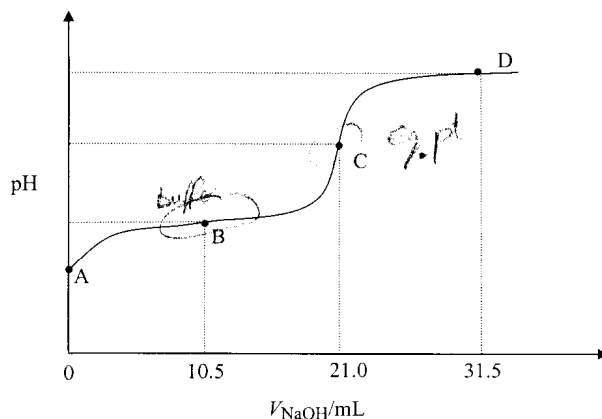


1. (24 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 20.0 mL sample of a solution of weak acid, HA, of unknown concentration,  $C_{HA}$ , is titrated with standardised NaOH solution. The NaOH solution has a concentration of  $0.100 \text{ mol L}^{-1}$  and  $V_{NaOH}$  represents the volume in mL of NaOH which has been added. [Data:  $K_a(\text{HA}) = 5.0 \times 10^{-8}$ ;  $K_w = 1.00 \times 10^{-14}$ ]

(a) What pieces of laboratory equipment would be used to measure out:

(i) the volume of HA solution?

pipette

(ii) the added volume of NaOH,  $V_{NaOH}$ ?

burette

(b) On the figure above, clearly indicate and label the following:

(i) the equivalence point;

C

(ii) a buffer region.

B

(c) Calculate  $C_{HA}$ .

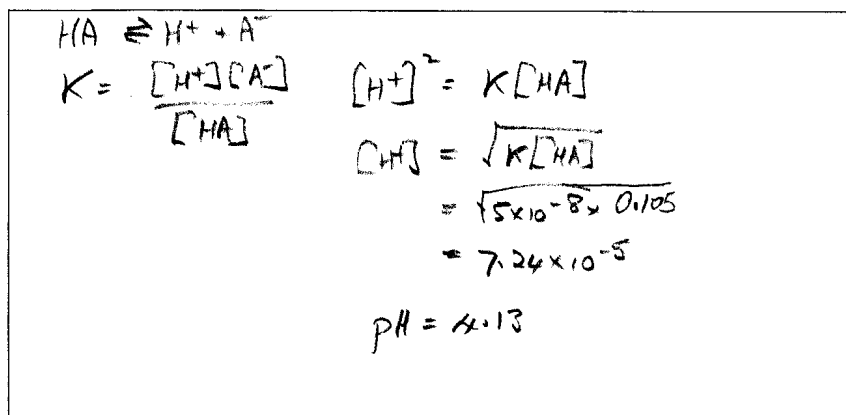
$$21 \times 0.1 = 20 \times x \quad x = 0.105 \text{ M}$$

$$V_{OH} \times [OH^-] = V_{HA} \times [H^+]$$

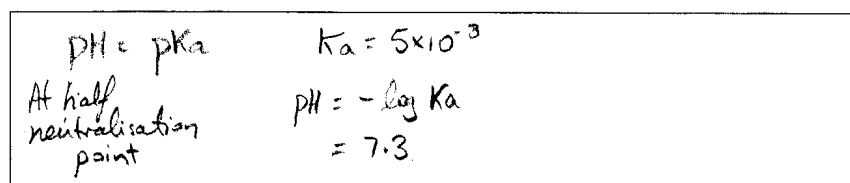
Question 1 continued on the following page  
TURN OVER

## Question 1 continued

- (d) Calculate the pH at point A.

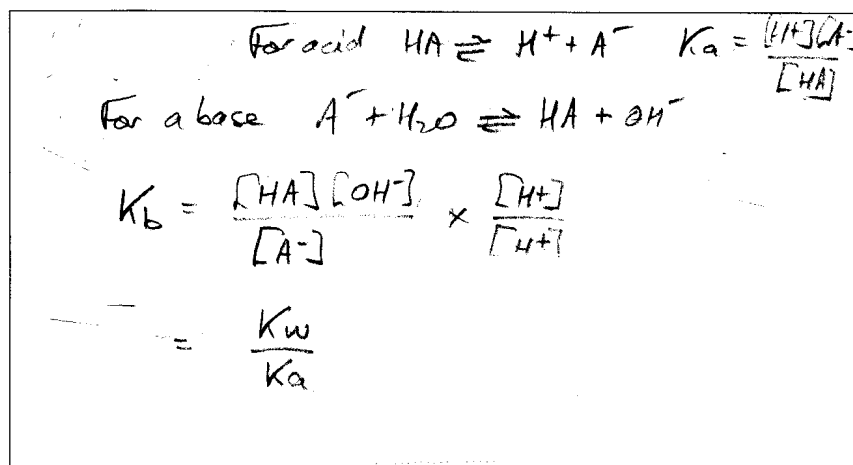


- (e) What is the pH at point B?



- (f) Prove the general result that
- $K_b$
- (base ionisation constant) for the base
- $\text{A}^-$
- (i.e. conjugate base of the acid, HA) is given by

$$K_b(\text{A}^-) = K_w / K_a(\text{HA})$$



Question 1 continued on the following page

TURN OVER

## Question 1 continued

- (g) Calculate the pH at the equivalence point in the titration.

At equiv. pt. all  $H^+$  consumed. can also use

$$\text{Need } [A^-] = \frac{0.1 \times 21}{20+21} = 0.0512 \text{ M} = \frac{0.105 \times 20}{41}$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \quad K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{[OH^-][HA]}{[A^-]} \quad = \frac{1 \times 10^{-14}}{5 \times 10^{-8}} = 2 \times 10^{-7}$$

$$2 \times 10^{-7} \times 0.0512 = [OH^-]^2$$

$$[OH^-] = 1 \times 10^{-4}$$

$$p[OH^-] = 4$$

$$pH = 14 - 4 = 10$$

Question 1 continued on the following page

TURN OVER

## Question 1 continued

4

- (h) The endpoint of this titration could be detected using an indicator. Of the indicators listed below, which would be the most suitable? Explain the reason for your choice.

Indicator	$pK_a$ (indicator)
Congo red	4.0
Brilliant yellow	7.2
Thymolphthalein	9.8
2,4,6-Trinitrotoluene	12.3

$$pK_{in} \pm 1 = pH \text{ at equiv. pt} = 9.8 \\ = \text{thymolphthalein}$$

- (i) What is the pH at point D?

Excess  $OH^-$ 

$$[OH^-] = \frac{31.5 - 21}{31.5 + 21} \times 0.1M <$$

common error  
to use 0.105M  
-16 [H<sup>+</sup>]

$$= 0.0203$$

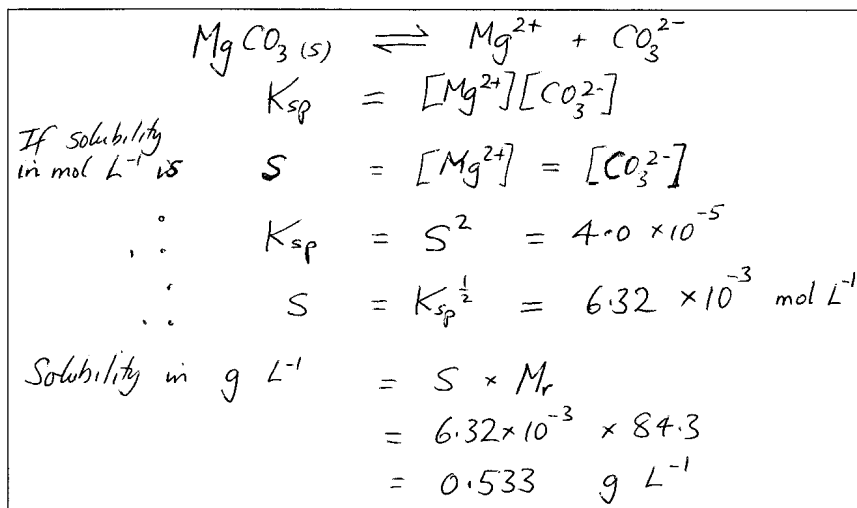
$$pOH = 1.69$$

$$pH = 14 - 1.69 \\ = 12.3$$

TURN OVER

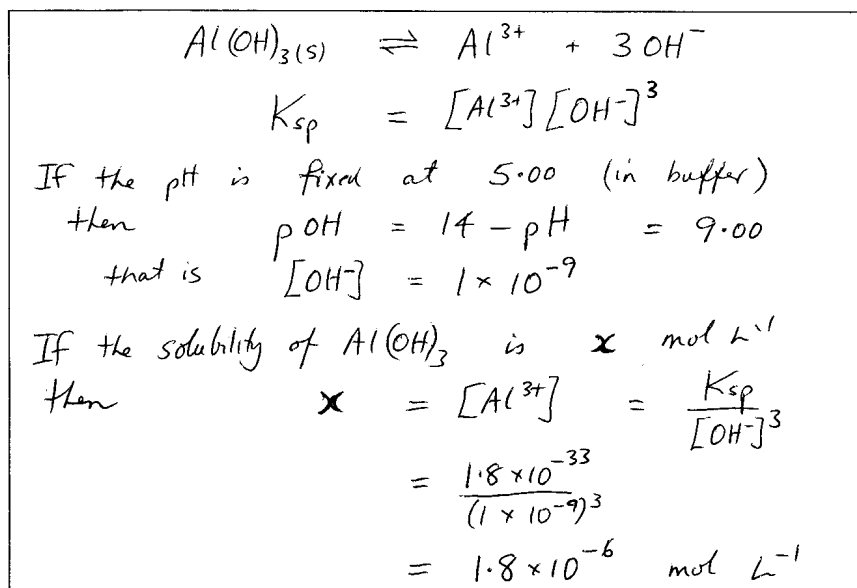
2. (18 marks)

- (a) Calculate the **molar** solubility (i.e. in mol L<sup>-1</sup>) and the **solubility** (in g L<sup>-1</sup>) of MgCO<sub>3</sub> in pure water. [Data:  $K_{sp}\{\text{MgCO}_3\} = 4.0 \times 10^{-5}$ ;  $M_r\{\text{MgCO}_3\} = 84.3$ ].



(6 marks)

- (b) Calculate the molar solubility of Al(OH)<sub>3</sub> in a buffered solution with pH = 5.00. [ $K_{sp}\{\text{Al(OH)}_3\} = 1.8 \times 10^{-33}$ ;  $K_w = 1.0 \times 10^{-14}$ ].



(7 marks)

Question 2 continued on the following page

TURN OVER

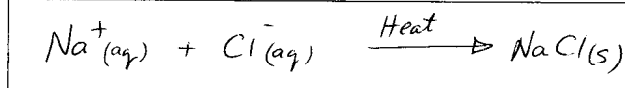
**Question 2 continued**

- (c) Name **THREE** industrial processes that illustrate applications of precipitation equilibria. For each of the named processes, write a balanced, chemical equation that is relevant to the process and describes the precipitation of a solid from solution.

*Possibilities include :-*

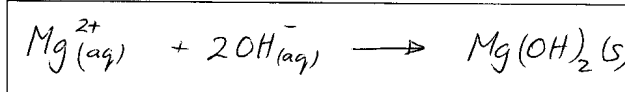
(i) Name of process: Salt recovery from Seawater

Equation:



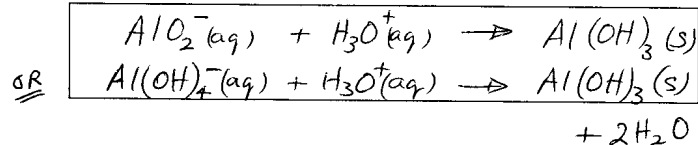
(ii) Name of process: Magnesium recovery from Seawater

Equation:



(iii) Name of process: Bauxite purification (Bayer process)

Equation:



*(Many other correct answers acceptable)*

*( 1 mark for each Name  
1 " " " Equation )*

**TURN OVER**

3. (10 marks)

(a) Give brief definitions of the following thermodynamic terms:

(i) state function;

A measurable property of a system the value of which depends only on the State of the system regardless of the pathway leading to that state. (i.e. independent of "history" of system)

(ii) surroundings;

The remainder of the universe other than a particular "system" which has been defined

(iii) equilibrium;

A system is at equilibrium when there is no change in any of its measurable properties with time.

(iv) third law.

The absolute Entropy of a perfect crystal of a pure substance is ZERO at a temperature of 0 Kelvin.

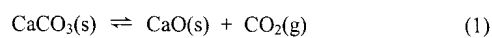
(b) Give the names of the functions  $G$ ,  $T$  and  $Q$  in the equation  $\Delta G = \Delta G^\circ + RT \log_e Q$

$G$  = (Gibbs) Free Energy  
 $T$  = Temperature in Kelvin  
 $Q$  = Reaction quotient

TURN OVER

4. (14 marks)

The thermodynamic data in the following table were obtained at 25°C for the reaction



substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CaCO <sub>3</sub> (s)	-1206.9	92.9
CaO(s)	-635.6	39.8
CO <sub>2</sub> (g)	-393.5	213.6

(a) Calculate  $\Delta H^\circ$  for reaction (1).

$$\begin{aligned} \Delta H^\circ &= \sum_{\text{prod}} \nu_{\text{prod}} \Delta H_f^\circ(\text{prod}) - \sum_{\text{react}} \nu_{\text{react}} \Delta H_f^\circ(\text{react}) \\ &= \Delta H_f^\circ(\text{CaO}(\text{s})) + \Delta H_f^\circ(\text{CO}_2(\text{g})) - \Delta H_f^\circ(\text{CaCO}_3(\text{s})) \\ &= (-635.6 - 393.5 + 1206.9) \text{ kJ mol}^{-1} \\ &= 177.8 \text{ kJ mol}^{-1} \end{aligned}$$

(b) Calculate  $\Delta S^\circ$  for reaction (1).

$$\begin{aligned} \Delta S^\circ &= \sum_{\text{prod}} \nu_{\text{prod}} S^\circ(\text{prod}) - \sum_{\text{react}} \nu_{\text{react}} S^\circ(\text{react}) \\ &= S^\circ(\text{CaO}(\text{s})) + S^\circ(\text{CO}_2(\text{g})) - S^\circ(\text{CaCO}_3(\text{s})) \\ &= (39.8 + 213.6 - 92.9) \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 160.5 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

(c) From your answers above, calculate  $\Delta G^\circ$  for reaction (1). (If you were unable to obtain answers in parts (a) and (b) above, use the **incorrect** values  $\Delta H^\circ = 150 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 200 \text{ J mol}^{-1} \text{ K}^{-1}$ .)

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 177.8 \text{ kJ mol}^{-1} - 298 \times 160.5 \times 10^{-3} \text{ kJ mol}^{-1} \\ &= 129.97 \text{ kJ mol}^{-1} \end{aligned}$$

OR

$$\begin{aligned} \Delta G^\circ &= (150 - 298 \times 200 \times 10^{-3}) \text{ kJ mol}^{-1} \\ &= 90.4 \text{ kJ mol}^{-1} \end{aligned}$$

Question 4 continued on the following page

TURN OVER

## Question 4 continued

- (d) If the substances in reaction (1) were permitted to come to equilibrium at 400 K, what would be the partial pressure of  $\text{CO}_2$ ?

$$\Delta G_{400}^{\circ} = (177.8 - 0.1605 \times 400) \text{ kJ mol}^{-1} = 113.6 \text{ kJ mol}^{-1}$$

$$K = \frac{a_{\text{CO}_2} a_{\text{CaO}}}{a_{\text{CaCO}_3}} = \frac{P_{\text{CO}_2} \times 1}{1} = P_{\text{CO}_2}$$

$$\Delta G^{\circ} = -RT \log_e K = -RT \log_e P_{\text{CO}_2}$$

$$P_{\text{CO}_2} = e^{-\Delta G^{\circ}/RT} = e^{(-113.6 \times 10^3 / (8.314 \times 400))}$$

$$= 1.76 \times 10^{-15} \text{ atm}$$

- (e) Consider the case where the process shown in reaction (1) has reached equilibrium. Predict, *with reasoning*, the direction (to the left or right) in which the equilibrium would shift if the following "stresses" were applied.

- (i) the volume of the system was decreased without changing the temperature;

To left (reverse direction)  
 Decrease volume  $\Rightarrow$  increase pressure  
 Le Chatelier says system will adjust to decrease pressure - i.e. to decrease the amount of gaseous  $\text{CO}_2$

- (ii) the temperature of the system was decreased without changing the volume;

To left (reverse direction)  
 System will adjust to increase the temperature - i.e. in the exothermic direction  
 The reaction is endothermic in the forward direction ( $\Delta H^{\circ} > 0$ ) so get a reverse adjustment.

- (iii) the pressure of the system was increased by adding  $\text{N}_2$  gas without changing the temperature or the volume.

No change.  
 $\text{N}_2$  is inert w.r.t this reaction so changes in its activity affect neither  $\Delta G^{\circ}$  nor  $K$ .

TURN OVER

5. (18 marks)

(a) Use the following table of standard reduction potentials to answer the questions below:

Reduction Half-reaction	$E^\circ / V$
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.920
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.771
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.91

(i) Which of the species in the table is the strongest oxidising agent?

1  $\text{Hg}^{2+}$  most +ve  $E^\circ$

(ii) Which of the species in the table is the strongest reducing agent?

1  $\text{Cr}(\text{s})$  most -ve  $E^\circ$

(iii) Which of the ions in the table will Ni(s) reduce?

2  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$  —  $E^\circ$  more +ve than  $\text{Ni}^{2+}/\text{Ni}$

(iv) Write down the conventional cell diagram for a cell that involves the nickel and iron half reactions above, and which also which has a positive standard cell potential. Calculate the standard cell potential for that cell.

3  
 oxid  $\text{Ni}(\text{s}) | \text{Ni}^{2+}(\text{aq}) || \text{Fe}^{3+}, \text{Fe}^{2+}(\text{aq}) | \text{Pt}$  reduction  
 anode (-) cathode (+)  
 2  
 $E^\circ = E_+ - E_- = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^\circ(\text{Ni}^{2+}/\text{Ni})$   
 $= 0.771 - (-0.25) = 1.021 \text{ V}$

9

Question 5 continued on the following page

TURN OVER

## Question 5 continued

- (v) Calculate the equilibrium constant for the reaction of Ni(s) with Fe
- <sup>3+</sup>
- (aq), to give Fe
- <sup>2+</sup>
- (aq).

4

$$\textcircled{1} E^{\circ} = \frac{RT}{nF} \ln K$$

$$\textcircled{1} \left\{ \begin{array}{l} \text{reaction } \text{Ni(s)} + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \\ n = 2 \end{array} \right.$$

$$\textcircled{1} 1.021 = 0.0128 \ln K$$

$$\ln K = 79.526 \quad \textcircled{1} \quad K = 3.4 \times 10^{34}$$

- (vi) Calculate the standard free energy change,
- $\Delta G^{\circ}$
- , for the reaction of Ni(s) with Fe
- <sup>3+</sup>
- (aq), to give Fe
- <sup>2+</sup>
- (aq).

3

$$\textcircled{1} \Delta G^{\circ} = -nE^{\circ}F$$

$$= -2 \times 1.021 \times 96489$$

$$\textcircled{2} = -197,030 \text{ J mol}^{-1}$$

$$= -197 \text{ kJ mol}^{-1}$$

$$\Delta G^{\circ} = -RT \ln K$$

$$= -8.314 \times 298 \times 79.526$$

$$= -197,030 \text{ J mol}^{-1}$$

$$= -197 \text{ kJ mol}^{-1}$$

- (b) Explain briefly (2-3 sentences only) how
- either**
- galvanising (coating with zinc)
- or**
- coating with paint protects iron from rusting.

2

galvanising — Zn oxidised rather than Fe if in electrical contact — protection until all Zn consumed.  
 $[ E^{\circ}(\text{Zn}^{2+}|\text{Zn}) < E^{\circ}(\text{Fe}^{3+}|\text{Fe}^{2+}) ]$

paint — prevents contact of metal surface with water and oxygen providing there is complete coverage.

9  
TURN OVER

6. (20 marks)

- (a) Platinum crystals have a face-centred cubic structure. The radius of a platinum atom is 139 pm. Calculate the density of a platinum crystal (in  $\text{g cm}^{-3}$ ).

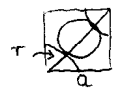
$$M(\text{Pt}) = 195.1 \text{ g mol}^{-1}; N_A = 6.022 \times 10^{23} \text{ mol}^{-1}; 1 \text{ pm} = 10^{-12} \text{ m}$$

For a unit cell

$$\begin{aligned} \text{Mass} &= 4 \times M / N_A \\ &= 4 \times 195.1 / 6.022 \times 10^{23} \\ &= 1.2959 \times 10^{-21} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Cell edge (a)} &= 4R/\sqrt{2} \\ &= 4 \times 139 \times 10^{-12} / \sqrt{2} \\ &= 3.93 \times 10^{-10} \text{ m} \end{aligned}$$

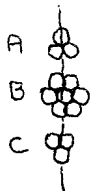
$$\begin{aligned} \text{Cell volume} &= a^3 \\ &= 6.077 \times 10^{-29} \text{ m}^3 \\ &= 6.077 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Density} &= \text{mass/volume} \\ &= 1.2959 \times 10^{-21} / 6.077 \times 10^{-23} \\ &= 21.33 \text{ g cm}^{-3} \end{aligned}$$


fcc 4 atoms/unit cell


- (b) Using **diagrams**, briefly explain the following terms:

- (i) cubic close-packed structure;



A  
B  
C

A close packing arrangement in a ABCBCA arrangement, CCP is equivalent to the face-centred cubic arrangement.



fcc

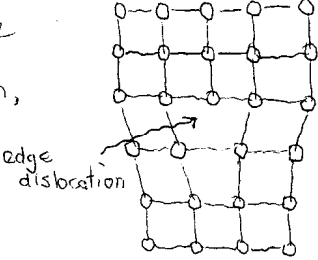
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Question 6 continued on the following page

Question 6 continued

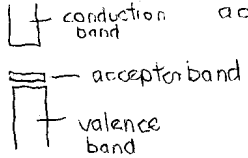
(ii) edge dislocation;

An edge dislocation is formed when there is a missing row (or plane) of atoms. In response to a shearing stress only one line of bonds needs to be broken,



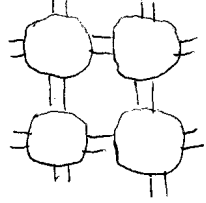
(iii) p-type semiconductor;

A semiconductor formed by doping an insulator with an element with fewer valence electrons eg Si (Gr 14) with In (Gr 13), leaving holes in the valence band. The holes form an acceptor band,



(iv) zeolite.

Zeolites are aluminosilicates (silica in which Si atoms are replaced by Al atoms). They are characterised by large holes or pores that lead to their use as molecular sieves and size-selective catalysts eg ZSM 5



TURN OVER

7. (16 marks)

- (a) The vapour pressure of ethanol and 1-propanol at 35°C are 100 Torr and 37.6 Torr respectively. 9.2 g of ethanol ( $M = 46.0 \text{ g mol}^{-1}$ ) and 18.0 g of 1-propanol ( $M = 60.0 \text{ g mol}^{-1}$ ) are mixed. Assuming that they form an ideal mixture, calculate:

(i) the mole fraction of 1-propanol in the mixture;

$$\begin{aligned} n_E &= 9.2 / 46.0 = 0.20 \text{ mol} \\ n_P &= 18.0 / 60.0 = 0.30 \text{ mol} \\ X_P &= n_P / (n_P + n_E) \\ &= 0.3 / (0.3 + 0.2) \\ &= 0.60 \end{aligned}$$

(ii) the vapour pressure of both ethanol and 1-propanol above the liquid mixture;

$$\begin{aligned} P_P &= X_P P_P^0 = 0.60 \times 37.6 = 22.56 \text{ torr} \\ X_E &= 1 - X_P = 1 - 0.60 = 0.40 \\ P_E &= X_E P_E^0 = 0.40 \times 100 = 40.0 \text{ torr} \end{aligned}$$

(iii) the total vapour pressure above the liquid mixture;

$$\begin{aligned} P_{\text{total}} &= P_P + P_E \\ &= 22.56 + 40.0 \\ &= 62.56 \text{ torr} \end{aligned}$$

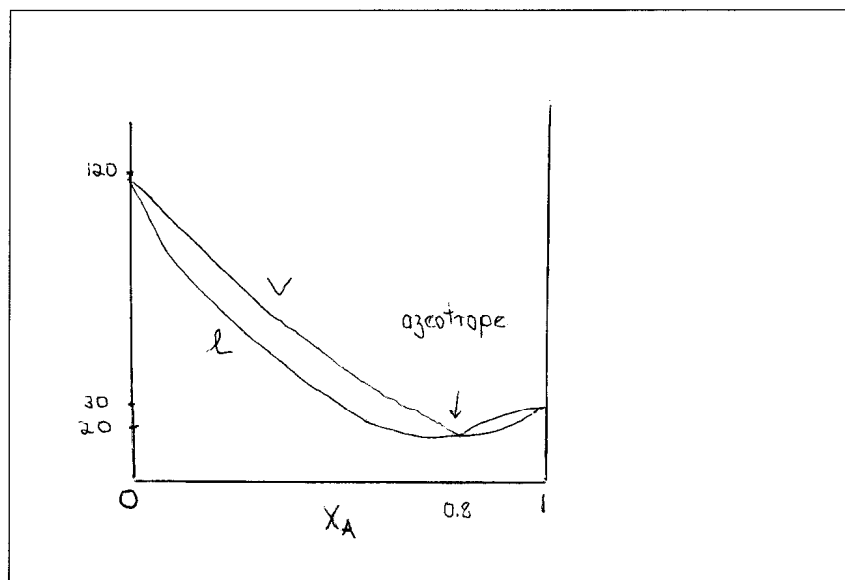
(iv) the composition of the vapour above the liquid mixture.

$$\begin{aligned} X_P^{\text{vap}} &= P_P / P_{\text{total}} = 22.56 / 62.56 = 0.36 \\ X_E^{\text{vap}} &= 1 - X_P^{\text{vap}} = 1 - 0.36 = 0.64 \end{aligned}$$

Question 7 continued on the following page  
TURN OVER

**Question 7 continued**

- (b) The boiling point of A is 30°C. The boiling point of B is 120°C. The boiling point of a mixture of A and B with composition  $x_A = 0.80$  is 20°C. The composition of the vapour above this mixture is also  $x_A = 0.80$ .
- (i) Draw the boiling point – composition ( $T-x_A$ ) diagram for a mixture of A and B showing the boiling points of mixtures of A and B and the composition of the vapour in equilibrium with the boiling mixtures. Label all curves.



- (ii) A mixture of A and B of composition  $x_A = 0.60$  is distilled in an efficient distillation column. What is the composition ( $x_A$ ) of the distillate (from the top of the column)? What composition does the liquid residue remaining in the bottom of the distillation still approach after a long time?

Distillate

0,80

Residue

0,0

- (iii) Is heat absorbed or given off when the two liquids are mixed? (Tick **one** box only)

Heat is absorbed

Heat is **NOT** absorbed**END OF PAPER**