \chi_b
\]

If we substitute in our expression for \(\chi_b\) we can solve for the solution vapour pressure.

\[
p = p_t^* + (p_b^* - p_t^*) \chi_b
= p_t^* + (p_b^* - p_t^*) \frac{1}{\frac{p_b^*}{p_t^*} + 1}
= 2.9 \text{kPa} + (9.9 \text{kPa} - 2.9 \text{kPa}) \frac{1}{\frac{9.9 \text{kPa}}{2.9 \text{kPa}} + 1}
= 4.4859
\]

**Solution**

- (a) 6.4 kPa
- (b) \(y_b = 0.77\) \(y_t = 0.23\)
- (c) 4.5 kPa
6 Exercise 5.27b pg 203

Exercise

Sketch the phase diagram of the system NH$_3$/N$_2$H$_4$ given that the two substances do not form a compound with each other, that NH$_3$ freezes at $T_m$(NH$_3$) = $-78^\circ$C and N$_2$H$_4$ freezes at $T_m$(N$_2$H$_4$) = $+2^\circ$C and that a eutectic is formed when the mole fraction of N$_2$H$_4$ is $\chi_{N_2H_4} = 0.07$ and that the eutectic melts at $T_m$(eutectic) = $-80^\circ$C.

In terms of given variables, this is written:

\[
\begin{align*}
T_m(NH_3) &= -78^\circ C \\
T_m(N_2H_4) &= +2^\circ C \\
\chi_{N_2H_4}(eutectic) &= 0.07 \\
T_m(eutectic) &= -80^\circ C
\end{align*}
\]

Strategy

For each component, we can use its pure melting/freezing temperature to determine one point on the coexistence curve between the phase where this component partially precipitates out of liquid (Liquid + X phase) and the phase where both liquids are completely miscible (Liquid phase). Additionally, the eutectic point falls on each coexistence curve and the rest of each coexistence curve can be estimated. The eutectic melting temperature also serves as the coexistence line between the solid phase and liquid phases. As an example of such a phase diagram showing similar information see Figure 5.51 on page 186 of the text book. The solution for this problem is shown on the next page.

It also worth mentioning the significance of the eutectic point. This is the moles fraction composition where both compounds are always well mixed; neither will ever precipitate out of solution regardless of temperature.

Although not requested, we have also included an example of determining the phase composition of a sample with $\chi_{N_2H_4} = 0.60$ and $T = -40^\circ$C. This point is shown as the blue open circle on the plot. At this temperature, tie lines are constructed between the sample point and the phase boundaries; the homogenous liquid mixture on the left and the pure solid N$_2$H$_4$ on the right. The endpoints of each tie line correspond to $\chi_{N_2H_4} = 0.34$ and $\chi_{N_2H_4} = 1.00$.

We can now use the lever rule (equation 5.46 on pg 178) to determine the phase composition of this sample.

\[
n_\alpha l_\alpha = n_\beta l_\beta
\]

where $n_\alpha$ denotes the moles of the $\alpha$-th phase and $l_\alpha$ is the length of the tie line between the $\alpha$-th phase and the sample point. For our sample we'll use this equation in the following form.

\[
n_{\text{liquid}} l_{\text{liquid}} = n_{N_2H_4(\text{solid})} l_{N_2H_4(\text{solid})}
\]

where $n_{\text{liquid}}$ and $n_{N_2H_4(\text{solid})}$ are the moles of the homogenous liquid mixture and the moles of the precipitated solid N$_2$H$_4$ respectively. The $l_{\text{liquid}}$ and $l_{N_2H_4(\text{solid})}$ similarly correspond to the tie line lengths of each phase.

The length of the each tie line is calculated as

\[
l_{\text{liquid}} = 0.60 - 0.34 = 0.26
\]

\[
l_{N_2H_4(\text{solid})} = 1.00 - 0.60 = 0.40
\]

Now we'll use the lever rule equation to solve for the mole fraction of the liquid phase $\chi_{\text{liquid}}$. 


\[ n_{\text{N}_2\text{H}_4(\text{solid})} = \frac{n_{\text{liquid}}}{n_{\text{N}_2\text{H}_4(\text{solid})}} \]

\[ \chi_{\text{liquid}} = \frac{n_{\text{liquid}}}{n_{\text{liquid}} + n_{\text{N}_2\text{H}_4(\text{solid})}} = \frac{n_{\text{liquid}}}{1.000 + \frac{n_{\text{liquid}}}{n_{\text{N}_2\text{H}_4(\text{solid})}}} \]

\[ = \frac{1.000}{1.000 + \frac{0.26}{0.40}} = 0.6061 \]

Therefore we’ve found that 61% of the sample will be in the mixed liquid phase with the remaining 39% in the precipitated solid \( \text{N}_2\text{H}_4 \) phase.

![Figure 1: Phase diagram of \( \text{NH}_3/\text{N}_2\text{H}_4 \) system](image-url)