

# Chemistry 240 Semester 01-2009

## Homework for Submission #7 – Key – 40 marks total

Answer the following questions and submit them for marking on or before 15<sup>th</sup> April 2009 in the chemistry drop box. If any answers show evidence of copying, the whole exercise will attract zero marks.

- 1) a) The osmotic pressure of seawater is 27 atm. Calculate (i) the minimum energy requirement in kilojoules and (ii) the electrical energy required in kilowatt-hours assuming 80% efficiency<sup>1</sup>, to produce 1000 gallons of pure water from seawater by reverse osmosis. (Consider this as a reversible expansion against a constant external pressure.) You can find appropriate conversions for units at <http://www.onlineconversion.com>

### Solution

The reversible work done would be  $w = -P\Delta V$  (since  $P_{in}$  is the same as  $P_{ex}$  for a reversible process). The pressure is 27 atm because this is the minimum pressure necessary to force pure water through the semipermeable membrane, leaving salt behind.  $\Delta V$  is volume of pure water produced, hence

$$w = -P\Delta V = -27 \text{ atm} \times 1000 \text{ gal} = -(27 \times 101325) \text{ Pa} \times (1000 \times 3.785 \times 10^{-3}) \text{ m}^3 \text{ since } 1 \text{ atm} = 101325 \text{ Pa, and } 1 \text{ gallon [US, liquid]} = 0.003785411784 \text{ m}^3.$$

$$\therefore w = -1.035 \times 10^7 \text{ J} = \underline{-1.0 \times 10^7 \text{ J to 2 sig. figs.}} \quad (3)$$

The sign can be ignored since it only means that the system must lose energy in the process of reverse osmosis. Numerically this is the minimum amount of energy necessary to purify 1000 gal of water.

The above figure (without the sign) would also be the amount of electrical energy necessary (to run the pumps) except that the process is only 80% efficient. Hence the above amount of energy is only 80% of that required. The actual amount of electrical energy is given by

$$1.035 \times 10^7 \text{ J} \times (100/80) = 1.294 \times 10^7 \text{ J} = 1.294 \times 10^7 \times 2.7777 \times 10^{-7} = 3.595 \text{ kW-hr} = \underline{3.6 \text{ kW-hr. to 2 sig. figs.}}, \text{ since } 1 \text{ joule} = 2.777777778 \times 10^{-7} \text{ kilowatt hour} \quad (2)$$

- a) Electricity in the Bahamas costs about \$0.23 per “unit” (kilowatt-hour) to the domestic consumer. What would be the cost of producing 1000 gallons of pure water from seawater on the above basis? How does this compare with Water & Sewerage’s \$6.00 per thousand gallons?

### Solution

The cost of this electricity is  $\$0.23 \times 3.595 = \$0.8270 = \underline{\$0.83}$  to 2 sig. figs. This is roughly one seventh of the price from water and sewerage, but purification only represents a small part of the cost of delivery to the home. (2)

- b) Why do you think that ground water rather than seawater is generally used as the feedstock for reverse osmosis?

### Answer

Ground water is generally less salty than seawater, giving a lower osmotic pressure and hence a lower energy cost. (1)

- 2) Naphthalene ( $C_{10}H_8$ ) steam distils at 98°C and an ambient pressure of  $1.01 \times 10^5$  Pa. At this temperature, the vapour pressure of water is  $9.50 \times 10^4$  Pa. Calculate the percentage by mass of naphthalene in the distillate. (Take the RAM of H=1, C=12, O=16.)

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<sup>1</sup> There are many factors influencing the efficiency of reverse osmosis. The quality of the membrane is just one of them. The amount of liquid pumped is another. In order to keep the osmotic pressure at a minimum the water in contact with the membrane must be changed frequently, which requires a lot of pumping with its attendant energy cost. To minimise pumping costs the water is allowed to spend a longer time in contact with the membrane until it is more concentrated than the original feed-stock water. This reduces the amount of water to be pumped but increases the osmotic pressure, which in turn makes pumping a given amount of water more expensive.

## Solution

The ratio of numbers of moles of naphthalene to water in the vapour is given by  $\frac{n_n}{n_w} = \frac{P_n}{P_w}$ . The distillate has the same composition. (5)

Since the total vapour pressure =  $1.01 \times 10^5$  Pa,  $P_n = P_{atm} - P_w$

$$\therefore \frac{n_n}{n_w} = \frac{P_n}{P_w} = \frac{1.01 \times 10^5 - 9.50 \times 10^4}{9.50 \times 10^4} = 6.316 \times 10^{-2}$$

but mass,  $m = nM$ , where  $M_n$  for naphthalene is  $128 \text{ g mol}^{-1}$  and  $M_w$  for water is  $18.0 \text{ g mol}^{-1}$ .

$$\therefore \frac{m_n}{m_w} = \frac{n_n \times M_n}{n_w \times M_w} = 6.316 \times 10^{-2} \times \frac{128}{18.0} = 6.316 \times 10^{-1}$$

$$\text{But \% by mass} = \frac{m_n}{m_w + m_n} = \frac{\left(\frac{m_n}{m_w}\right)}{1 + \left(\frac{m_n}{m_w}\right)} = \frac{6.316 \times 10^{-1}}{1 + 6.316 \times 10^{-1}} = 0.3871 = \underline{\underline{38.7\%}} \text{ to 2 sig. figs.}$$

3) Define the term *molality*.

## Answer

The molality of a solution is the number of moles of solute per kilogram of solvent. (1)

In terms of the molality,  $\mu$ , of an undissociated solute, the freezing point depression ( $\Delta T$ ) is given by

$$\Delta T = -k_f \mu$$

From this, derive the equation

$$\Delta T = -k_f \frac{m}{M} \times \frac{1}{W}$$

where  $k_f$  is the freezing point depression constant,  $m$  is the mass of solute in grams,  $M$  is the molar mass of the solute in  $\text{g mol}^{-1}$ , and  $W$  is the mass of solvent in kilograms.

## Solution

$$\Delta T = -k_f \mu$$

But  $\mu = \frac{n}{W}$ , where  $n = \#$  of moles of solute and  $W =$  mass of solvent in kg.

$$\therefore \Delta T = -k_f \frac{n}{W}$$

$$\text{But } n = \frac{m}{M}$$

$$\therefore \Delta T = -k_f \frac{m}{M} \times \frac{1}{W}$$

4) a) The vapour pressure of one component of an ideal liquid mixture is given by  $P_1 = x_1 P_1^0$  (Raoult's law), where  $P_1$  represents the vapour pressure (partial pressure in the mixture of vapours) of component (1),  $x_1$  its mole fraction in the mixture, and  $P_1^0$  the vapour pressure of the component when pure. Show that the composition of the vapour in equilibrium with an ideal mixture of two liquids is always richer in the more volatile component. (That is, prove that  $\frac{n_{1vap}}{n_{2vap}} > \frac{n_{1liq}}{n_{2liq}}$  when component (1) is more volatile than

component (2)).

### Solution

Considering the vapour as a mixture of ideal gases, we have, from the ideal gas law<sup>2</sup>, (6)

$$\frac{n_{1vap}}{n_{2vap}} = \frac{p_1}{p_2} \text{----- (A) where } p_1 \text{ and } p_2 \text{ are the vapour pressures of substances (1) and (2) (which are the same}$$

as their partial pressures in the mixture of vapours) and  $n_{1vap}$  and  $n_{2vap}$  are the numbers of moles of the two substances in the vapour.

But from Raoult's law,

$$p_1 = x_{1liq} p_1^0 \text{ and } p_2 = x_{2liq} p_2^0$$

$$\therefore \frac{p_1}{p_2} = \frac{x_{1liq} p_1^0}{x_{2liq} p_2^0} \text{----- (B)}$$

But

$$x_1 = \frac{n_1}{n_1 + n_2} \text{ and } x_2 = \frac{n_2}{n_1 + n_2}$$

$$\therefore \frac{x_{1liq}}{x_{2liq}} = \frac{n_{1liq}}{n_{2liq}} \text{----- (C)}$$

And substituting (A) and (C) in (B), we have

$$\frac{p_1}{p_2} = \frac{n_{1vap}}{n_{2vap}} = \frac{n_{1liq}}{n_{2liq}} \frac{p_1^0}{p_2^0}$$

But if component (1) is more volatile than component (2), its vapour pressure is higher. Hence  $\frac{p_1^0}{p_2^0} > 1$

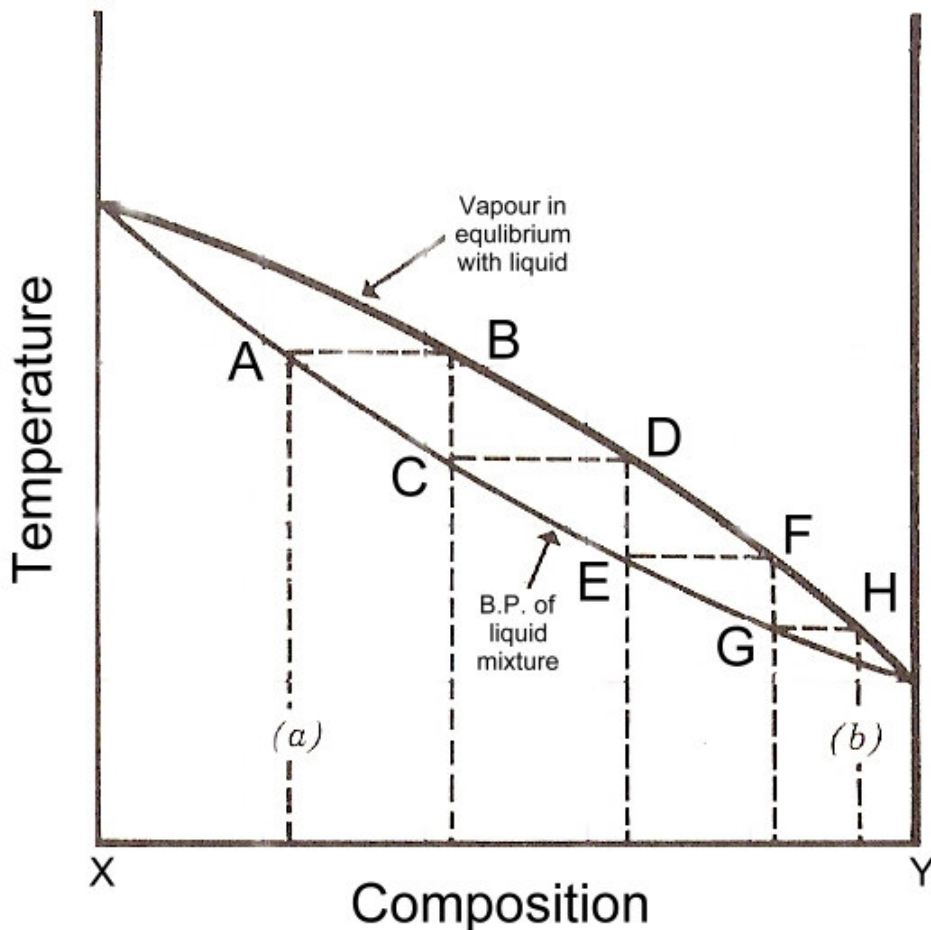
And so  $\frac{n_{1vap}}{n_{2vap}} > \frac{n_{1liq}}{n_{2liq}}$  QED<sup>3</sup>

- b) Sketch a phase diagram of temperature against composition for a mixture of two volatile liquids which behave ideally, showing the boiling point of the mixture and the composition of the vapour in equilibrium with the mixture.

<sup>2</sup> Whatever volume of vapour is considered, the volume is occupied by the two vapours equally, and of course their temperatures are the same, so, from  $pV=nRT$ ,

$$\frac{p_1 V}{p_2 V} = \frac{n_1 RT}{n_2 RT} \text{ and } V, R \text{ and } T \text{ cancel.}$$

<sup>3</sup> QED is a Latin abbreviation for "Quod Erat Demonstrandum" meaning "Which was to be demonstrated".



(3 for diagram)

What is meant by the term “tie-line”? Draw tie-lines on your graph to illustrate (i) simple distillation and (ii) fractional distillation. Use the tie-lines to describe and explain these processes. (7)

A tie-line is one which joins phases in equilibrium (1), on the above graph at a given temperature, showing their compositions. A-B is a tie-line. (1)

In simple distillation, a liquid mixture of composition (a) boils at the temperature at point A (1). The vapour produced has composition represented by the position of point B on the horizontal axis. (1) (Note the temperature is the same as at A.) When B condenses it produces a liquid of the same composition which is richer in the more volatile component, Y. (1)

In fractional distillation it is as if a series of simple distillations is performed, (1) taking the vapour from B and producing a liquid C, which again gives a vapour D, and so through liquid E, vapour F, liquid G, vapour H and finally liquid (b), which is almost pure Y. (1)

- c) What are meant by positive and negative deviations from Raoult’s law? What, in terms of intermolecular forces, leads to such behaviour? What are “high boiling” and “low-boiling” azeotropes? (7)

A positive deviation from Raoult’s law gives a higher vapour pressure for a liquid mixture than predicted by Raoult’s law, (1) a negative deviation, one which is lower. (1) A positive deviation results when the intermolecular forces X/Y are weaker than X/X or Y/Y. (1) A negative deviation results when the intermolecular forces between X/Y are stronger than X/X or Y/Y. (1) An azeotrope is a liquid mixture which boils to give a vapour of the same composition. (1) A “high-boiling” azeotrope is a mixture which has a boiling point higher than that of either pure liquid (1), whereas a low-boiling azeotrope is one which has a lower boiling point than either pure liquid (1).