PART A - STRUCTURED ESSAY

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Answer all four questions. Each question carries 10 marks.

1.	(a)	Con	sider	the follow	ing elen	nents of	the perio	dic table	and ans	wer the questions given below.
			H	11	111	$\mathbb{I}\mathbf{V}$	v	VI	VII	VIII
			Li	Be	В	C	N	O	F	Ne
		(i)	Whic	h elemen	t has the	e largest	atomic	radius?		
		(ii)	Which	h element	t has the	highes	melting	point?		
	(i	ii)	Which	element	has the	highest	second	ionizatio	n enthal	ру?
			••••••							
	(i	v) '	Which	elements	are cap	pable of	forming	a triple	bond b	etween its atoms?
						••••••	•••••			
	()	') \	Which	elements	do not	show a	any posit	ive oxid	ation sta	ites?
	<i>(</i>		n							
	(VI	, n	vnicn	elements	form c	ompoun	ds that a	ct as Le	wis acid	ls?
		••	•••••							(2·7 marks)
(b)	Giv	e or	e exp	erimental	evidenc	e in eac	ch case to	demons	trate the	discontinuous nature of matter:
	(i)	air	Ē,				••••••	··········		
	(ii)	wa	ter .							
			,	·····		•••••				
	(iii)	ап	netal.							
								•••••		(2·5 marks)
A	A diss	solve	es in a	e three c queous N s hydroly	NaOH so	olution.	E forms	a chlorid	e which	ne periodic table. The oxide of is a liquid at room temperature.
I	denti	fy A	A, D	and E by	y writin	g their	chemic	al symb	ols in tl	he space below:
	A	<u> </u>				D =	=			E =
										(2·4 marks)

[See page three

2,

...

Do not write anything in this column

(c) Two pure liquids A and B mix together at temperature T to give a homogeneous solution AB in which

$$f_{A-A} = f_{B-B} = f_{A-B}$$

where f_{X-Y} for example refers to the force of attraction between two molecules X and Y.

Two pure liquids B and C mix together at the same temperature T to give a homogeneous solution BC in which the force of attraction f_{B-C} is very slightly greater than f_{B-B} and f_{C-C} .

Some of the physical properties of liquids A, B and C together with the liquid quantities mixed to give the above mentioned solutions AB and BC are given in the table below:

Liquid	Number of moles mixed	Number of molecules mixed	Vapour pressure at temperature T	Relative molecular mass	Boiling point
A	x	d ·	J	M	U
B	у	e	K	L	v
С	z	f	j	N	W

The volume occupied by the vapour in equilibrium with each of the solutions AB and BC is S at the same temperature T. There are no intermolecular interactions between molecules in the vapour phase.

Universal gas constant = R.

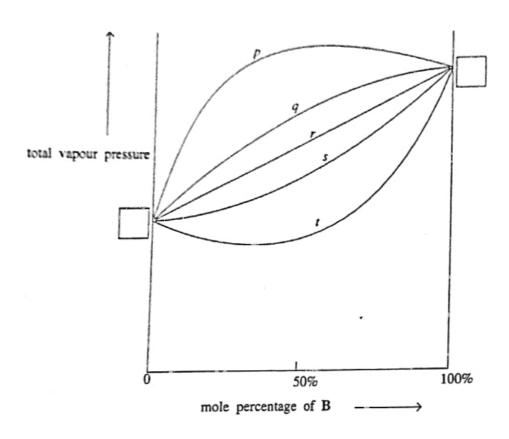
Using only symbols given above as may be necessary, (but using no other), answer the following.

- (i) Write down a mathematical expression for the Avogadro Constant.
- (ii) Write down in respect of the vapour phase in equilibrium with the solution AB, mathematical expressions for,
 - (I) the equilibrium vapour pressure of A
 - (II) the total equilibrium vapour pressure
 - (III) the total number of molecules
 - (IV) the ratio of the number of molecules of A and B
 - (V) the number of molecules of B
 - (VI) the mean square speed $\overline{c_{\mathbb{B}}^2}$ of \mathbb{B} molecules

(3.6 marks)

(iii) Possible variations of the total vapour pressure of binary liquid solutions containing B with the mole percentage of B in solution at temperature T are indicated as p, q, r, s and t in the phase diagram below.

Do not write anything in this column



(I) Identify the most appropriate variation p, q, r, s and t in the above diagram relevant to each of the following solutions by writing same in the appropriate space below.

Solution AB:

Solution BC:

(II) Mark in the two boxes of the above diagram, the appropriate symbols for the vapour pressures corresponding to 0% B and 100% B in both solutions AB and BC.

(1.6 marks)

 $\sqrt{\frac{100}{100}}$

3. (a) Consider the following:

Selecting relevant reactants and reagents from amongst those given above,

- (i) write down the mechanism for a nucleophilic addition reaction.
- (ii) write down the mechanism for an electrophilic substitution reaction.

(4-0 marks)

column

(b) Consider the scheme of reactions given below:

$$C_4H_8$$
 \xrightarrow{HBr} C_4H_9Br $\xrightarrow{aqueous\ NaOH}$ $C_4H_{10}O$

(A) ethanolic KOH (B) (C)

 H_2/Pt
 C_4H_{10}
(D)

Compound A exhibits geometric isomerism while compound B exhibits optical isomerism.

(i) Write down the structure of B.

Identify each of the carbon atoms in B which underwent a change in hybridisation in its formation from A. Mark these carbon atoms by drawing a circle around each of them in the structure of B written by you above.

- (ii) Strike out the incorrect terms/symbols within the brackets in the sentences given below. Note that these sentences refer to the carbon atoms circled by you in (i) above.
 - (I) The hybridisation changes from $\left[sp/sp^2/sp^3\right]$ in A to $\left[sp/sp^2/sp^3\right]$ in B.
 - (II) The geometry around the carbon atoms changes from [linear/planar triangular/tetrahedral/octahedral] in A to [linear/planar triangular/tetrahedral/octahedral] in B.

(iii)	Name	the	reaction	mechanism	that	operates	in	the	conversion	of
-------	------	-----	----------	-----------	------	----------	----	-----	------------	----

(I)	A		\mathbb{B}	:	

(II)	$\mathbb{B} \longrightarrow$	C:	
------	------------------------------	----	--

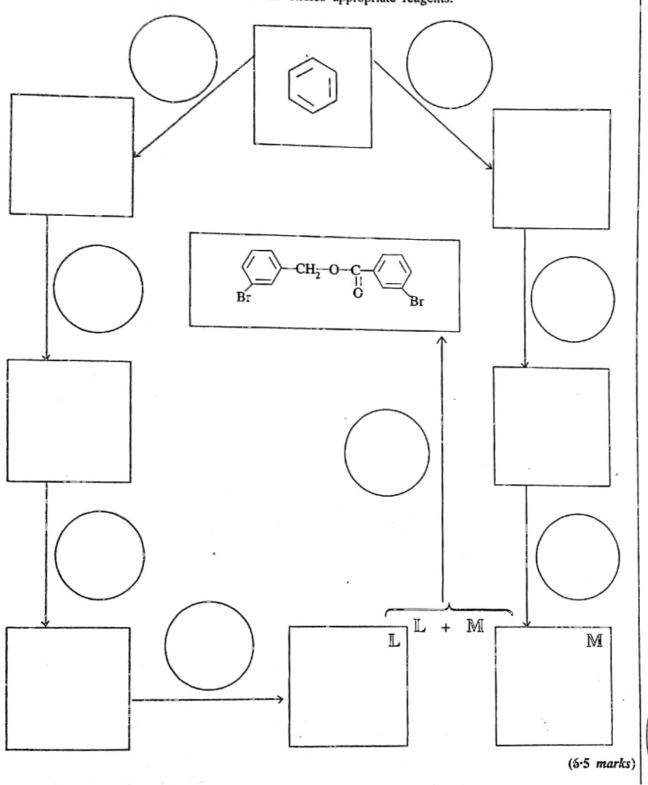
(3.0 marks) [See page seven

			4.40
	(6)	Citral is a colourless natural product	Do not write
			poythin in this
		CH, CoCH-CH, CH, CH, CH, CH,	column
		(i) From what plant can citral be industrially extracted in Sri Lanka?	
		Manager	
		(ii) Give the name of the technique used in the extraction of citral.	1
		Company of the Compan	
		(iii) Give one chemical test (with observation) in each case to show the presence of the following in citral:	
		(1) carbon carbon double bond	
		test	
		observation:	
		(il) aidehyde group	
		test :	
		observation:	
		(iv) Draw the stereoisomers of citral.	
		(v) Citral may be reduced to an alcohol E with relative molecular mass = 156. E exhibits	
		optical isomerism. Write down the structure of E.	
			100
		(3·0 marks)	100
4	(a)	A compound X (C ₅ H ₁₀ O ₅) on reaction with PCI ₅ gives a compound Y having a relative molecular	
•	(5)	mass of 205.5. Reaction of one mole of X with Na ₂ CO ₃ gives one mole of CO ₂ .	
		Calculate the number of alcoholic hydroxyl groups present in the compound X.	
		(C = 12.0; H = 1.0, O = 16.0; C1 = 35.5)	
		ı	

(3.5 marks)

(b) Using benzene as the starting material, show how you would synthesize the following compound

by completing the scheme given below. For this purpose, write in the boxes structures of appropriate compounds and in the circles appropriate reagents.



100

A STATE OF THE PROPERTY OF THE (උසස් පෙළ) විතාගය පොදු සහතික පතු கல்விப் பொதுத் தராதரப்பத்திர(உயர் தர)ப் பரீட்சை, 2003 ஏப்பிரல் General Certificate of Education (Advanced Level) Examination, April 2003 Sem proceeding & see Sem proceedings of may seembers & a value of as a ment of Examinations, So Larka Department Sem proceeding & see Sem proceedings of may seembers. රසායන විද**ත**ාව II ඉතා විශාව අතුව පත්වරවාදීම ඉත. විදුනු අතුව පත්වරවලි waster with may discontinuit ar very இரசாயனவியல் II Department of Examinations, Sri Lanka Department 1 mel fremsterne Sa saute of Ludes and the attendent & are the attend amount utimes formesome. Chemistry II Department of Examinations, Sri Lanka Departm

PART B - ESSAY

Answer two questions only. Each question carries 15 marks.

- (a) (i) Write down chemical equations for the reactions appropriate to each of the following statements relevant to 298 K.
 - (I) The standard electron gain enthalpy, ΔH_{EA}, of chlorine is 350 kJ mol⁻¹.
 - (II) The standard lattice energy, ΔH_L° , of sodium fluoride is -620 kJ mol⁻¹.
 - (III) The standard enthalpy of formation, ΔH_f° , of $H_2O(1)$ is -300 kJ mol⁻¹.
 - (IV) The standard enthalpy of formation, ΔH_f, of trinitrotoluene (TNT), C₇H₅N₃O₆(s), is -250 kJ mol⁻¹.
 - (V) The standard enthalpy of combustion, ΔH_c° , of $CH_4(g)$ is -800 kJ mol⁻¹.

(3-0 marks)

(ii) TNT can react with O2(g) according to the following equation.

$$2 C_7 H_5 N_3 O_6(s) + 8 O_2(g) \longrightarrow 3 N_2(g) + 5 H_2(g) + 14 CO_2(g)$$

For this reaction, the standard reaction enthalpy at 298 K is -2.550 kJ per mole of TNT.

Obtaining the necessary data from part (i) above, calculate the standard enthalpy of formation of CO₂(g) at 298 K.

(1.2 marks)

(iii) In the presence of sunlight and a suitable catalyst A, CH₄(g) reacts with CO₂(g) according to the equation

$$CH_4(g) + CO_2(g) \xrightarrow{hv} 2CO(g) + 2H_2(g)$$

with a standard enthalpy change of x kJ at 298 K.

The standard enthalpy change for the reaction,

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

at 298 K is 125 kJ.

Calculate the value of x using the necessary thermochemical data given/calculated in parts (i) and (2.5 marks)

(iv) The products of the catalysed reaction given in part (iii) above may be reacted under different conditions and over a different catalyst B according to the equation

$$2CO(g) + 2H_2(g) \longrightarrow CH_4(g) + CO_2(g)$$

to yield the starting materials once again. This sequence of reactions may be used to convert solar energy into heat energy.

Give two advantages of such a cyclic process over the coal combustion process for the production of heat to generate electric power in Sri Lanka.

(2**-0** marks)

(v) TNT, which is used as an explosive detonates according to the equation

$$2C_7H_5N_3O_6(s) \longrightarrow 3N_2(g) + 7C(s) + 7CO(g) + 5H_2O(l)$$

with a standard enthalpy change of -850 kJ per mole of TNT. Use some of the data given in part (i) above to calculate the standard enthalpy of formation of CO(g) at 298 K.

(1.3 marks)

(b) N₂O₅(g) decomposes according to the equation,

$$2 N_2 O_3(g) \longrightarrow 4 NO_2(g) + O_2(g)$$
.

The reverse reaction can be neglected at 400 K.

The order of the above reaction, with respect to $N_2O_5(g)$, was determined by placing a mixture of $N_2O_5(g)$ and an inert gas in an evacuated bulb of volume 8.314 dm³, maintained at 400 K and measuring the pressure of the gas mixture as a function of time (t).

- (i) Using the data given in the following table, calculate,
 - (I) the amount of N₂O₅(g) reacted after 5s in each of the experiments A and B given below.
 - (II) the order of the reaction with respect to N₂O₅(g), assuming that the time taken for the reactant to reach 400 K is negligible.

State any other assumptions you make.

Experiment	Contents of	Total pressure (in Pa) inside the bulb	
	N ₂ O ₅ (g)/mol	inert gas/mol	at $t = 5 s$
A	0.125	0-125	1·012 × 10 ⁵
B	0.250	0-125	1·524 × 10 ⁵

- (ii) Explain, in molecular terms, the effect of increase in pressure of N₂O₅(g), at a constant temperature, on the rate of the above reaction.
- 6. (a) Write down balanced equations for all theoretically possible half reactions that could occur when a dilute aqueous solution of CuCl₂ is electrolysed using inert electrodes.

In each case mention whether the half reactions occur at the cathode or the anode.

(3-0 marks)

3)

(b) (i) When SO₂(g) dissolves in water, the following equilibrium is established.

$$SO_2(g) \longrightarrow SO_2(aq)$$

Write down an expression for the equilibrium constant, K_c , for this process.

Also write down balanced chemical equations and expressions for the relevant equilibrium constants, K_c , to represent all the other equilibria that exist in the above solution.

- (ii) Compare qualitatively the pH of a SO₂(aq) solution with that of pure water.

 Predict, giving reasons, what would happen to the pH of an aqueous solution of SO₂ when it is aerated by bubbling air through it.
- (iii) Giving reasons in brief, name one chemical substance in each case that you would add to a solution of SO₂ in water to
 - (I) increase the concentration of SO₂(aq).

(II) decrease the concentration of SO₂(aq).

(4.0 marks)

A gaseous compound A dissociates at temperatures above 10 °C giving gaseous products B and D and reaches the equilibrium represented by the equation

$$A(g) \rightleftharpoons B(g) + D(g)$$

- (i) Write down expressions for K_p and K_c for the above equilibrium. Derive the relationship between K_p and K_c mentioning any assumptions you make. Identify the terms in that relationship.
- (ii) An elastic balloon is filled by introducing 6.5 mol of He(g) and 2.0 mol of A(g) at a temperature below 5°C. The system is next allowed to reach the equilibrium given above at 27°C. Under these conditions it is found that the total pressure inside the balloon is 1×10^5 Pa, and the balloon contains 0.5 mol of A(g).

Calculate K_p and K_c at 27 °C for the above equilibrium. (Express the value of K_c in mol dm⁻³).

- (iii) The balloon referred to in (ii) above is then released to rise in the atmosphere. At a certain altitude when the temperature inside the balloon is 17°C, it was found that the total pressure in it is 4.9×10^4 Pa and the partial pressure of He(g) is 3.5×10^4 Pa. Calculate K_p for the above equilibrium at 17°C.
- (iv) Considering the equilibrium mole fractions of A(g), B(g) and D(g) at 27°C and 17°C in (ii) and (iii) respectively, deduce whether the forward reaction is exothermic or endothermic.
- (v) Consider the equilibrium existing at 27 °C in (ii) above. Assume that the system takes 10 minutes to reach equilibrium at this temperature. More D(g) is next introduced into the equilibrium system. State, giving reasons, the changes that would happen to the volume of the balloon within the first 15 minutes from the time of introduction of D(g).
- 7. (a) At a certain temperature the concentration of each salt NaCl and K₂CrO₄ in a given aqueous solution is 0.01 mol dm⁻³. An aqueous solution of 0.1 mol dm⁻³ AgNO₃ is slowly added into this solution. The solubility products of AgCl and Ag_2CrO_4 at this temperature are $1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ and $1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$ respectively.
 - (i) Deduce which of the salts AgCl or Ag2CrO4 will be precipitated first from the solution.
 - (ii) At the instant the second silver salt just begins to precipitate, calculate the concentration of the anion of the silver salt that precipitated first which still remains in the solution.
 - (iii) State the most important assumption you used during the above calculations. (5.0 marks)
 - (b) A weak monobasic organic acid HA is soluble in both solvents, water and CHCl₃. 500·0 cm³ of a solution of HA in CHCl₃, in which the concentration of HA is 0.057 mol dm⁻³, is shaken well with 500.0 cm3 of water and allowed to attain equilibrium at 27°C. An aqueous layer and CHCl3 layer then separate out; the pH of the aqueous layer is found to be 3.21 under these conditions.

The dissociation constant of HA in water at 27°C is 1 × 10⁻⁵ mol dm⁻³.

- (i) Calculate the partition coefficient at 27 °C for the partitioning of HA between water and CHCl₃.
- (ii) In a second experiment, a further 500·0 cm³ portion of the same HA solution in CHCl₃ in which the concentration of HA is 0.057 mol dm⁻³, is shaken well with 500.0 cm³ of a 0.027 mol dm⁻³ aqueous NaOH solution and allowed to reach equilibrium at 27 °C.

Calculate the pH of the aqueous layer under these conditions.

- (iii) State the assumptions you make, if any, in the above calculations.
- (iv) An organic amine and a carboxylic acid which are both solids, are soluble in water and CHCl3. An aqueous solution containing this amine and the acid is provided. Suggest a method of separation, using CHCl₃ for extraction and any other reagents required, to obtain samples of the pure amine and the pure acid.
- (c) Marine life depends on oxygen dissolved in sea water. This oxygen comes from air and the following equilibrium exists between oxygen in air and in sea water.

$$O_2(g) \longrightarrow O_2(aq)$$

It has been found that a major portion of the oxygen in sea water comes from the cold currents from the Antarctica (southern pole region) spreading through the oceans.

Using your knowledge of equilibria, explain the above observation.

(2.0 marks)

[See page twelve

PART C - Essay

Answer two questions only. Each question carries 15 marks.

& (a) X is an element with atomic number less than 40. Some properties relevant to X are given below.

Maximum oxidation state	+5
Electrical conductivity	Comparable to that of Al
Highest oxide	Weakly acidic
Density	6·1 g cm ⁻³

- (i) To which block of elements does X belong?
- (ii) Write down the chemical symbol of X.
- (iii) Write down the complete electronic configuration of X.
- (iv) Write down the chemical formula of the highest oxide of X.
- (v) Write down one industrial use of the highest oxide of X.
- (vi) What are the other oxidation states, if any, shown by X?

(4-2 marks)

- (b) How would you identify the compounds in each of the following groups (i) (iv), using only the method specified for each group.
 - (i) (NH₄)₂CO₃(s) Ag₂CO₃ (s) Na₂CO₃ (s)

by heating

(ii) Pb(NO₃)₂ solution dilute HCl dilute H₂SO₄

by mixing the solutions pair-wise followed by heating.

(iii) CH₃COONH₄ solution (NH₄)₂SO₄ solution Ca(OH)₂ solution

by using the blue litmus paper provided to you.

(iv) 0·1 mol dm⁻³ Na₂S₂O₃ solution 0·5 mol dm⁻³ Na₂S₂O₃ solution 0·5 mol dm⁻³ HCl solution

by mixing the solutions pair-wise.

(6.0 marks)

- (c) (i) H₂O₂ decomposes into H₂O and O₂ on heating. Write down a balanced chemical equation for this reaction and indicate the changes in the oxidation state of oxygen(O).
 - (ii) H₂O₂ reacts in acidic medium converting Sn²⁺ ions to Sn⁴⁺ ions. O₂ is not evolved in this reaction.
 Write down the relevant oxidation reduction half reactions.
 - (iii) H₂O₂ reacts in acidic medium converting Ag₂O to Ag metal. O₂ is evolved in this reaction. Write down the relevant oxidation reduction half reactions.
 - (iv) 100·0 cm³ of a 0·1 mol dm⁻³ H₂O₂ solution is reacted with 50·0 cm³ of 0·1 mol dm⁻³ Sn²+ ion solution in acid medium. The resultant solution is then reacted with excess Ag₂O.
 Calculate the number of moles of O₂ produced.

(4.8 marks)
[See page thirteen

(a) has crystallised out from sea water (bittern), contains significant concentrations of Cl and Br ions.

- (i) Using sea water as the only source of raw/starting materials and no other, and using your knowledge only required).
 (In your answer, wherever possible, reference should be made to established industrial processes and the conditions used.)
- (ii) Consider any three chemicals produced in the process proposed by you in fi).
 Write down one industrial use for each such chemical excluding its use in the proposed process.
- (iii) Mention two economic and two environmental considerations that should be taken into account in setting up such an industry in Sri Lanka.

(5-1) marks)

(b) A mixture contains of the sulphides of two metallic elements A and B only. The following tests were performed with the mixture and the observations made are given below.

	Test	Observation
(i)	Dissolved the mixture in dilute HCl and boiled the solution with a few drops of conc HNO ₃ until the evolution of gas ceased.	A clear solution was obtained on cooling
(ii)	Added NH ₄ C! and excess of NH ₄ OH to solution from (i).	A precipitate was formed.
(iii)	The precipitate from (ii) was washed with water, dissolved in dilute HCl and shaken with. KI and CHCl ₃ .	CHCl ₃ layer turned violet.
(iv)	Added (NH ₄) ₂ CO ₃ to filtrate from (ii).	A white precipitate was formed.
	discolved in dilute	A yellow precipitate was formed.

Identify the elements A and B, giving as completely as possible, the inferences you can make from each of these tests.

(5.0 marks)

(c) Hardness of water is usually expressed in terms of mg dm⁻³ CaCO₃, using the following relationship:

these of water is usually expressed in terms of mg dm
$$^{\circ}$$
 CaCO₃, using the following Hardness
(in mg dm $^{\circ}$ CaCO₃) =
$$\begin{cases} \text{Concentration of } \\ \text{Ca}^{2+} \text{ and/or Mg}^{2+} \\ \text{ions / mol dm}^{-3} \end{cases} \times \begin{cases} \text{Relative molecular mass} \\ \text{of CaCO}_3 \end{cases} \times 10^3$$

A water sample contains the compounds Mg(HCO₃)₂, Ca(HCO₃)₂, CaSO₄, MgCl₂ and NaCl dissolved in it.

- (i) Identify the compound(s) responsible for temporary hardness.
- (ii) Identify the compounds(s) responsible for permanent hardness.
- (iii) State two problems in everyday life that arise due to hardness of water,
- (iv) The above water sample was analysed in the following manner to determine its hardness.
 - (A) 100 0 cm³ of water sample required 16 0 cm³ of 0 02 mol dm⁻³ HCl for complete neutralization using methyl orange as the indicator.
 - (B) 200·0 cm³ of the water sample was boiled with 18·0 cm³ of 0·05 mol dm⁻³ Na₂CO₃ solution, filtered and the filtrate diluted to 250 0 cm³ with distilled water in a volumetric flask. 50·0 cm³ of this solution required 14·0 cm³ of 0·02 mol dm⁻³ HCl for complete neutralization using methyl orange as the indicator.

Calculate the temporary hardness and the permanent hardness of the water sample and express them as mg dm⁻³ CaCO₃.

$$(Ca = 40.0; C = 12.0; O = 16.0)$$
 (5.0 marks)
[See page fourteen]

- (a) (i) Give the chemical formulae and the names of two minerals used to extract iron, using the blast furnace.
 - (ii) What are the other materials required to extract iron by this process?
 - (iii) Indicate the role of the materials mentioned by you in (ii).
 - (iv) What are the reducing agents involved in this process?
 - (v) Indicating the relevant temperatures, write down the balanced chemical equations for the reactions occurring in a blast furnace.
 - (vi) Write down three ill-effects on the environment due to the use of a blast furnace.

 (4-8 marks)
 - (b) Some chemical compounds relevant to the polymer industry are listed below.

HCHO, HOCH₂CH₂OH,
$$CF_2 = CF_2$$
, $COCI$ CH_3 $CH_2 = CH = CH_2$ $COCI$

Considering only the polymers manufactured from one or more of these compounds, answer the following questions.

- (i) Give the names of four commonly used polymers.
- (ii) Give one use of each of the four polymers you have mentioned in (i).
- (iii) Draw the structure of a repeat unit of the polymer which is most resistant to heat.
- (iv) Draw the structure of a repeat unit of a polymer having the highest elasticity.
- (v) Give one example of a thermosetting polymer.

(5.0 marks)

(c) A solution B contains CrO_4^{2-} and SO_4^{2-} ions. The following procedure was employed to determine the concentrations of these ions.

25.0 cm³ of solution B was reacted with excess $Pb(NO_3)_2$ solution to completely precipitate CrO_4^{2-} and SO_4^{2-} ions as $PbCrO_4$ and $PbSO_4$. The mass of the precipitate so obtained after drying was 0.929 g. This precipitate was then treated with excess dilute HCl and excess aqueous KI solution. The liberated I_2 required 30.0 cm³ of 0.1 mol dm⁻³ $Na_2S_2O_3$ solution for complete reaction.

Calculate the concentrations of CrO_4^{2-} and SO_4^{2-} ions in solution B.

(Pb =
$$.207.0$$
; Cr = $.52.0$; S = $.32.0$; O = $.16.0$)

(5.2 marks)