

Mid Year Examination and Test Period 2007

Prescription Number(s):	CHEM 113
Paper Title:	Engineering Chemistry

Time Allowed: 2.5 HOURS

Number of pages: 18

FAMILY NAME:

Answer **ALL** questions

GIVEN NAMES:

Total marks = 120

STUDENT ID#:

NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

For examiners use only

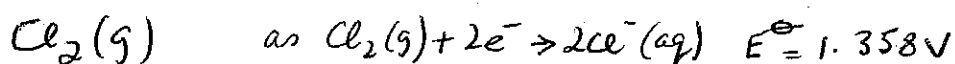
1	2	3	4	5	6	Total

1. (22 marks)

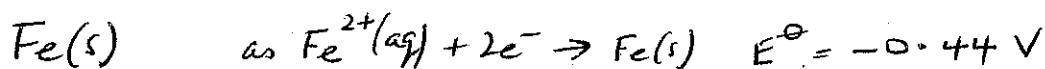
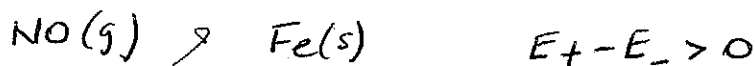
Use the following table of standard reduction potentials to answer the questions below:

<u>Reduction Half-reaction</u>	<u>E°/V</u>
(i) $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.358
(ii) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
(iii) $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
(iv) $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44

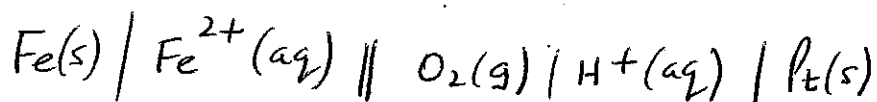
(a) Which of the species in the table is the strongest oxidising agent?



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

(c) Which of the species in the table will $\text{O}_2(\text{g})$ oxidise under acidic conditions?

(d) Write down the conventional cell diagram for a cell involving the oxygen and iron couples ((ii) and (iv) in the list above) which has a positive standard cell potential.



Question 1 continued on following page

Question 1 continued

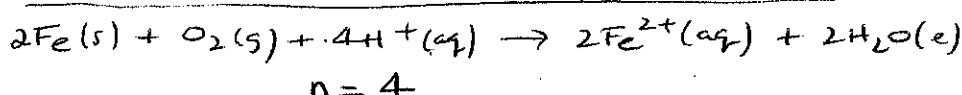
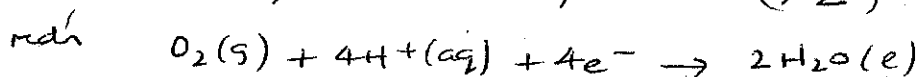
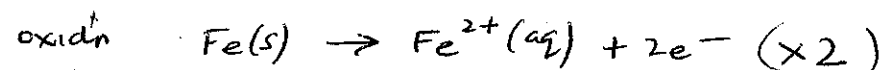
- (e) Calculate the standard cell potential for the cell in (d).

$$E_{\text{cell}}^{\ominus} = E_{+}^{\ominus} - E_{-}^{\ominus} = E_{\text{O}_2|\text{H}_2\text{O}}^{\ominus} - E_{\text{Fe}^{2+}|\text{Fe}}^{\ominus}$$

$$= 1.23 - (-0.44) = 1.67 \text{ V}$$

- (f) Calculate the standard free energy change,
- ΔG^{\ominus}
- , for the reaction of
- $\text{O}_2(\text{g})$
- with
- $\text{Fe}(\text{s})$
- in acid.

$$\Delta G^{\ominus} = -nFE^{\ominus}$$



$$\Delta G^{\ominus} = -4 \times 96485 \text{ C mol}^{-1} \times 1.67 \text{ V}$$

$$= -644.05 \text{ kJ mol}^{-1}$$

- (g) Calculate the thermodynamic equilibrium constant,
- K
- , for the reaction of
- $\text{O}_2(\text{g})$
- with
- $\text{Fe}(\text{s})$
- in acid.

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

$$-644500 = -8.314 \times 298 \times \ln K$$

$$\ln K = 2.6013 \times 10^2$$

$$K = e^{260.13}$$

ANS

$$E^{\ominus} = \frac{0.0591}{n} \log_{10} K$$

$$1.67 = 1.4775 \times 10^{-2} \log_{10} K$$

$$\log_{10} K = 1.1303 \times 10^2$$

ANS

Question 1 continued on following page

Question 1 continued

- (h) Write down the Nernst equation for an electrochemical cell in which the cell reaction is the reaction of $O_2(g)$ and $Fe(s)$ under acidic conditions.

$$E = E^\ominus - \frac{RT}{nF} \ln \frac{a_{Fe^{2+}}^2}{a_{O_2} a_{H^+}^4}$$

$$E^\ominus = 1.67V$$

$$n = 4$$

- (i) Describe one method of corrosion prevention and explain how it relates to the equation in part (h).

Galvanize with Zn, Zn more easily oxidized than Fe
as Zn acts as the anode and Fe as the cathode.

In above eqn: $a_{Fe^{2+}} \downarrow$

Also, with painting or Zn or Sn coating O_2 and H^+ cannot
react the surface and a_{O_2} & $a_{H^+} \downarrow$

2. (10 marks)

(a) Provide definitions of the following terms in the context of acid-base equilibria:

(i) A Brønsted acid

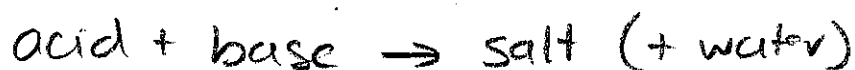
A proton donor

(ii) A Brønsted base

A proton acceptor

(iii) A salt

The product of a reaction between an acid and a base



(iv) A buffer solution

A solution that contains significant and comparable amounts of a weak acid-weak base conjugate pair. It can reduce the effect of added acid or base on the pH of the system

Question 2 continued on following page

Question 2 continued

- (b) A chemist discovers a new, water-soluble compound, exoticaine. A 1.5×10^{-6} mol L⁻¹ aqueous solution of exoticaine has a pH of 8.18. Circle, below, two words that best describe the acid-base properties of exoticaine:

STRONG

WEAK

ACID

BASE

$$pOH = -\log_{10} 1.5 \times 10^{-6} = 5.82$$

$$pH = 14 - pOH = 8.18$$

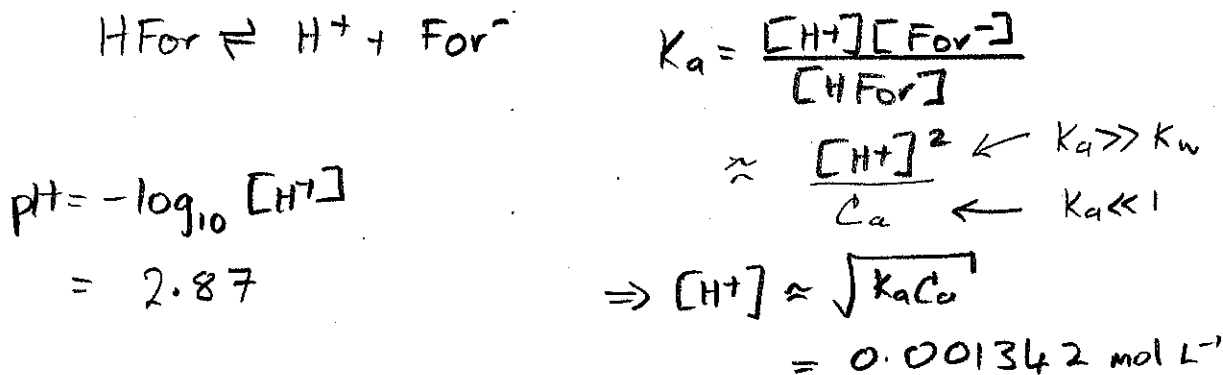
3. (18 marks)

Formic acid (HCOOH) is an organic compound with $K_a = 1.8 \times 10^{-4}$.

- (a) What is the
- pK_a
- of formic acid?

$$pK_a = -\log_{10} K_a = 3.74$$

- (b) What is the pH of a 0.0100 mol L
- ⁻¹
- solution of formic acid?



- (c) What is the
- pK_b
- of the formate anion (HCOO
- ⁻
-)?

$$pK_a + pK_b = 14$$

$$pK_b = 14 - pK_a$$

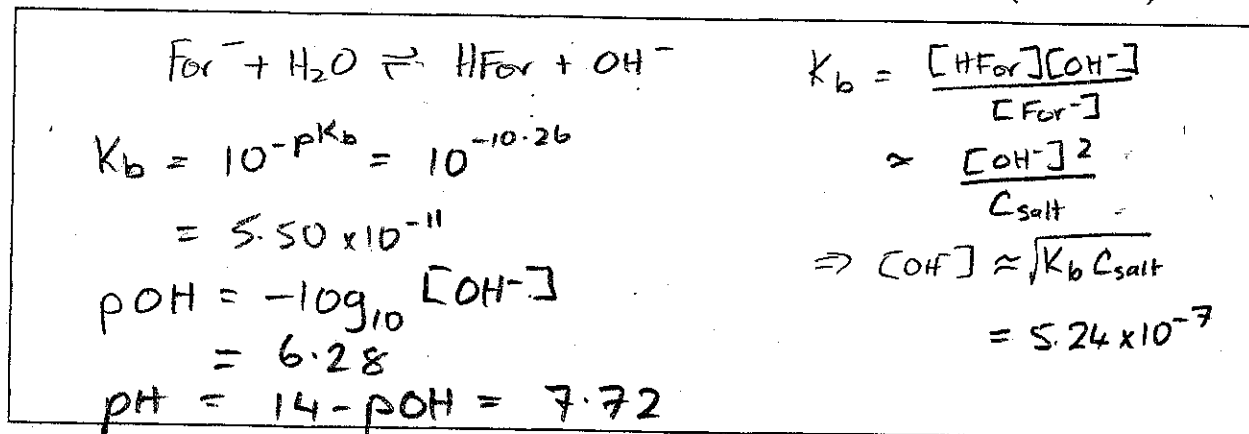
$$= 14 - 3.74$$

$$= 10.26$$

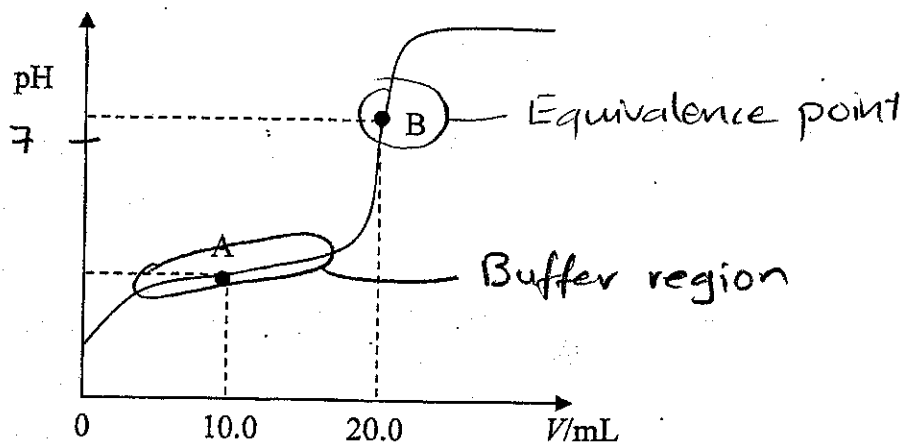
Question 3 continued on following page

Question 3 continued

- (d) What is the pH of a 0.0050 mol L⁻¹ solution of sodium formate (HCOONa)?



- (e) The plot below was obtained from a titration involving 0.0100 mol L⁻¹ solutions of formic acid and sodium hydroxide.



- (i) Tick the box that correctly describes the titration:

Formic acid solution is being added to sodium hydroxide solution

OR sodium hydroxide solution is being added to formic acid solution

- (ii) Indicate and clearly label the following on the above plot:

- The equivalence point
- The buffer region
- The approximate position of pH = 7 on the pH (y) axis

Question 3 continued on following page

Question 3 continued

- (iii) Using your answers to earlier parts of this question, what is the pH corresponding to point A of the plot? *Provide an explanation for your answer.*

$$\text{pH}_{1/2\text{eq}} = \text{p}K_a = 3.74 \quad \text{from (a)}$$

- (iv) Using your answers to earlier parts of this question, what is the pH corresponding to point B? *Provide an explanation for your answer.*

At equivalence we have a salt solution with a concentration of $C_a/V_{\text{total}} = 0.005 \text{ mol L}^{-1}$. So

$$\text{pH}_{\text{eq}} = 7.72 \quad \text{from (d)}$$

- (v) 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	$\text{p}K_a$ (indicator)
Bromophenol blue	3.8
Brilliant yellow	7.2
Thymolphthalein	10.0
2,4,6-Trinitrotoluene	12.3

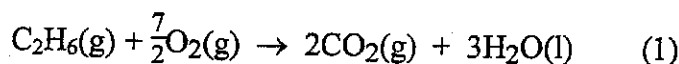
We want an indicator with

$$\text{p}K_a(\text{indicator}) \approx \text{pH}_{\text{eq}}$$

Best choice is brilliant yellow

4. (28 marks)

- (a) For the combustion of ethane (1), use the thermodynamic data given below to calculate the following parameters at 298 K. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{C}_2\text{H}_6(\text{g})$	-84.7	-32.8	unknown
$\text{O}_2(\text{g})$	0	0	+205.1
$\text{CO}_2(\text{g})$	-393.5	-394.4	+213.7
$\text{H}_2\text{O}(\text{l})$	-285.8	-237.2	+69.9

(i) ΔH°

$$\begin{aligned} \Delta H^\circ &= 2 \cdot \Delta H_f^\circ(\text{CO}_2) + 3 \cdot \Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{C}_2\text{H}_6) \\ &= 2(-393.5) + 3(-285.8) - (-84.7) \\ &= -1559.7 \text{ kJ mol}^{-1} \end{aligned}$$

(3 mark)

(ii) ΔG°

$$\begin{aligned} \Delta G^\circ &= 2 \cdot \Delta G_f^\circ(\text{CO}_2) + 3 \cdot \Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{C}_2\text{H}_6) \\ &= 2(-394.4) + 3(-237.2) - (-32.8) \\ &= -1467.6 \text{ kJ mol}^{-1} \end{aligned}$$

(3)

(iii) ΔS°

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \cdot \Delta S^\circ \\ \therefore \Delta S^\circ &= (\Delta H^\circ - \Delta G^\circ) / T \\ &= \frac{[-1559.7 - (-1467.6)] \times 1000}{298} \quad \left(\frac{\text{kJ}}{\text{mol}} \times \frac{\text{J}}{\text{kJ}} \times \frac{1}{\text{K}} \right) \\ &= \frac{-92.1 \times 1000}{298} = -309.1 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(3)

Question 4 continued on following page

Question 4 continued

(iv) S° for ethane ($C_2H_6(g)$)

$$\begin{aligned}\Delta S^\circ &= 2 \times S^\circ(CO_2) + 3 \times S^\circ(H_2O) - S^\circ(C_2H_6) - \frac{7}{2} \times S^\circ(O_2) \\ \therefore S^\circ(C_2H_6) &= 2 \times S^\circ(CO_2) + 3 \times S^\circ(H_2O) - \frac{7}{2} \times S^\circ(O_2) - \Delta S^\circ \\ &= 2 \times 213.7 + 3 \times 69.9 - \frac{7}{2} \times 205.1 - (-309.1) \\ &= +228.4 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

(4 marks)

(v) K (the thermodynamic equilibrium constant) at 298 K

$$\begin{aligned}\Delta G^\circ &= -RT \cdot \ln K \\ \therefore K &= \exp(-\Delta G^\circ / RT) \\ &= \exp\left\{\frac{+1467.6 \times 1000}{8.314 \times 298}\right\} \\ &= \exp(592.35) \quad (= 1.8 \times 10^{257})\end{aligned}$$

↖ Full marks to here ("calculator overflow") ↘

(4)

(vi) K at 400 K (assume that ΔH° and ΔS° are constant between 298 and 400 K)

$$\begin{aligned}\ln\left(\frac{K_2}{K_1}\right) &= \frac{\Delta H^\circ}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\} \quad \left(\begin{array}{l} T_1 = 298 \text{ K} \\ T_2 = 400 \text{ K} \end{array} \right) \\ \therefore \ln\left(\frac{K_{400}}{K_{298}}\right) &= \frac{-1559.7 \times 1000}{8.314} \left\{ \frac{1}{298} - \frac{1}{400} \right\} \\ &= -160.53 \\ \therefore K_{400}/K_{298} &= \exp(-160.53) = 1.92 \times 10^{-70} \\ K_{400} &= 1.92 \times 10^{-70} \times K_{298} \quad (= 3.44 \times 10^{187})\end{aligned}$$

(4)

Question 4 continued on following page

Full marks to here ("calculator overflow")

Question 4 continued

- (b) By considering the phase and number of moles of each reaction component in reaction (1), comment on the sign you have obtained for ΔS° .

Reactants comprise $1 + \frac{1}{2} = 4.5$ moles of gas
 Products " 2 moles of gas + 3 moles of liquid
 \therefore Lower total entropy expected as reaction proceeds
 because liquid phase is more ordered (than gas).
 $\therefore \Delta S^\circ$ expected to be NEGATIVE

(2 marks)

- (c) Calculate the changes of entropy of the surroundings ($\Delta S_{\text{surr}}^\circ$) and of the universe ($\Delta S_{\text{univ}}^\circ$) induced by reaction (1) under standard thermodynamic conditions.

$$\begin{aligned}\Delta S_{\text{surr}}^\circ &= \frac{\Delta H_{\text{surr}}^\circ}{T} = -\frac{\Delta H_{\text{system}}^\circ}{T} \quad (\text{1st Law}) \\ &= \frac{+1559.7 \times 1000}{298} \\ &= +5233.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta S_{\text{universe}}^\circ &= \Delta S_{\text{system}}^\circ + \Delta S_{\text{surr}}^\circ \\ &= -309.1 + 5233.8 = +4925 \text{ (J K}^{-1} \text{ mol}^{-1})\end{aligned}$$

(3)

- (d) Comment on the direction of spontaneous change for reaction (1) under standard thermodynamic conditions.

Under standard conditions: $\Delta G = \Delta G^\circ = -1467.6$
 (kJ mol⁻¹)
 This is a large NEGATIVE quantity
 therefore under standard conditions (all gas pressures
 at 1 atm + pure liquid H₂O) the reaction will
 proceed spontaneously in the FORWARD direction

(2)

5. (24 marks)

(a) Barium metal crystallizes in a body-centred cubic lattice. The density of the metal is 3.50 g cm^{-3} . Calculate the radius (**in pm**) of a barium atom.

$$M(\text{Ba}) = 137.3 \text{ g mol}^{-1}; N_A = 6.022 \times 10^{23} \text{ mol}^{-1}; 1 \text{ pm} = 10^{-12} \text{ m}.$$

$$\text{For 1 unit cell: } m = 2 \times 137.3 / 6.022 \times 10^{23}$$

$$= 4.56 \times 10^{-22} \text{ g}$$

$$V = m/\rho$$

$$= 4.56 \times 10^{-22} / 3.5$$

$$= 1.303 \times 10^{-22} \text{ cm}^3$$

$$= 1.303 \times 10^{-28} \text{ m}^3 \quad 1 \text{ cm} = 10^{-2} \text{ m}; 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

$$= 1.303 \times 10^{+8} \text{ pm}^3 \quad 1 \text{ m} = 10^{12} \text{ pm}; 1 \text{ m}^3 = 10^{+36} \text{ m}^3$$

$$\text{Cell side length } a = V^{1/3} = 506.9 \text{ pm}$$

$$\text{Cell diagonal length} = 4r = \sqrt{3}a$$

$$\text{Atomic radius } r = \sqrt{3}/4 a = 219.5 \text{ pm}$$

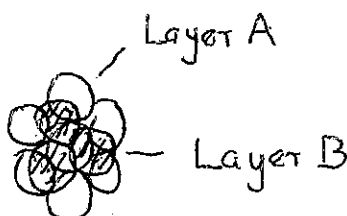
Question 5 continued on following page

Question 5 continued

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

(i) Hexagonal close-packed structure;

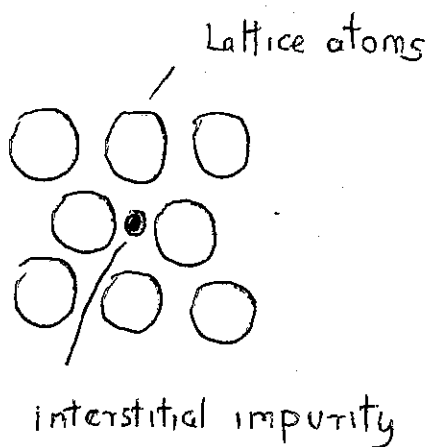
A close-packed arrangement, where an atom in a plane is surrounded by six other atoms in a hexagonal arrangement and the planes are stacked on each other in a ABABA arrangement i.e. the 3rd layer lies above the first layer. The second layer atoms lie over half the channels in the first layer.



(ii) interstitial impurity;

An atom or ion in a lattice which is:

- i) Not a lattice site – hence interstitial
- ii) A different species to the lattice atoms or ions

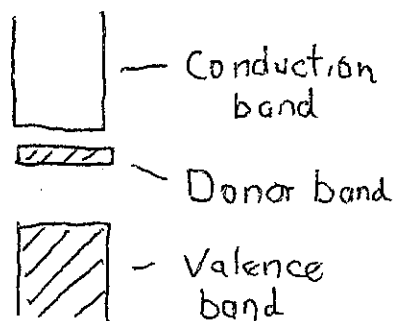


Question 5 continued on following page

Question 5 continued

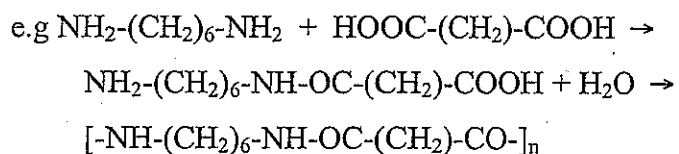
(iii) n-type semiconductor (give an **example** of an n-type semiconductor);

An n-type semiconductor is an insulator **doped** with an element with more valence electrons
e.g. **Si doped with As**. This gives rise to a **donor band** close to the conduction band

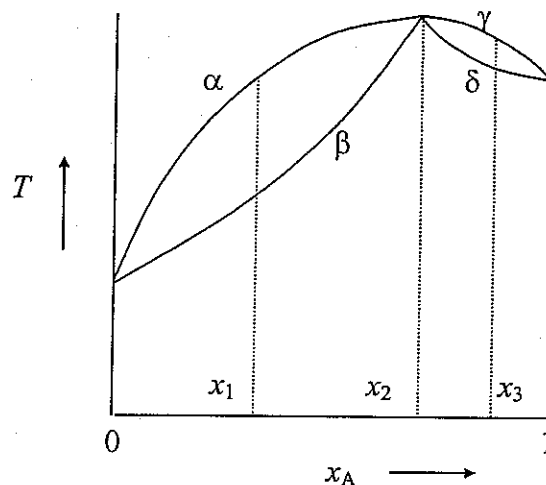


(iv) condensation polymer (give an **example** of a condensation polymer).

Polymer formed from 2 different monomers with different functional groups at the ends or a monomer with 2 different groups at the ends. The formation of the polymer involves the formation of a smaller molecule, usually water.



6. (18 marks)



The boiling point-composition ($T - x_A$) diagram for a mixture of A and B is given above.

- (a) Of the four curve segments labelled as α , β , γ and δ in the diagram above, which **two** segments indicate the composition of the **vapour**, in equilibrium with the liquid? (Tick **one** of the following boxes.)

α and β

β and γ

α and δ

β and δ

α and γ

γ and δ

- (b) Which pure liquid, A or B, would you expect to have the **higher** vapour pressure at a particular temperature? (Tick **one** of the following boxes.)

A

B

- (c) Which of the following occurs when the two liquids are mixed? (Tick **one** of the following boxes.)

Heat is absorbed
(endothermic process)

No heat is absorbed
or released

Heat is released
(exothermic process)

Question 6 continued on following page

Question 6 continued

- (d) What is the composition of the distillate formed when **each** of the following liquid mixtures is distilled in an efficient distillation column?

	liquid mixture	distillate composition
(i)	x_1	$x_A = 0$
(ii)	x_2	$x_A = x_2$
(iii)	x_3	$x_A = 1$

- (e) What is the composition of the residue left when **each** of the following liquid mixtures is boiled in an efficient distillation column until the boiling point is constant?

	liquid mixture	residue composition
(i)	x_1	$x_A = x_2$
(ii)	x_2	$x_A = x_2$
(iii)	x_3	$x_A = x_2$

Question 6 continued on following page

Question 6 continued

- (f) Ethanol and methanol form an ideal solution. At 293 K, the vapour pressure of ethanol is 44.5 Torr, and that of methanol is 88.7 Torr. Consider a mixture of these liquids where the mole fraction of ethanol is 0.60 and the temperature is 293 K.

- (i) Calculate the **partial** pressure of ethanol above the mixture.

$$\begin{aligned}
 p_E &= x_E p_E^\circ \\
 &= 0.60 \times 44.5 \\
 &= 26.7 \text{ Torr}
 \end{aligned}$$

- (ii) Calculate the **total** pressure above this mixture.

$$\begin{aligned}
 p_M &= x_M p_M^\circ & p_{\text{Total}} &= p_E + p_M \\
 &= (1 - x_E) p_M^\circ & &= 26.7 + 35.48 \\
 &= 0.4 \times 88.7 & &= 62.2 \text{ Torr} \\
 &= 35.48 \text{ Torr}
 \end{aligned}$$

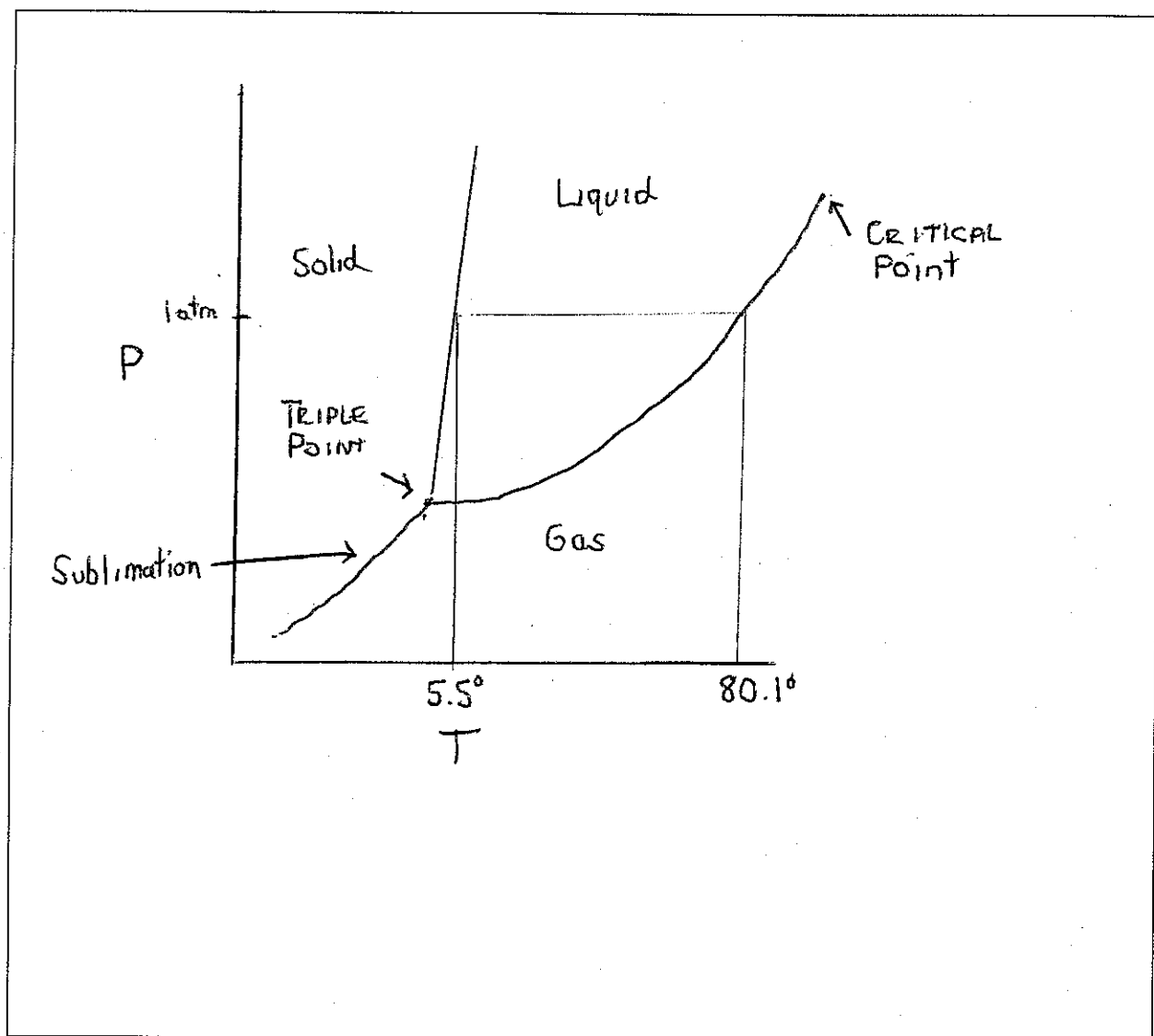
- (iii) Calculate the mole fraction of ethanol **in the vapour** above the mixture.

$$x_E^{\text{vap}} = p_E / p_{\text{Total}} = 26.7 / 62.2 = 0.429$$

Question 6 continued on following page

Question 6 continued

- (g) Sketch the p - T phase diagram for a pure substance (one-component) whose normal boiling point is 80.1°C and whose normal freezing point is 5.5°C .
- (i) Indicate on the diagram the positions of the triple point and the critical point.
- (ii) Indicate where sublimation would occur rather than melting or boiling.

**END OF PAPER**