

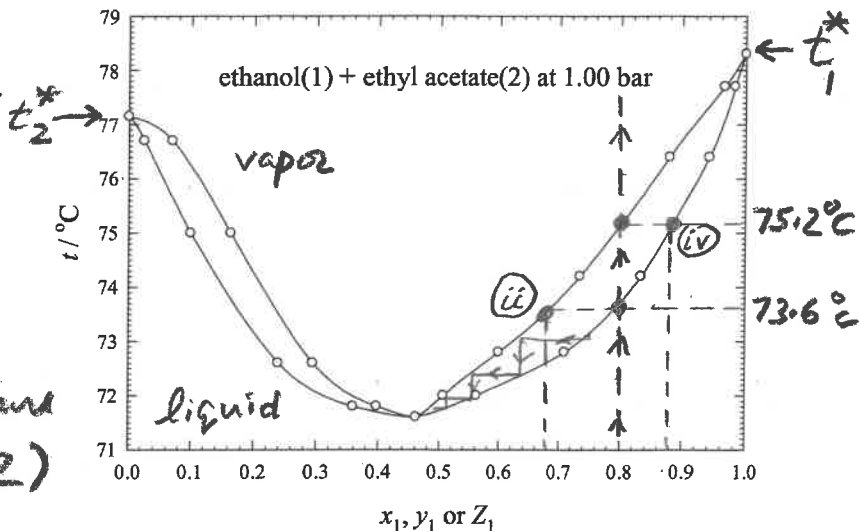
- please answer all 5 questions in the spaces provided
- this is a two-hour test
- a calculator and the equation sheet provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

Q1. Use the liquid-vapor phase diagram given below to answer this question.

a) Is ethanol more volatile than ethyl acetate? Justify your answer.

No
 $t_1^* = 78.4^\circ\text{C}$
 $t_2^* = 77.2^\circ\text{C}$
 ethanol (1) boils at a higher temperature than ethyl acetate (2)



b) A liquid solution consisting of 0.400 mole ethanol(1) and 0.100 mole ethyl acetate(2) initially at 25 °C and 1.00 bar is heated at constant pressure. Give:

i) the temperature at which first vapor forms

73.6 °C

ii) the mole fraction of ethanol in the first vapor

$y_1 = 0.68$ (ii on graph)

iii) the temperature at which the last liquid disappears

75.2 °C

iv) the mole fraction of ethanol in the last liquid

$x_1 = 0.88$ (iv on graph)

c) Given a liquid ethanol(1) + ethyl acetate(2) solution of composition $x_1 = 0.750$, can pure ethanol be obtained by fractional distillation of this solution? Explain briefly.

No. Azeotrope ($x_1 = y_1 = 0.46$) is produced by fractional distillation.

Q2. Use the phase diagram given below to answer this question.

a) Give the number of degrees of freedom in region A.

$$C = 2$$

$$P = 2 \text{ (l + solid naphth.)}$$

$$F = C + 2 - P - 1$$

$$= 2 + 2 - 2 - 1$$

$$F = 1$$

b) Give the number of degrees of freedom in region B.

$$C = 2$$

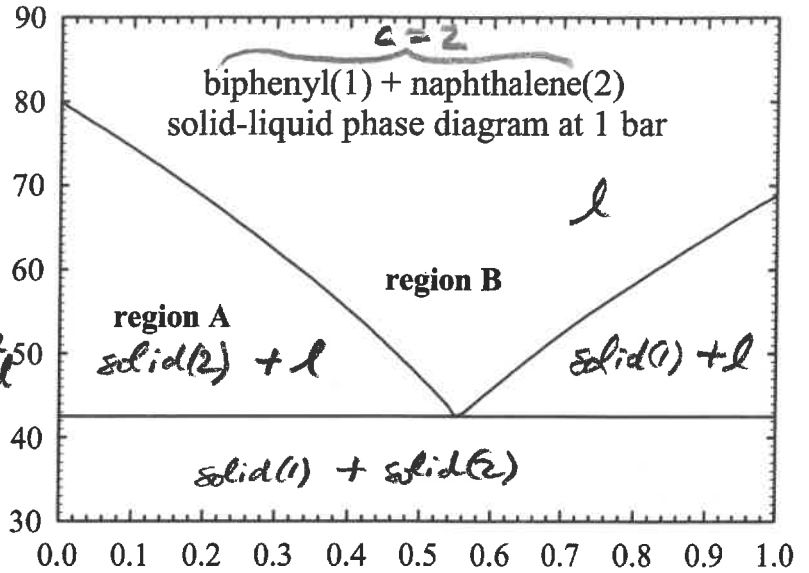
$$P = 1 \text{ (liquid)}$$

$$F = C + 2 - P - 1$$

$$= 2 + 2 - 1 - 1$$

$$F = 2$$

pressure fixed



c) 0.350 moles biphenyl and 0.150 moles naphthalene are placed in a container at 25 °C and 1.00 bar pressure. Describe the phase (or phases) present at equilibrium.

25 ° < eutectic temperature (42.5 °C)
⇒ no liquid

solid biphenyl and solid naphthalene present

d) Crystallization is an important purification technique. In a typical application, a solution is cooled, causing one of the components to precipitate as crystals, which are collected.

If pure biphenyl is to be obtained from a liquid biphenyl(1) + naphthalene(2) solution by crystallization:

i) Why must the mole fraction of biphenyl in the solution be greater than 0.55?

if $x_1 < 0.55$, then naphthalene crystallizes first

ii) Why must the temperature not drop below 42.5 °C?

at 42.5 °C (eutectic temperature)

both biphenyl(1) and naphthalene(2)

crystallize — won't get pure biphenyl

(biphenyl crystals mixed with naphthalene crystals, like salt mixed with sugar)²

- Q3. a) Pure water and an aqueous NaCl solution, both at 25 °C and 1.00 bar, are separated by a membrane permeable to water but impermeable to Na⁺ and Cl⁻ ions.

Water is observed to flow spontaneously across the membrane, from the pure water into the NaCl solution. Give a thermodynamic explanation for this behavior.

The chemical potential of water in the NaCl solution is lower than the chemical potential of water in the pure water: spontaneous flow of water to lower chem. potential

- b) As a practical application of the process described in a, explain why salt (NaCl) preserves food by preventing microbial spoilage.

Salting food (e.g., fish) draws water out of microbes by osmotic flow (part a), killing them by desiccation.

- c) The osmotic pressure of an ideal solution containing c moles of solute molecules per unit volume of solution is $\pi = cRT$. Show that this result closely resembles the ideal gas equation.

$$\pi = cRT = \frac{\text{moles of solute}}{V} RT \sim \frac{nRT}{V}$$

analogous to $p = \frac{nRT}{V}$

- d) Liquid coolant is pumped through channels in car and truck engines to prevent engine overheating. Water is an unsuitable coolant in cold climates because it freezes at 0 °C.

Calculate the freezing point of a water(1) + propylene glycol(2) solution containing 60 weight % propylene glycol antifreeze.

Data $T_1^* = 273.15 \text{ K}$
MW(H₂O) 18.0 g mol⁻¹

$\Delta H_{\text{fus,m},1} = 6010 \text{ J mol}^{-1}$
MW(propylene glycol) 76.1 g mol⁻¹

For 100 grams of solution (40 g water + 60 g PG):

moles water $n_1 = \frac{40 \text{ g}}{18.0 \frac{\text{g}}{\text{mol}}} = 2.22 \text{ mol}$

moles PG $n_2 = \frac{60}{76.1} = 0.788 \text{ mol}$

water mole fraction $x_1 = n_1 / (n_1 + n_2) = 2.22 / (2.22 + 0.788)$
($x_2 = 0.262$) $x_1 = 0.738$

b.p. depression $\Delta T = - \frac{R(T_1^*)^2}{\Delta H_{\text{fus,m},1}} \ln x_1 = - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})^2}{6010 \text{ J mol}^{-1}} \ln(0.738)$

$\Delta T = 31.4 \text{ K}$

b.p. = (273.15 - 31.4) K = 241.8 K

b.p. = -31.4 °C

$$m_{Ca^{2+}} = 12.0 \text{ mol kg}^{-1}$$

$$m_{Cl^{-}} = 24.0 \text{ mol kg}^{-1}$$

Q4. a) For an aqueous solution containing 12.0 moles CaCl_2 per kilogram of water:

i) Calculate the calcium chloride activity assuming the solution is ideal.

$$\begin{aligned} a_{\text{CaCl}_2} &= a_{\text{Ca}^{2+}} a_{\text{Cl}^{-}}^2 = (\gamma_+ m_{\text{Ca}^{2+}}) (\gamma_- m_{\text{Cl}^{-}})^2 \\ &= \gamma_+ \gamma_-^2 m_{\text{Ca}^{2+}} m_{\text{Cl}^{-}}^2 = (1)(1)^2 (12.0 \frac{\text{mol}}{\text{kg}}) (24.0 \frac{\text{mol}}{\text{kg}})^2 \end{aligned}$$

$$a_{\text{CaCl}_2} (\text{ideal}) = \boxed{6912 \text{ mol}^3 \text{ kg}^{-3}}$$

ii) Calculate the calcium chloride activity using the measured mean ionic activity coefficient $\gamma_{\pm} = 14.6$.

$$\begin{aligned} a_{\text{CaCl}_2} &= \gamma_+ \gamma_-^2 m_{\text{Ca}^{2+}} (m_{\text{Cl}^{-}})^2 = \gamma_{\pm}^3 m_{\text{Ca}^{2+}} m_{\text{Cl}^{-}}^2 \\ &= (14.6)^3 (12.0 \frac{\text{mol}}{\text{kg}}) (24.0 \frac{\text{mol}}{\text{kg}})^2 \end{aligned}$$

$$a_{\text{CaCl}_2} = \boxed{2.15 \times 10^7 \text{ mol}^3 \text{ kg}^{-3}} \quad (\text{3112 times larger than if ideal})$$

iii) Explain how ion hydration causes the actual calcium chloride activity (ii) to be much larger than the calcium chloride activity expected for an ideal solution (i).

Ca^{2+} ions are strongly hydrated in aqueous solutions, reducing the amount of "free" water to act as the solvent, making the solution effectively more concentrated than for an ideal solution (no ion hydration)

b) The thermodynamic properties of individual ions cannot be measured. But Table 10.1 in the notes gives $\Delta H_{\text{fm}}^{\circ}$, $\Delta G_{\text{fm}}^{\circ}$ and S_{m}° values for $\text{Ca}^{2+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$, $\text{Ag}^{+}(\text{aq})$, $\text{Br}^{-}(\text{aq})$, ... ! Account for this *apparent* contradiction.

The tabulated $\Delta H_{\text{fm}}^{\circ}$, $\Delta G_{\text{fm}}^{\circ}$ and S_{m}° values are relative to the corresponding values for $\text{H}^{+}(\text{aq})$

$$\text{e.g. } \Delta H_{\text{fm}}^{\circ}(\text{Ca}^{2+}, \text{aq}) = \Delta H_{\text{fm}}^{\circ}(\text{Ca}^{2+}, \text{aq})_{\text{actual}} - \Delta H_{\text{fm}}^{\circ}(\text{H}^{+}, \text{aq})_{\text{actual}}$$

Q5. Indicate whether each of the following statements is true or false. If false, briefly explain why, or give an example to show the statement is false.

- a) The vapor in equilibrium with a liquid mixture of two components is always richer than the liquid in the more volatile component. T **F**

Not true for azeotropic systems.

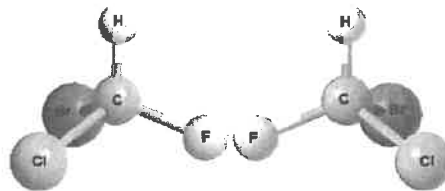
On page 1, the vapor is richer in ethanol, (less volatile component)

- b) The chemical potential μ_i of component i in an ideal liquid solution is always lower than the chemical potential μ_i^* of the pure liquid. **T** F

$$\mu_i - \mu_i^* = RT \ln x_i \leftarrow \text{always negative for a solution}$$

- c) The optical isomers of bromochlorofluoromethane are not expected to form ideal solutions. T **F**

The optical isomers have identical sizes, shapes, polarities, and interactions.



- d) Raoult's law $p_i = x_i p_i^*$ accurately describes the vapor pressures of solutions. T **F**

Not for nonideal solutions:

$$p_i < x_i p_i^*$$

$$p_i > x_i p_i^*$$

- e) Liquid sodium chloride is an electrolyte. **T** F

$\text{NaCl}(l)$ has mobile Na^+ and Cl^- ions, and is a good ionic conductor.

- f) Solid sodium chloride is not an electrolyte. **T** F

Na^+ and Cl^- are locked in the crystal lattice, not free to move.

Q1
Q2
Q3
Q4
Q5