Exercises 7.4(b): The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 cm$^3$/mole and 176.14 cm$^3$/mole, respectively. The molar masses of A and B are 241.1 g/mol and 198.2 g/mol.

What is the volume of a solution of mass 1.000 kg?

\[ V = V(n_a,n_b) \\
\]
\[ dV = (?V/?n_a)_{nb}dn_a + (?V/?n_b)_{na}dn_b \\
\]
where \( (?V/?n_a)_{nb} \) & \( (?V/?n_b)_{na} \) are the partial molar volumes \( V_a \) & \( V_b \).

\[ dV = V_adn_a + V_bdn_b \quad \text{Integrates to:} \quad V = V_an_a + V_bn_b \]

where the mole fractions are \( x_a = n_a/n \), \( x_b = n_b/n \) and \( n \) is total moles.

1000 g = (241.1 g/mol* 0.3713 + 198.2 g/mol*0.6287) mole

Solve for \( n = 1000 g / (241.1 g/mol* 0.3713 + 198.2 g/mol*0.6287) \) = 4.671 mole

Solve for \( V = (188.2 ml/mol* 0.3713 + 176.14ml/mol*0.6287)*4.671 \) mole = 843.67 ml

Exercises 7.6(b): At 310 K the partial vapor pressure of a substance B dissolved in a liquid A as follows:

<table>
<thead>
<tr>
<th>( x_B )</th>
<th>0.010</th>
<th>0.015</th>
<th>0.020</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_B/\text{kPa} )</td>
<td>82.0</td>
<td>122.0</td>
<td>166.1</td>
</tr>
</tbody>
</table>

Show that the solution obeys Henry’s law in this range of mole fractions, and calculate Henry’s law constant at 310 K.

\[
\begin{align*}
\text{Henry’s Law Plot} \\
\text{Vapor Pressure (kPa)} & \quad \text{Mole Fraction} \\
\text{y} & = 8234.5x \\
R^2 & = 0.9997 \\
\end{align*}
\]

\( p_B = K_Bx_B \)

The Henry’s law constant \( K_B = 8234.5 \) kPa at 310 K.

Exercises 7.7(b): Predict the partial vapor pressure of component B above its solution in A when the molality of B is 0.25 mol/kg. The molar mass of A is 74.1 g/mol
Convert 0.25 mol/kg to mole fraction.

1000 g A • (mol/74.1 g) = 13.5 mole
mole fraction A = 0.25 mo/(13.5 mol + 0.25 mol) = 0.0182
This is within the range of our graph.

\[ p_B = K_B x_B = 8234.5 \text{ kPa} \times 0.0182 = 149.8 \text{ kPa} \]

Exercises 7.11(b): The osmotic pressure of an aqueous solution at 288 K is 99 kPa. Calculate the freezing point of the solution.

\[ \Pi = [x]RT \]
\[ [x] = 99 \text{ kPa}/8.314 \text{ J/mole-K} \times 288 \text{ K} \]
\[ = 0.041 \text{ kPa} (1000 \text{ Pa/kPa})(J/m^3/Pa)(mole-K/J)(1/K)(1 \text{ m}^3/1000 \text{ L}) \]
\[ = 0.041 \text{ M} \]
\[ 0.048 \text{ mole/L} \times (1 \text{ L}/1000 \text{ g}) = 0.048 \text{ mole/kg} \]
\[ \Delta T = K_f(b) = 1.86 \text{ K/mol/kg} \times 0.041 \text{ mol/kg} = -0.077 \text{ K} \]

Exercises 7.13(a): Air is a mixture with a composition given in Self-test 1.5. Calculate the entropy of mixing when it is prepared from pure and perfect gases.
EXCEL is useful for this calculation.

\[ \Delta S_{\text{mix}} = -n_{\text{tot}} R \sum x_i \ln(x_i) \]

<table>
<thead>
<tr>
<th>Component</th>
<th>% mass</th>
<th>mole/kg</th>
<th>mole frac.</th>
<th>x_iLN(x_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>7.553E+01</td>
<td>2.698E+01</td>
<td>7.810E-01</td>
<td>-1.931E-01</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.314E+01</td>
<td>7.231E+00</td>
<td>2.094E-01</td>
<td>-3.274E-01</td>
</tr>
<tr>
<td>Argon</td>
<td>1.280E+00</td>
<td>3.200E-01</td>
<td>9.265E-03</td>
<td>-4.337E-02</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>4.700E-02</td>
<td>1.068E-02</td>
<td>3.093E-04</td>
<td>-2.499E-03</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.000E-04</td>
<td>1.000E-03</td>
<td>2.895E-05</td>
<td>-3.025E-04</td>
</tr>
<tr>
<td>Neon</td>
<td>1.300E-03</td>
<td>6.500E-04</td>
<td>1.882E-05</td>
<td>-2.048E-04</td>
</tr>
<tr>
<td>Helium</td>
<td>7.200E-05</td>
<td>1.800E-04</td>
<td>5.211E-06</td>
<td>-6.339E-05</td>
</tr>
<tr>
<td>Methane</td>
<td>1.100E-04</td>
<td>6.875E-05</td>
<td>1.990E-06</td>
<td>-2.613E-05</td>
</tr>
<tr>
<td>Krypton</td>
<td>3.20E-04</td>
<td>3.810E-05</td>
<td>1.103E-06</td>
<td>-1.513E-05</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>1.700E-06</td>
<td>5.667E-07</td>
<td>1.641E-08</td>
<td>-2.941E-07</td>
</tr>
<tr>
<td>Xenon</td>
<td>1.200E-05</td>
<td>9.160E-07</td>
<td>2.652E-08</td>
<td>-4.627E-07</td>
</tr>
<tr>
<td>Ozone</td>
<td>1.200E-05</td>
<td>2.500E-06</td>
<td>7.238E-08</td>
<td>-1.190E-06</td>
</tr>
<tr>
<td>Total</td>
<td>1.000E+02</td>
<td>3.454E+01</td>
<td>1.000E+00</td>
<td></td>
</tr>
</tbody>
</table>

Entropy Of Mixing
all
\[ 4.713E+00 \text{ J/K-mol} \]

\[ 3.454E+01 \text{ Entropy of mixing 1, 2, 3, 4} \]
\[ 4.708E+00 \text{ J/K-mol} \]

Problem 7.2: The volume of an aqueous solution of NaCl at 25 °C was measured at a series of molalities \( b \) and it was found that the volume fit the expression
\[ V/cm^3 = 1003 + 16.62b + 1.77b^{3/2} + 0.12b^2 \]

where \( V \) is the volume of a solution formed from 1.000 kg of water and \( b \) is understood to as \( b/b° \).

Calculate the partial molar volume of the components in a solution of molality 0.100 mol/kg.

\[ V_i = (\frac{?\text{V/}\eta_i}{\eta_i}) \]

\[ V_{\text{NaCl}} = (\frac{?\text{V/}\eta_{\text{NaCl}}}{\eta_{\text{NaCl}}}) = 16.62 + 2.655b^{1/2} + 0.24b \]

\[ V = 1004.683 \text{ cm}^3 = n_{\text{H}_2\text{O}} + n_{\text{NaCl}}V_{\text{NaCl}} \]

\[ n_{\text{H}_2\text{O}} = 1000 \text{ g}/18 = 55.56 \text{ mole} \]

\[ V = 1004.683 \text{ cm}^3 = n_{\text{H}_2\text{O}} + n_{\text{NaCl}}V_{\text{NaCl}} \]

\[ n_{\text{H}_2\text{O}} = \frac{1004.683 \text{ cm}^3}{55.56 \text{ mole}} = 18.051 \text{ cm}^3/\text{mol} \]

Problem 7.18: The table below lists the vapor pressures of mixtures of iodoethane (I) and ethyl acetate (A) at 50 °C. Find the activity coefficients of both components on (a) the Raoult’s Law basis and (b) the Henry’s Law basis with I as solute.

\[
\begin{array}{cccccc}
 x_I & 0 & 0.0579 & 0.1095 & 0.1918 & 0.2353 \\
p_I/\text{torr} & 0 & 20.0 & 52.7 & 87.7 & 105.4 \\
p_A/\text{torr} & 280.4 & 266.1 & 252.3 & 231.4 & 220.9 \\
 x_I & 0.3718 & 0.5478 & 0.6349 & 0.8253 & 0.9093 \\
p_I/\text{torr} & 155.4 & 213.3 & 239.1 & 296.9 & 322.5 \\
p_A/\text{torr} & 187.9 & 144.2 & 122.9 & 66.6 & 38.2 \\
\end{array}
\]

Raoult’s Law: \( a_i = p_i/p_i^* \) & \( \gamma_i = a_i/x_i \)

Henry’s Law: \( a_i = p_i/K \) & \( \gamma_i = a_i/x_i \)

Problem 7.16: The excess Gibbs energy of solutions of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 303.15 K were found to fit the expression:

\[ G^e = RTx(1-x)[0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2] \]

where \( x \) is the mole fraction of
MCH. Calculate the Gibbs energy of mixing when a mixture of 1.0 mole MCH and 3.0 mole of THF is prepared.

\[ \Delta G_{\text{mix}} = \Delta G_{\text{mix}}^E + \Delta G_{\text{ideal-mix}} \]

\[ x = 1/(1+3) = 0.25 \]

\[ \Delta G_{\text{mix}}^E = RT(0.25)(0.75)[0.4857 - 0.1077(-0.5) + 0.0191(-0.5)^2] \]

\[ \Delta G_{\text{mix}}^E = 8.314 \text{ J/mol-K} \times 303.15 \text{ K} \times 0.102 = 0.257 \text{ kJ/mol} \]

\[ \Delta G_{\text{ideal-mix}} = RT(x \ln(x) + (1-x) \ln(1-x)) \]

\[ \Delta G_{\text{ideal-mix}} = 8.314 \text{ J/mol-K} \times 303.15 \text{ K} \times (0.25 \ln(0.25) + 0.75 \ln(0.75)) = -1.417 \text{ kJ/mol} \]

\[ \Delta G_{\text{mix}} = 0.257 \text{ kJ/mol} - 1.417 \text{ kJ/mol} = -1.160 \text{ kJ/mol} \]

Problem 7.23: Suppose that two equal volumes of 0.200 M NaCl(aq) are separated by a membrane and that an anionic protein P of mass 55 kg/mol, which cannot pass through the membrane, is added as its sodium salt Na\textsubscript{6}P to a concentration of 50 g/L to the left hand compartment of the apparatus. Calculate the molar concentrations of Na\textsuperscript{+} and Cl\textsuperscript{-} in each compartment.

The ions will diffuse through the membrane until the chemical potentials are equal on both sides of the membrane.

\[ \mu_{\text{NaCl L}} = \mu_{\text{NaCl}}^* + RT \ln(x_{\text{NaCl L}}) = \mu_{\text{NaCl R}} = \mu_{\text{NaCl}}^* + RT \ln(x_{\text{NaCl R}}) \]

Simplifies to: \[ x_{\text{NaCl L}} = x_{\text{NaCl R}} \]

Therefore \([\text{NaCl}]_L = [\text{NaCl}]_R\) which is \([\text{Na}][\text{Cl}]_L = [\text{Na}][\text{Cl}]_R\) due to equilibrium.

Maintaining Electrical Neutrality Requires that

\[ [\text{Na}]_L = [\text{Cl}]_L + 6[P] \quad [\text{Na}]_R = [\text{Cl}]_R \]

Assume a 1 L total volume for each chamber

\[ P = 50 \text{ g/L} / 55,000 \text{ g/mol} = 9.09 \times 10^{-4} \text{ mol} \]

\[ \text{Na}_\text{Tot} = [\text{Na}]_L^*1L + [\text{Na}]_R^*1L = 0.4 + 6 \times 9.09 \times 10^{-4} = 0.4055 \text{ mol} \]

\[ \text{Cl}_\text{Tot} = \text{Cl}_L + \text{Cl}_R = 0.4 \text{ mol} \]

Therefore \[ \text{Na}_L Cl_L = \text{Na}_R Cl_R \]

\[ \text{Na}_L (\text{Na}_L - 6P) = \text{Na}_R \text{Na}_R \]

\[ \text{Na}_L^2 - 6P \text{Na}_L = \text{Na}_R^2 = (0.4055 - \text{Na}_L)^2 \]

\[ \text{Na}_L^2 - 6P \text{Na}_L = 0.1644 - 0.8110 \text{Na}_L + \text{Na}_L^2 \]

\[-0.1644 = (-0.8110 + 0.0055) \text{Na}_L \]

Convert from moles to M by using the 1 L volumes.

\[ [\text{Na}]_L = 0.2041 \]

\[ [\text{Cl}]_L = 0.1959 \]

\[ [\text{Na}]_R = 0.2014 \]

\[ [\text{Cl}]_R = 0.2014 \]

Problem 7.25: K. Sato, F.R. Eirich and J.E. Mark (J. Polymer Sci., Polymer Phys. 14, 619, 1976) have reported the data below for the osmotic pressure of polychlorprene
(ρ = 1.25 g/cm³) in toluene (ρ = 0.858 g/cm³) at 30 °C. Determine the molar mass of polychlorpene and its second osmotic virial coefficient.

c(mg/cm³ or g/L) 1.33 2.10 4.52 7.18 9.87
Π(N/m²) 30 50 132 246 390

Graph Π/c vs. c

\[ \Pi = [C]RT(1 + B[C]) \] where \([C]\) is concentration in mol/L \[ [C] = \frac{c(g/L)}{M(g/mol)} \]

\[ \Pi/c = \frac{RT}{M} + cBRT/M^2 \]

\[ 19.857 = \frac{RT}{M} \]

\[ M = \frac{RT}{19.857(Pa-L/g)} \]

\[ = \frac{0.08205 \ (L-atm/K-mol) \times 101,325 \ Pa/atm \times 303 \ K}{19.857(Pa-L/g)} \]

\[ = 1.269 \times 10^5 \ g/mol \]

\[ 2.0023 = BRT/M^2 \]

\[ B = \frac{2.0023M^2}{RT} \]

\[ = \frac{2.0023(Pa-L/g)(1.269 \times 10^5 \ g/mol)^2}{[0.08205 \ (L-atm/K-mol) \times 101,325 \ Pa/atm \times 303 \ K]} \]

\[ = 1.28 \times 10^4 \ g^2/L-mol \]