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

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

Q1.   This question refers to an ideal solution prepared by dissolving 2.31 grams of a compound in 100.0 grams of water. The freezing point of the solution is $-0.352\ ^{\circ}C$.

a) Use $\Delta T = K_f m$ to calculate the molecular weight of the compound. *Data*: $K_f = 1.86$ K kg mol^{-1}

$$\Delta T = 0.352\ K \quad (\text{the freezing point depression})$$

$$m = \frac{\text{solute}}{\text{molality}} = \frac{\Delta T}{K_f} = \frac{0.352\ K}{1.86\ K\ kg\ mol^{-1}} = 0.1892\ \frac{mol}{kg}$$

$$m = \frac{\text{moles of solute}}{kg\ of\ water} = \frac{2.31\ g\ /\ M}{0.1000\ kg} \longleftarrow \text{solute molecular weight}$$

$$M = \frac{2.31\ g}{(0.1000\ kg)\ m} = \frac{2.31\ g}{(0.1000\ kg)(0.1892\ \frac{mol}{kg})}$$

$$\boxed{M = 122\ g\ mol^{-1}}$$

b) If the compound is a salt, the molecular weight calculated in **a** would be incorrect. Why?

Should use $\Delta T = K \nu m$ for salts, where ν is the number of moles of ions per mole of salt (e.g., $\nu = 2$ for NaCl, $\nu = 3$ for CaCl$_2$, etc.)

c) If the compound is a salt, would the molecular weight calculated in **a** be too large? Explain.

No. For a salt such as NaCl, the freezing point depression is $\Delta T = K(2m)$ because there are **two** moles of dissolved ions per mole of salt and the calculated MW would be $1/2$ of the correct value.

d) Calculate the Raoult's law activity of water (MW 18.0 g mol^{-1}) in the solution.

$$a_w^{(RL)} = \gamma_w^{(RL)} x_w = x_w \text{ for the ideal solution } (\gamma_w^{(RL)} = 1)$$

$$x_w = \frac{\text{moles of water}}{\text{moles of water} + \text{moles of solute}} = \frac{5.556\ mol}{5.556\ mol + 0.0189\ mol}$$

$$= \frac{(100.0\ g)/(18.0\ g\ mol^{-1})}{\frac{100.0\ g}{18.0\ g\ mol^{-1}} + \frac{2.31\ g}{122\ g\ mol^{-1}}} = \boxed{0.9966}$$

1

Q2. **a)** Show the equation $\pi = RTc$ for the osmotic pressure resembles the ideal gas law.

osmotic pressure $\quad \pi = RTC = RT\dfrac{n}{V}$

molar concentration $\quad c = \dfrac{\text{moles of solute}}{\text{volume of solution}}$

b) Calculate the osmotic pressure of seawater at 25 °C, assuming seawater is an ideal solution containing 0.47 mol L^{-1} NaCl and 0.04 mol L^{-1} MgCl$_2$.

$\pi = RTC \qquad\qquad C = \text{total concentration of ions}$

$\pi = RT(C_{Na^+} + C_{Mg^{2+}} + C_{Cl^-})$

$= 0.08314 \dfrac{L\ bar}{J\ K}\,(298.15 K)\,(0.47 + 0.04 + 0.55)\,\dfrac{mol}{L}$

$\boxed{\pi = 26.3\ bar}$

$\left(\text{note: } C_{Cl^-} = C_{NaCl} + 2C_{MgCl_2} = \left[0.47 + 2(0.04)\right]\dfrac{mol}{L}\right.$
$\left. = 0.55\ mol\ L^{-1}\right)$

c) Explain how **reverse osmosis** is used to produce drinking water from seawater.

A large pressure (ΔP), up to about 400 bar, much larger than the osmotic pressure of seawater, is applied to seawater, forcing pure water to flow out of the seawater, across semipermeable membranes, for collection
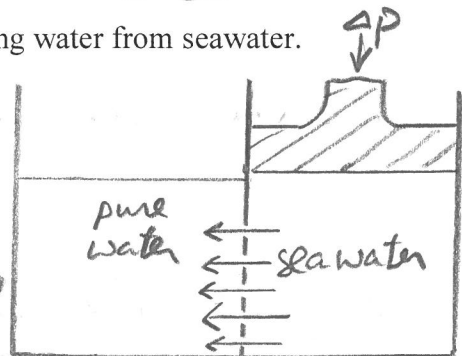
d) Give a thermodynamic explanation for the ability of NaCl to prevent the microbial spoilage of food products.

water spontaneously flows out of microbes into the salt solution where the water chemical potential is low

the "dried" microbes die

concentrated aqueous NaCl $\xleftarrow{H_2O}$ solution

bacterium cell
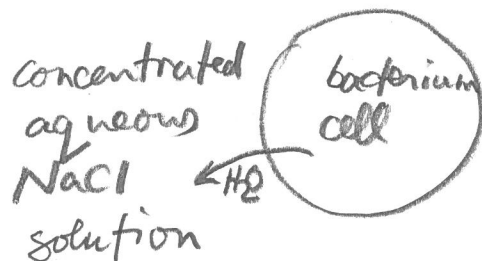
Q3. The diagram below gives the vapor pressures of liquid carbon disulfide(1) + acetone(2) mixtures at 20 °C plotted against the mole fraction of carbon disulfide in the liquid. The vapor pressures of the pure liquids at this temperature are $p_1^* = 510$ Torr and $p_2^* = 342$ Torr.

a) Carbon disulfide and acetone molecules are nonpolar and polar, respectively. Why would you expect mixtures of these compounds to show positive deviations from Raoult's law? Do these mixtures show positive deviations from Raoult's Law? Explain.
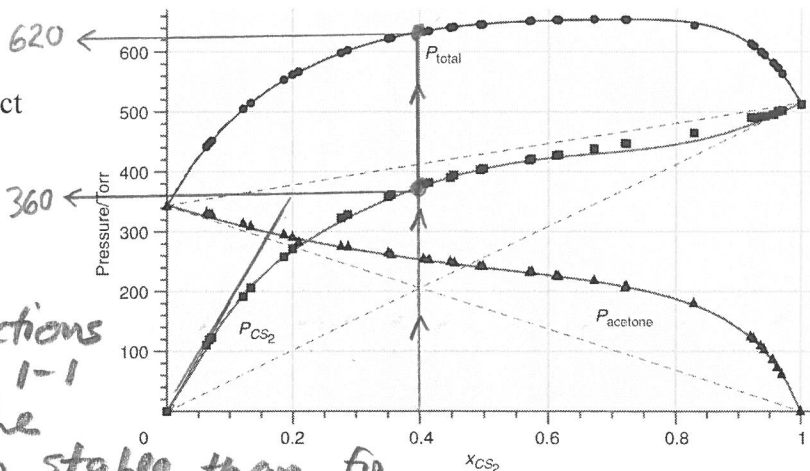
2-2 (polar-polar) attractions are stronger than 2-1, 1-1 attractions, making the liquid mixtures less stable than for ideal mixtures. Positive deviations are observed:
$$p_i (actual) > x_i p_i^* \quad (\text{the dashed lines})$$

b) Calculate the mole fraction of carbon disulfide in the vapor in equilibrium with a liquid mixture of composition $x_{CS2} = 0.40$. $(= x_1)$

at $x_1 = 0.40$, read total pressure $p = 620$ Torr
$p_1 = 360$ Torr

$$y_1 = \frac{p_1}{p} = \frac{360 \text{ Torr}}{620 \text{ Torr}} = \boxed{0.58}$$

c) Is the vapor described in **b** richer in the more volatile component? Justify your answer.

$\boxed{yes}$ $y_1 = 0.58$ $x_1 = 0.40$
1 (CS$_2$) is the more volatile component
$$y_1 > x_1$$

d) Calculate the Raoult's law activity coefficient $(\gamma_1^{(RL)})$ of carbon disulfide at $x_{CS2} = 0.40$.

$$\gamma_1^{(RL)} = \frac{p_1}{x_1 p_1^*} = \frac{360 \text{ Torr}}{0.40 (510 \text{ Torr})}$$

$$= \boxed{1.76}$$

$\left(\begin{array}{c} \gamma_1^{(RL)} > 1 \\ positive\ deviations \\ from\ Raoult's\ law \end{array} \right)$

e) Use the diagram to estimate k_{CS2}, the Henry's law constant of carbon disulfide.

k_{CS2} = slope of p_{CS2} against x_{CS2} at small x_{C2} values

$$\approx \frac{rise}{run} = \frac{360 \text{ Torr}}{0.20} = \frac{\Delta p_{CS2}}{\Delta x_{CS2}} \quad (\text{see graph})$$

$$= \boxed{1800 \text{ Torr}}$$

3

Q4. a) A beaker containing aqueous NaCl at molality 0.500 mol kg^{-1} and a second beaker containing aqueous CaCl$_2$ at molality 0.500 mol kg^{-1} are placed in a sealed chamber, as illustrated below. The volume of the NaCl solution is observed to decrease, and the volume of the CaCl$_2$ solution is observed to increase. Why does this happen?

CaCl$_2$ has 3 moles of ions per mole of CaCl$_2$, compared to only 2 moles ions per mole of NaCl, so the water mole fraction and chemical potential of water are lower than for the NaCl solution.

$\rightarrow H_2O(g)$

lower μ_{H2O}

0.500 mol kg^{-1} aqueous NaCl

0.500 mol kg^{-1} aqueous CaCl$_2$
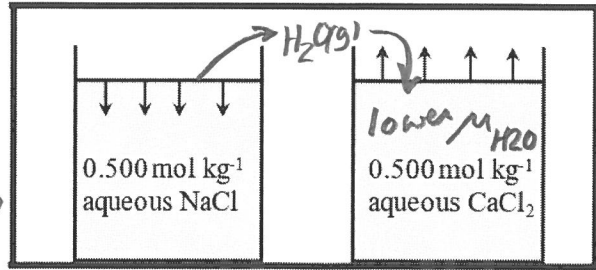
b) Solid water (ice), solid NaCl and an aqueous NaCl solution are in equilibrium at the eutectic point at 1 atm. Use the phase rule to calculate the number of degrees of freedom (F) for this system.

$P = 3$ (2 solids, liquid)
$C = 2$ (H$_2$O, NaCl)
$F = C + 2 - P = 1$
$\boxed{F' = F - 1 = 0}$ (constant pressure)

NaCl forms Na$^+_{(aq)}$ + Cl$^-_{(aq)}$
but $m_{Na^+} = m_{Cl^-}$
so NaCl is a single chemical component

c) The eutectic temperature of aqueous NaCl solutions is $-15\,°C$, compared to $-42\,°C$ for aqueous CaCl$_2$ solutions. Explain why CaCl$_2$ is better than NaCl for melting road ice at low temperatures.

NaCl can't melt ice at temperatures below the eutectic temperature (no liquid possible). CaCl$_2$ can melt ice down to $-42\,°C$.

d) It is impossible to measure the thermodynamic properties of aqueous Na$^+$ ions.

i) Why? Electroneutrality makes it impossible to measure the properties of aqueous Na$^+$ ions alone

ii) But Table 10.1 in the course notes gives:

$S_m°(Na^+, aq) = 59.0$ J K^{-1} mol^{-1} $\Delta H_{fm}°(Na^+, aq) = -240.1$ kJ mol^{-1} $\Delta G_{fm}°(Na^+, aq) = -261.9$ kJ mol^{-1}

How is this possible? These are not absolute values. They are relative values.

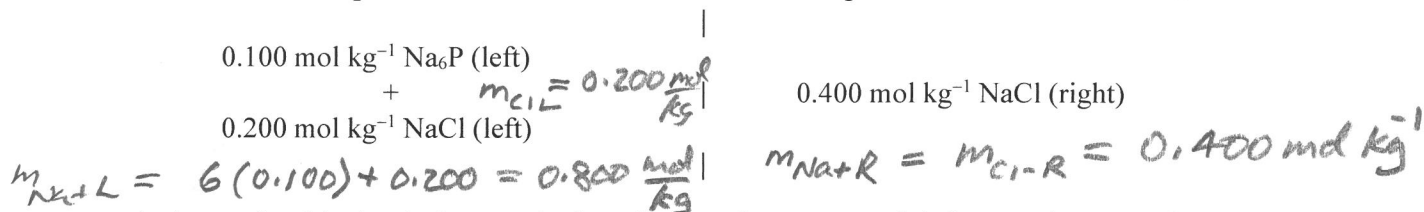e.g. $S_m°(Na^+) = \underset{actual}{S_m°(Na^+)} - \underset{actual}{S_m°(H^+)}$

e) An experiment is performed by adding phenol to a beaker of water equipped with a stir bar. The solution, initially clear, turns cloudy. But as more phenol is added, the cloudy solution becomes clear again! Explain.

The solution turns cloudy because the water becomes saturated (can't dissolve any more phenol), and a second phenol-rich phase appears. Adding more phenol produces a clear solution because there is enough phenol to dissolve all the water

T

clear

clear again

cloudy

0 x_{phenol} 1

4
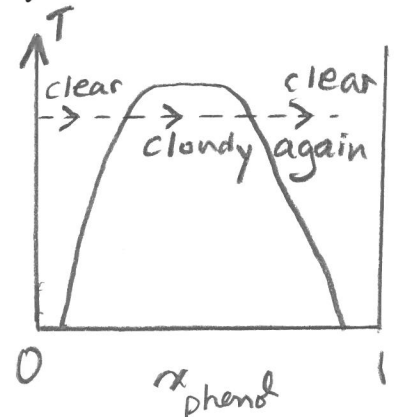
Q5. A 0.100 mol kg^{-1} solution of protein Na$_6$P (six moles of Na$^+$ ions per mole of protein) also containing 0.200 mol kg^{-1} NaCl is separated from a 0.400 mol kg^{-1} NaCl solution by a membrane that is permeable for Na$^+$ and Cl$^-$ ions but impermeable for the P^{6-} ions.

$$|$$

0.100 mol kg^{-1} Na$_6$P (left)
　　　　+　　　　$m_{Cl^-L} = 0.200 \frac{mol}{kg}$|　　0.400 mol kg^{-1} NaCl (right)
0.200 mol kg^{-1} NaCl (left)

$m_{Na^+L} = 6(0.100) + 0.200 = 0.800 \frac{mol}{kg}$ |　　$m_{Na^+R} = m_{Cl^-R} = 0.400 \, mol \, kg^{-1}$

a) Assuming ideal solutions, calculate the membrane potential $\phi_{Right} - \phi_{Left}$ at 25 °C.

$$\phi_R - \phi_L = \frac{RT}{F} \ln\left(\frac{m_{Na^+L}}{m_{Na^+R}}\right)$$

$$= \frac{(8.314 \, JK^{-1}mol)(298.15 \, K)}{96485 \, C \, mol^{-1}} \ln\left(\frac{0.800}{0.400}\right) = \boxed{0.0178 \, V}$$

b) Assuming ideal solutions, show the left and right solutions are in chemical equilibrium. *Suggestion:* Calculate the NaCl activity in the left and right solutions.

$$a_{NaCl \, L} = (m_{Na^+L})(m_{Cl^-L}) = (0.800)(0.200) = 0.160 \frac{mol^2}{kg^2}$$

$$a_{NaCl \, R} = (m_{Na^+R})(m_{Cl^-R}) = (0.400)(0.400) = 0.160 \frac{mol^2}{kg^2}$$

$$a_{NaCl \, L} = a_{NaCl \, R} \quad so \quad \mu_{NaCl \, L} = \mu_{NaCl \, R} \left(\begin{array}{c} chemical \\ equilibrium \end{array}\right)$$

$$\left(\mu_{NaCl} = \mu^{\circ}_{NaCl} + RT \ln a_{NaCl}\right)$$

c) Everyone knows substances spontaneously move from higher to lower concentrations, but:

i) NaCl at 0.400 mol kg^{-1} on the right does not move into the less concentrated 0.200 mol kg^{-1} NaCl solution on the left! Why?

chemical equilibrium : $\quad a_{NaCl \, L} = a_{NaCl \, R}$

$$\boxed{\mu_{NaCl \, L} = \mu_{NaCl \, R}}$$

ii) Cl$^-$ ions at 0.400 mol kg^{-1} on the right do not move into the less concentrated 0.200 mol kg^{-1} Cl$^-$ solution on the left! Why?

electrochemical equilibrium $\boxed{\tilde{\mu}_{Cl^-L} = \tilde{\mu}_{Cl^-R}}$

$$RT \ln m_{Cl^-L} - F\phi_L = RT \ln m_{Cl^-R} - F\phi_R$$

Cl$^-$ ions on the right have higher chemical potential $\left(\frac{0.400}{> 0.200}\right)$ but lower electric potential $-F\phi_R$ (<0)

d) Give an important biological application of membrane potentials.

nerve operation