1.    a) According to the phase rule, what is the maximum number of phases that can exist in one-, two- and three-component systems?

b) For certain systems, especially those involving solids, the maximum number of phases that can exist is larger than the number predicted by the phase rule. Why?

2.    a) Methanol and ethanol form very nearly ideal liquid solutions. Why?

b) At 20 °C, the vapor pressures of methanol and ethanol are 11.93 kPa and 5.93 kPa, respectively. For a liquid solution prepared by mixing 0.270 mol methanol(1) and 0.552 mol ethanol(2), calculate the total vapor pressure $p$ and the vapor composition $y_1$ at 20 °C.

3.    a) If two liquids are completely immiscible, the two-phase liquid mixture will boil when the pressure is $p = p_1^* + p_2^*$. Show that the vapor mole fraction of component 1 under these conditions is $y_1 = p_1^*/(p_1^* + p_2^*)$.

b) The boiling point of the immiscible system naphthalene(1) + water(2) is 98 °C at a pressure of 97.7 kPa. The vapor pressure of pure water at this temperature is 94.3 kPa. Calculate the mole fraction of naphthalene in the vapor during the steam distillation of naphthalene at 98 °C.

4.    The osmotic pressure of an unknown substance is measured at 298 K. Determine the molecular weight of the substance if its concentration is 31.2 grams per liter of solution and the osmotic pressure is 53.0 kPa. The density of the solution is 0.997 $g \; cm^{-3}$.

5.    68.4 g sodium chloride (58.44 $g \; mol^{-1}$) is dissolved in 750.0 g water. What is the freezing point of the solution? What is the vapor pressure of the solution at 20 °C?

Data: $K_f = 1.86 \; K \; kg \; mol^{-1}$. The vapor pressure of water is 2.3149 kPa at 20 °C..

6.    The following data have been obtained for isopropanol(1) + n-decane(2) mixtures at 25 °C.

| $p$/Torr | $x_2$ | $y_2$ |
|---|---|---|
| 942.6 | 0.1312 | 0.0243 |
| 868.4 | 0.3360 | 0.0362 |
| 758.7 | 0.6036 | 0.0489 |

a) Use Raoult's law to calculate the activity coefficients of isopropanol(1) and n-decane(2) at each composition. The vapor pressures of the pure components are $p_1^* = 1008$ Torr and $p_2^* = 48.3$ Torr at 25 °C.

b) Do isopropanol + n-decane mixtures show negative deviations from Raoult's law? Explain.

**7.** Use the boiling point diagram for ethanol + ethyl acetate below to answer this question.

**a)** Which is the more volatile component?

**b)** A liquid ethanol(1) + ethyl acetate(2) mixture of composition $x_1 = 0.100$ initially at 25 °C is heated at 1.013 bar. Give the temperature at which the liquid starts to boil and the composition $y_1$ of the first vapor. Show that the vapor is richer than the liquid in the *less* volatile component. Why is this unusual?

**c)** Give the azeotrope temperature and composition. Why is it unnecessary to specify $x_1$ or $y_1$ for the azeotrope composition?

**d)** If a liquid ethanol(1) + ethyl acetate(2) mixture of composition $x_1 = 0.100$ is distilled at 1.013 bar, what is the maximum possible mole fraction of ethanol in the distillate?

**e)** If a liquid ethanol(1) + ethyl acetate(2) mixture of composition $x_2 = 0.100$ is distilled at 1.013 bar, what is the maximum possible mole fraction of ethyl acetate in the distillate?



ethanol(1) + ethyl acetate(2) at 1.013 bar

c) azeotrope at 71.6 °C $x_1 = y_1 = 0.46$

$x_1, y_1 \text{ or } Z_1$
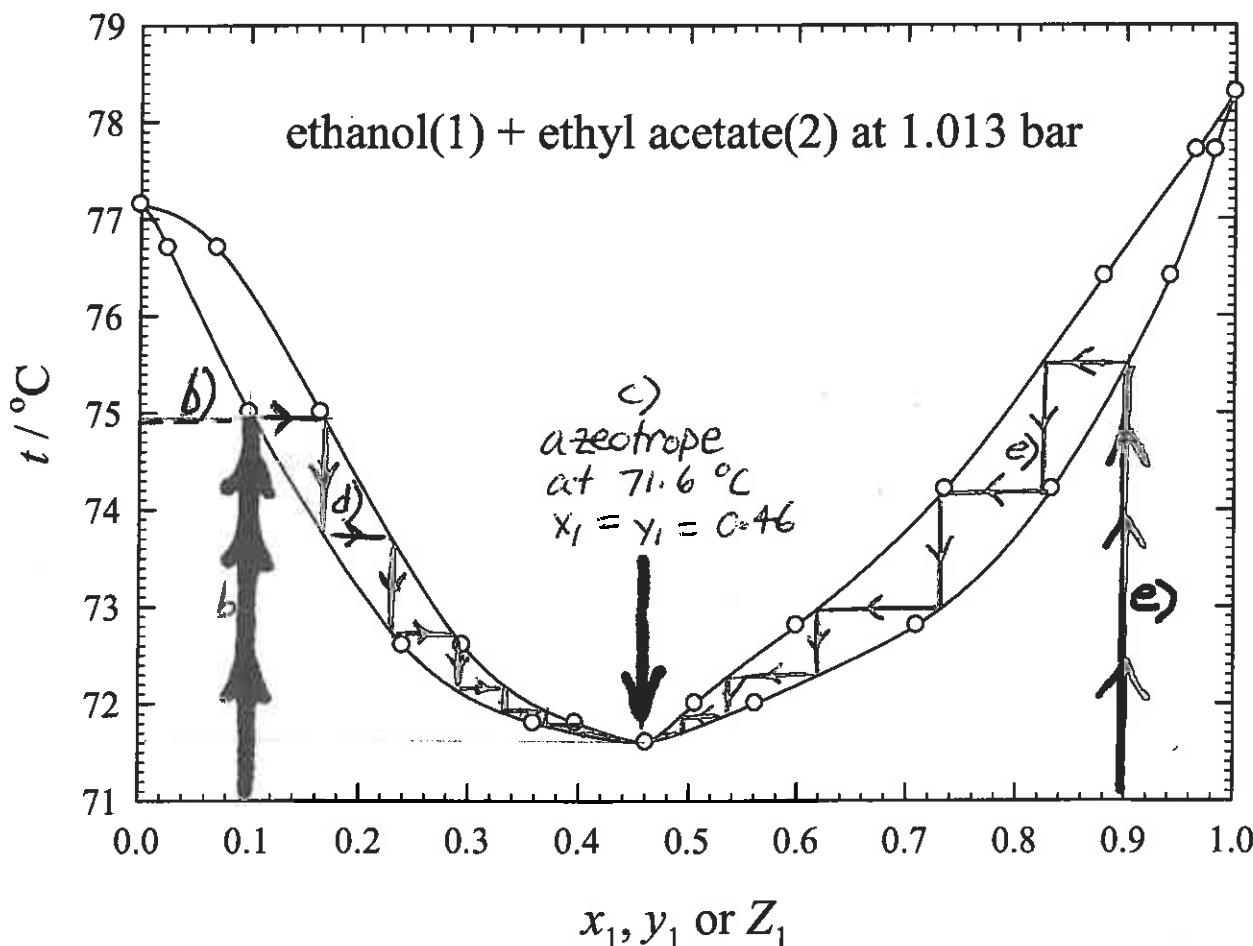
**8.** The expression for the freezing point depression $\Delta T = T^* - T$ of component 1 derived in class

$$-RT\ln x_1 = \Delta H_{\text{fusion, m(1)}} \frac{T^* - T}{T}$$

can be rearranged to give

$$\ln x_1 = -\frac{\Delta H_{\text{fusion, m(1)}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

where $\Delta H_{\text{fusion,m(1)}}$ is the enthalpy of fusion of component 1.

a) The equation for $\ln x_1$ does not contain any parameters for the solute (component 2). Why?

b) Remarkably, the equation for $\ln x_1$ can be used to show that the solubility of component 1 is the same in all solvents that form ideal solutions! For example, calculate the solubility of naphthalene(1) in any ideal solution at 25 °C. The melting point of naphthalene is 80 °C and the enthalpy of fusion is 19.29 kJ mol$^{-1}$. (The measured solubility of naphthalene in benzene at 25 °C is $x_1 = 0.296$.)

Chemistry 232     Tutorial #1

(1)  a)  $F = C + 2 - P$

maximum number of phases when $F = 0$ (invariant)

$$\max P = C + 2$$

for $C = 1, 2, 3$
maximum $F$ is $3, 4, 5$

b) $F = C + 2 - P$ is derived for equilibrium systems, does not apply to systems with nonequilibrium phases

diamond, for example, is not at equilibrium at $25°$, 1 bar, but is stable indefinitely due to the very slow rate of conversion of diamond to graphite

many other "metastable" solid phases exist

(2) a) $CH_3OH$ and $CH_3CH_2OH$ have similar polarities, functional groups, and molecular sizes $\rightarrow$ ≈ ideal solutions

b) for the liquid, $x_1 = \dfrac{n_1}{n_1 + n_2} = \dfrac{0.270}{0.270 + 0.552} = 0.3285$

$$P_1 = x_1 P_1^* = 0.3285\,(11.93\ kPa) = 3.919\ kPa$$

$$P_2 = x_2 P_2^* = (1 - x_1)P_2^* = 0.6715\,(5.93\ kPa) = 3.982\ kPa$$

total vapor pressure $p = P_1 + P_2 = 7.90\ kPa$

mole fraction
methanol in vapor
$(y_1 > x_1)$
$$y_1 = \left(\dfrac{n_1}{n_1 + n_2}\right)_{vap} = \dfrac{P_1}{P} = 0.496$$
(vapor richer in more-volatile $CH_3OH$)

(3)
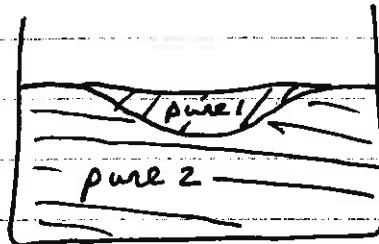


total pressure $p$

vapor pressure of pure liquid 1 = $p_1^*$
" " " " liquid 2 = $p_2^*$

a) $y_1$ = mole fraction of component 1 in the vapor phase

$$= \frac{p_1}{p_1 + p_2} = \frac{p_1}{p} \quad (\text{why?} \quad p_i \text{ proportional to } n_{igas})$$

$$= \frac{p_1^*}{p_1^* + p_2} \quad \text{in this case where both liquids are pure}$$

b) $\quad p = 97.7 \ kPa \quad (\text{total pressure})$
$\quad p_1^* = 94.3 \ kPa$

water (1)
+
naphthalene (2)

$$y_1 = \frac{94.3}{97.7} = \frac{p_1^*}{p} = 0.9652 \qquad y_2 = 1 - y_1 = 0.0348$$
$$(\text{naphthalene mole fraction})$$

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(4) $\quad$ unknown compound = component 2

osmotic pressure $\quad \pi = \frac{n_2}{V} RT$

$T = 298 \ K$
$V = 1.00 \ L = 10^{-3} \ m^3$
$\pi = 53000 \ Pa$
mass of component 2 = 31.2 g

$$n_2 = \frac{\pi V}{RT}$$

$$= \frac{(53000 \ Pa)(10^{-3} \ m^3)}{(8.314 \ J \ K^{-1} mol^{-1})(298 \ K)} = 0.02139 \ mol$$

$$M_2 = \frac{31.2 \ g}{0.02139 \ mol} = 1458 \ g \ mol^{-1}$$

(5)  1 = water        2 = NaCl

a) $\Delta T$ = freezing point depression $= T^* - T$
$$= K_f\, 2m_2$$

why $2m_2$ ?
$NaCl \rightarrow Na^+ + Cl^-$
2 moles of solute ions per mole of dissolved NaCl

$K_f = 1.86\ K\ kg\ mol^{-1}$

$$m_2 = \frac{\text{moles NaCl}}{\text{kg water}} = \frac{(68.4\ g)/(58.44\ g\ mol^{-1})}{0.750\ kg}$$

$$m_2 = 1.560\ mol\ kg^{-1}$$

$$\Delta T = K_f\, 2m_2 = \left(1.86\ K\ kg\ mol^{-1}\right) 2\left(1.560\ mol\ kg^{-1}\right) = 5.80\ K$$

b) vapor pressure of the solution at 20 °C

important: $Na^+$ and $Cl^-$ ions are not volatile

$$Na^+(aq) \rightarrow Na^+(g)$$
$$Cl^-(aq) \rightarrow Cl^-(g)$$
negligible at 25 °C
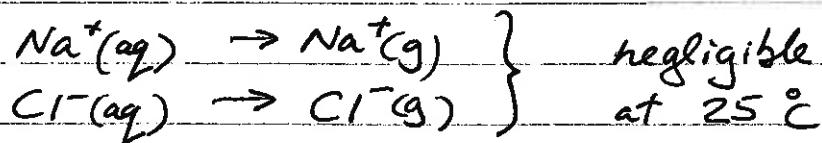
$Na^+(g)$ and $Cl^-(g)$ are "high" energy species found in plasmas

vapor pressure of a water(1) + NaCl(2) solution is entirely due to water (volatile)

assume Raoult's law (no activity coefficient data provided):
$$P_1 = x_1 P_1^*$$

$$P_1 = \frac{n_1}{n_1 + 2n_2}\ P_1^* = \frac{\dfrac{750.0\ g}{18.015\ g\ mol^{-1}}}{\dfrac{750}{18.015} + 2\dfrac{68.4}{58.44}}\ 2.3149\ kPa = 2.192\ kPa$$

each mole of NaCl
→ two moles of ions

(6) isopropanol (1) + decane (2) liquid $\rightleftharpoons$ vapor
equilibrium at 25 °C

pure isopropanol, vapor pressure $P_1^* = 1008$ Torr
pure decane, vapor pressure $P_2^* = 48.3$ Torr

a) Raoult's law activity coefficients       ($p$ = total pressure
                                                  $= P_1 + P_2$)

$$\gamma_1 = \frac{P_1}{x_1 P_1^*} = \frac{y_1 P}{x_1 P_1^*} = \frac{(1-y_2) P}{(1-x_2) P_1^*}$$

$$\gamma_2 = \frac{P_2}{x_2 P_2^*} = \frac{y_2 P}{x_2 P_2^*}$$

$\underline{P = 942.6 \text{ Torr} \qquad x_2 = 0.1312 \qquad y_2 = 0.0243}$

$$\gamma_1 = \frac{1 - 0.0243}{1 - 0.1312} \frac{942.6}{1008} = 1.050$$

$$\gamma_2 = \frac{0.0243}{0.1312} \frac{942.6}{48.3} = 3.614$$

$\underline{P = 868.4 \text{ Torr} \qquad x_2 = 0.3360 \qquad y_2 = 0.0362}$

$$\gamma_1 = \frac{1-0.0362}{1-0.3360} \frac{868.4}{1008} = 1.250 \qquad \gamma_2 = \frac{0.0362}{0.3360} \frac{868.4}{48.3} = 1.937$$

$\underline{P = 758.7 \text{ Torr} \qquad x_2 = 0.6036 \qquad y_2 = 0.0489}$

$$\gamma_1 = \frac{1-0.0489}{1-0.6036} \frac{758.7}{1008} = 1.806 \qquad \gamma_2 = \frac{0.0489}{0.6036} \frac{758.7}{48.3} = 1.272$$

b)    positive deviations from Raoult's law
$$P_1 > x_1 P_1^* \implies \gamma_1 > 1$$
$$P_2 > x_2 P_2^* \implies \gamma_2 > 1$$

ethanol (1) + ethyl acetate (2)

(7) a) pure ethanol b.p. ($x_1 = 1$)  78.4 °C
pure ethyl acetate b.p. ($x_1 = 0$)  77.2 °C

ethyl acetate is more volatile because it boils at a lower temp.

b) heat a one-phase liquid mixture with $x_1 = 0.100$

read from graph (lines shown): boiling at 74.9 °C
$y_1 = 0.17$
$\overset{0.17}{\swarrow} \quad \overset{0.100}{\swarrow}$
$y_1 > x_1$  vapor richer in methanol, the less-volatile
component

for ideal, or moderately nonideal, systems, the
vapor is usually richer in the more volatile component

c) azeotrope at 0.46 mole fraction ethanol
and 71.6 °C   (see graph)

d) vaporize a liquid of composition $x_1 = 0.100$,
get vapor of composition 0.17, condenses to
liquid of composition 0.17, vaporizes to give
vapor of composition 0.230, etc.   (see graph)

reach azeotrope composition at $x_1 = y_1 = 0.46$
no further change in composition because
vapor composition = liquid composition

e) vaporize liquid of composition $x_1 = 0.900$  ($x_2 = 0.100$),
get vapor $y_1 = 0.82$, liquid 0.72, ...
to azeotrope at $x_1 = y_1 = 0.46$   (see graph)

⑧  a) freezing point depression is a colligative property, independent of the nature of solute ions or molecules dissolved in liquid naphthalene, only dependent on the number of dissolved ions or molecules, which gives $x_1$

for example, naphthalene should have the same solubility (assuming ideal solutions) in benzene, toluene, cyclohexane, ...

b)    naphthalene (1)  +  solvent (2)

at 80°C (melting point of naphthalene), pure liquid naphthalene exists, $x_1 = 1.00$   (100% solubility)

at  25°C :                               $T^* = 353.15K$   (80°C)
                                          $T = 298.15K$      (25°C)

$$\ln x_1 = - \frac{\Delta H_{fus,m,1}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

$$= - \frac{19290 \, J \, mol^{-1}}{8.314 \, J \, K^{-1} mol^{-1}} \left( \frac{1}{298.15K} - \frac{1}{353.15K} \right)$$

$$= -1.212$$

$$x_1 = e^{-1.212} = 0.298$$

naphthalene solubility
(mole fraction)

( measure $x_1 = 0.296$
  in benzene
  WOW!
  (good agreement) )