2013 MI PU3 H2 CHEMISTRY PRELIM II PAPER 3 SOLUTIONS

1. (a) State and explain in terms of electronic structure, **two** characteristic chemical properties of transition metals or their compounds.

- Transition metal ions possess variable oxidation states; variable number of 4s and 3d electrons can be removed to form ions of similar stability.
- Transition metal ions form complexes; the ions have energetically accessible vacant orbitals to accommodate the lone pair of electrons from ligands to form dative bond which results in the formation of complexes.
- Transition metals have catalytic properties; transition metals and their compounds are good heterogeneous catalyst because of the vacant and availability of d orbitals for temporary bond formation OR Transition metals and their compounds are good homogenous catalyst because of their ability to exist in variable oxidation states.

Any two
1m for each characteristic with 1m for each complete matching explanation

[4]

(b) Transition element complexes such as those of iron are common reagents in colourful demonstrations of redox reactions. In one particular demonstration, the following observations were made.

When aqueous iron(III) sulfate was added to aqueous sodium iodide, the reaction mixture turned brown. The brown colour is discharged upon addition of aqueous sodium hexacyanoferrate(II), $Na_4Fe(CN)_6$.

On the other hand, when aqueous sodium hexacyanoferrate(III), $Na_3Fe(CN)_6$, was added to a fresh sample of the aqueous sodium iodide, the colour of the reaction mixture remained unchanged.

(i) Explain the above observations using relevant data from the Data Booklet.

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77$ V

$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\theta = +0.36$ V

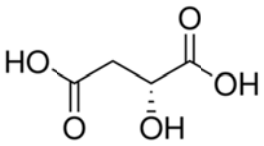
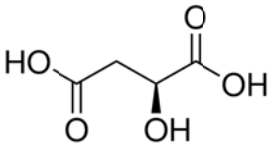
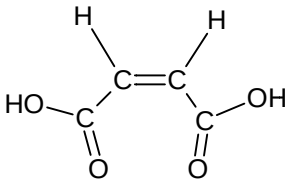
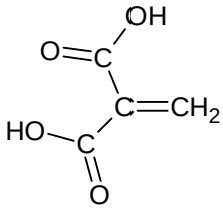
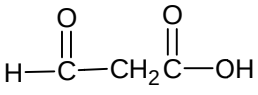
$\frac{1}{2} I_2 + e^- \rightleftharpoons I^-$ $E^\theta = +0.54$ V

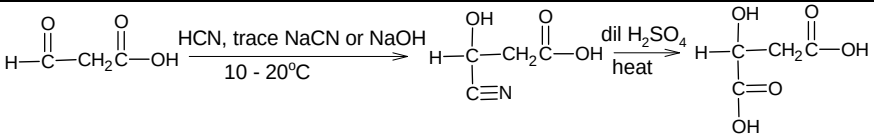
When Fe^{3+} is added to I^-, the oxidation of I^- to brown I_2 by Fe^{3+} is feasible.
$\Rightarrow E^\theta_{cell} = +0.23$ V ($E^\theta_{cell} > 0$; reaction is feasible)

			When $[Fe(CN)_6]^{4-}$ is added to I_2, brown I_2 is reduced to I^-. $\Rightarrow E^\theta_{cell} = +0.18$ V ($E^\theta_{cell} > 0$; reaction is feasible) The oxidation of I^- to brown I_2 by $[Fe(CN)_6]^{3-}$ is not feasible. $\Rightarrow E^\theta_{cell} = -0.18$ V ($E^\theta_{cell} < 0$; reaction is not feasible) *1m for quoting all 3 correct E^θ* from Data Booklet *1m for each calculation of E^θ_{cell} to explain observation*
		(ii)	Comment on the relative stability of the different oxidation states of iron in the presence of different ligands.
			Since the E^θ (Fe^{3+}/Fe^{2+}) is more positive compared to the E^θ ($[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{2-}$), in the presence of the CN^- ligand, Fe^{3+} is stabilised with respect to Fe^{2+}. *1m for complete answer*
			[5]
	(c)	Haemoglobin (Hb) is composed of 4 polypeptide chains: two alpha chains and two beta chains of polypeptides. Each chain contains one haem group, each of which contains one iron ion. The iron is the site of oxygen binding; each iron can bind one O_2 molecule thus each haemoglobin molecule is capable of binding a total of four O_2 molecules. The iron–oxygen interaction is very weak; the two can easily be separated without damaging the haem unit or the oxygen molecule. The binding of an oxygen molecule to the iron in a haem unit is therefore completely reversible.	
		(i)	Explain how O_2 molecule binds to the Fe of the haem group.
			Oxygen contains lone pairs which can coordinate to the centre Fe ion through coordinate (or dative) bonding. 1m for explanation
		(ii)	Each Hb molecule has a *complex quaternary structure*. Briefly describe what this means.
			• The quaternary structure refers to the three dimensional structure of proteins consisting of more than one polypeptide chain coming together to form the complete protein. • The structure is stabilized by R group interactions such as hydrogen bonding, disulphide bridges, van der Waals' forces and ionic linkages. *1m for each point*

		(iii)	A haemoglobin molecule in which the iron has separated from the oxygen molecule is called *deoxyhaemoglobin*. Blood containing red-blood cells filled with O_2 is brighter red. Suggest an explanation for the observation of this colour.
			When O_2 binds to Fe ion centre, the light-absorbing property of the heme group is changed due to the change in structure. Oxyhaemoglobin absorbs light in the blue-green range, and reflect red light. *1m for correct answer*
		(iv)	Haemoglobin is susceptible to denaturation. Explain the term *denaturation* as applied to proteins and state two types of R group interactions that can be disrupted when heat is applied to proteins.
			Denaturation is a process where the original conformations of secondary, tertiary and quaternary structures are destroyed through the breaking of non-covalent interactions and disulfide linkages. ; Van der Waals' or hydrophobic interactions ; hydrogen bonds ;
			[7]
	(d)	Iron(II) ethanedioate, FeC_2O_4, reacts with manganate(VII), MnO_4^-, forming Fe^{3+} and carbon dioxide. In an experiment, 0.144g of FeC_2O_4 reacted with 20.0 cm^3 of 0.150 mol dm^{-3} of MnO_4^-.	
		(i)	Write an ion-electron equation for the oxidation of FeC_2O_4 to Fe^{3+} and carbon dioxide.
			$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2 + 3e$;
		(ii)	Determine the oxidation number of manganese in the product formed after the reduction of manganate(VII).
			amount of FeC_2O_4 = 0.144/(55.8 + 24.0 + 64.0) = 0.001001 mol amount of e = 3 × 0.001001 = 0.003003 mol ; amount of MnO_4^- = 0.020 × 0.150 = 0.00300 mol 1 mol of MnO_4^- takes in 1 mol of e ; oxidation no. of Mn in product = +7 – 1 = +6 ;
			[4]
			[Total: 20]

2.	**(a)**	Malic acid is an organic dicarboxylic acid found in wines, sour apples and some other fruits. Malic acid has two stereoisomeric forms as shown

		below:  D-Malic acid  L-Malic acid	
		(i)	State a characteristic difference between D- and L-Malic acid.
			The enantiomers rotate plane-polarized light in opposite direction? D. Do not accept 'They are mirror image of each other.'
		(ii)	With the aid of a diagram, explain why malic acid is soluble in water.
			1m for diagram showing at least one hydrogen bond formed between malic acid and water, with partial charges and lone pair shown. 1m for stating hydrogen bond
		(iii)	Malic acid can be dehydrated to give compound **K**. Compound **L** is an isomer of compound **K**.  compound **K**  compound **L** State the type of isomerism exhibited.
			Structural isomerism ;
		(iv)	Compound **L** in **(a)(iii)** decolourises acidified potassium manganite(VII). Draw the structure of the organic product.
			$CO(COOH)_2$;
		(v)	The structure of 3-oxopropanoic acid is shown below.  3-oxopropanoic acid Suggest how you can make malic acid from 3-oxopropanoic acid in **two** steps, showing the reagents and conditions necessary as well as the structure of the intermediate.



1m for each set of reagents and conditions
1m for intermediate

[8]

(b) A student carried out an experiment to investigate the rate of reaction between sodium and malic acid. A freshly cut piece of sodium weighing 0.0690 g was added to a large excess of malic acid.

The volume of gas evolved was measured at room temperature and pressure over a 30-min time interval. The following results were obtained.

Time /min	0	5	10	15	20	25	30
Volume of gas /cm^3	0.0	8.5	15.0	20.5	25.0	27.5	31.0

(i) Write a balanced equation for the reaction between sodium and malic acid.

$(COOH)CH(OH)CH_2COOH + 3Na \rightarrow (COO^-Na^+)CH(O^-Na^+)CH_2COO^-Na^+ + 3/2\ H_2$;

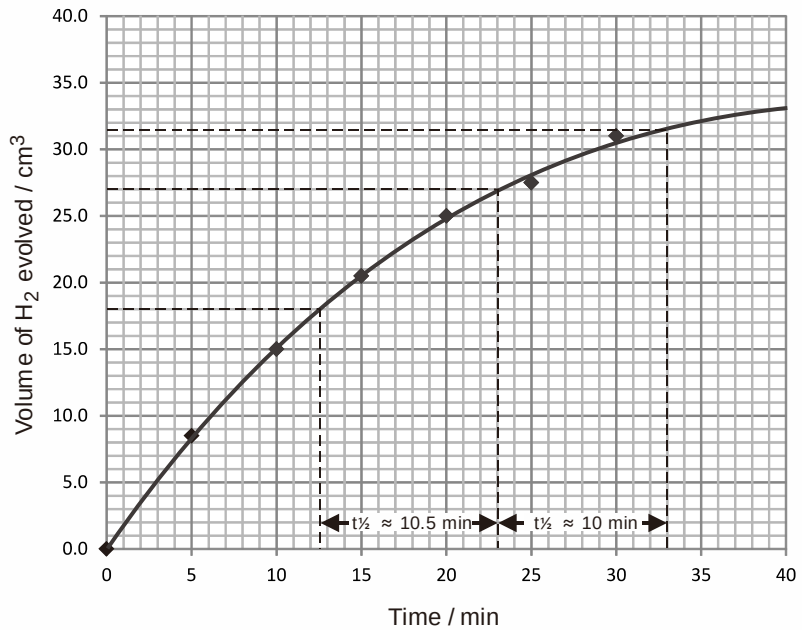
(ii) Calculate the maximum volume of gas evolved at room temperature and pressure if the reaction goes to completion.

amount of Na = 0.0690/23 = 0.00300mol
amount of H_2 = 0.00300/2 = 0.00150 mol
vol of H_2 = 0.00150(24) = 0.036 dm^3 = 36.0 cm^3 ;

(iii) What do you understand by the term *order of reaction*?

The order of reaction is defined as the power to which the concentration of the reactant is raised to in the experimentally determined rate equation. ;

(iv) Using the graphical method, show that the overall kinetics of the reaction is first order.



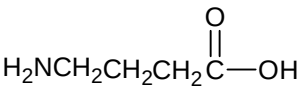
1m Graph correctly plotted with labeled axes
1m to show 2 half lives on graph
1m to conclude that since half lives are constant, first order

(v) In this experiment, the kinetics appears to be zero order with respect to malic acid initially. Suggest a reason for this.

malic acid is in large excess, hence the change in its concentration is negligible. Therefore its concentration does not seem to affect the rate. ;

[7]

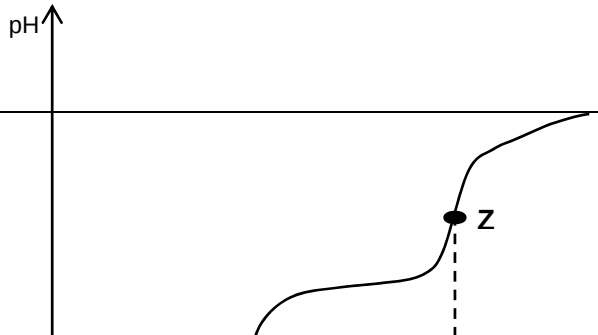
(c) 4-aminobutanoic acid, also known as GABA, can also be synthesised from 3-oxopropanoic acid in a few steps.



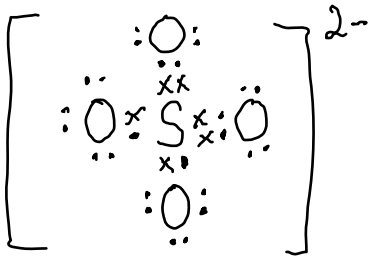
GABA

The two pK_a values associated with 4-aminobutanoic acid are 4.23 and 10.43.

A sample of GABA requires 20 cm^3 of 1.0 mol dm^{-3} NaOH for complete neutralisation. The following diagram is a titration curve, showing how the pH of GABA changes with volume of NaOH added.



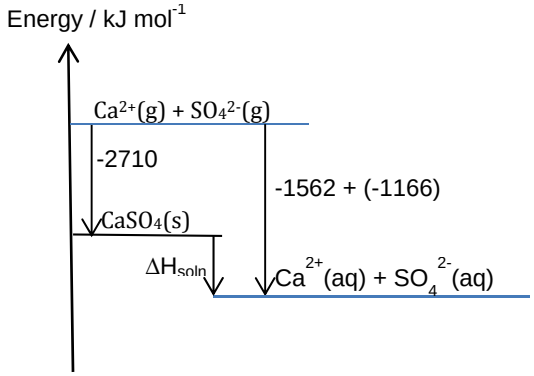
		(i)	Draw the structures of the predominant species of GABA at **X**, **Y** and **Z**.
			X: $H_3N^+CH_2CH_2CH_2COOH$ **Y**: $H_3N^+CH_2CH_2CH_2COO^-$ **Z**: $H_2N\ CH_2CH_2CH_2COO^-$ 1m each structure
		(ii)	State the pH and the volume of NaOH added when **Y** and **Z** are equimolar.
			pH = 10.43 ; vol = 15 cm^3 ;
			[5]
			[Total: 20]

3.	**(a)**	Calcium is a mineral that is found naturally in foods. Calcium is necessary for many normal functions of the body, especially bone formation and maintenance. Calcium sulphate, $CaSO_4$, is a salt of calcium. It is used as a coagulant in products like tofu.	
		(i)	Draw the dot-and-cross diagram to show the bonding in sulfate ion. State the shape and the bond angle.
			 tetrahedral 109.5°

1m for dot-cross
1m for both bond angle and shape

(ii) Using the following data, construct an energy level diagram to calculate the enthalpy change of solution of $CaSO_4$.
Include state symbols in your diagram.

enthalpy change of hydration of calcium ion	– 1562 kJ mol^{-1}
enthalpy change of hydration of sulfate ion	– 1166 kJ mol^{-1}
lattice energy of calcium sulfate	– 2710 kJ mol^{-1}



ΔH_{soln} = -(-2710) + (-1562) + (-1166) = -18.0 kJ mol^{-1}
1m for each step of the energy level diagram (total 3m)
1m for answer + units

(iii) Hence predict whether $CaSO_4$ becomes more or less soluble when temperature increases. Explain your answer.

$CaSO_4(s) \leftrightarrows Ca^{2+}(aq) + SO_4^{2-}(aq)$
When temperature increases,

- the position of equilibrium will shift to the left to reduce the temperature
- by favouring the endothermic reaction.
- $CaSO_4$ becomes less soluble

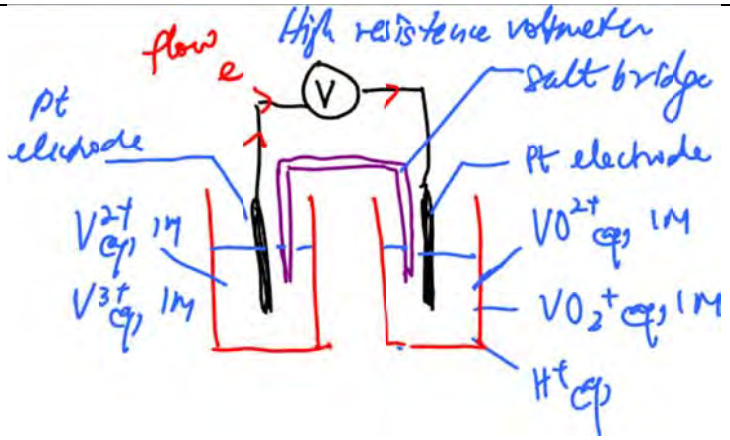
1m for each point.

[9]

(b) Calcium sulfate is a component of the grout used in between the tiles in swimming pools. Calcium chloride is added into swimming pools to prevent calcium sulfate in the grout from dissolving.
The solubility product of $CaSO_4$ at 25°C is 2.4×10^{-5} mol^2 dm^{-6}.

(i) Write an expression for the solubility product, K_{sp}, of $CaSO_4$.

			$K_{sp} = [Ca^{2+}][SO_4^{2-}]$;
		(ii)	If 5.555 kg of calcium chloride was added to a wading pool containing 3000 dm^3 of water, calculate the maximum concentration of sulfate ions in the water.
			amount of $CaCl_2$ = 5555 / (40.1+71) = 50.0 mol ; $[Ca^{2+}]$ = 50.0 / 3000 = 0.01667 mol dm^{-3} ; $[SO_4^{2-}] = K_{sp} / [Ca^{2+}]$ = 0.00144 mol dm^{-3} (3 sf) ;
		(iii)	Explain qualitatively how the added calcium chloride helps to prevent calcium sulfate in the grout from dissolving.
			$CaSO_4(s)$ ←→ $Ca^{2+}(aq) + SO_4^{2-}(aq)$ $CaCl_2(s)$ → $Ca^{2+}(aq) + 2Cl^-(aq)$ • $CaCl_2$ dissolves in water to give Ca^{2+} ions, increasing $[Ca^{2+}]$. • Equilibrium will shift to the left to reduce the concentration of Ca^{2+} hence making $CaSO_4$ less soluble. 1m for each point No credit for stating 'Common Ion Effect' only
			[6]
	(c)	Calcium iodate(V) is another calcium salt with the formula $Ca(IO_3)_2$. At high temperatures, solid calcium iodate(V) undergoes decomposition to form a white solid, violet vapour and a colourless gas which relights a glowing splint.	
		(i)	Construct a balanced equation, with state symbols, for the decomposition process.
			$Ca(IO_3)_2$ (s) → $CaO(s) + I_2(g) + 5/2\ O_2(g)$;
		(ii)	Describe and explain how the thermal stabilities of the Group II iodate(V) vary down the group.
			Going down the group • charge density decreases polarizing power of metal ion decreases • electron cloud of iodate(V) is less distorted thermal stability increases 1m each point
		(iii)	Predict the relative thermal stability of calcium chlorate(V) compared to calcium iodate(V). Explain your answer.
			Calcium chlorate(V) is more stable. ; Chlorate(V) ion is smaller in size hence less easily distorted. ;
			[5]
			[Total: 20]

4.	**(a)**	A rechargeable battery contains inert platinum electrodes immersed in solutions containing a mixture of vanadium compounds in different oxidation states. One half cell contains a mixture of $VO_2^+(aq)$ and $VO^{2+}(aq)$ and the other half cell contains $V^{2+}(aq)$ and $V^{3+}(aq)$.	
		(i)	By reference to the Data Booklet, choose two half-equations to construct the full equation for the reaction that occurs during discharge. Calculate the $E°_{cell}$.
			$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O \quad E = +1.00V$ $V^{3+} + e \rightleftharpoons V^{2+} \quad E = -0.26V$ $VO_2^+(aq) + 2H^+(aq) + V^{2+}(aq) \rightleftharpoons VO^{2+}(aq) + V^{3+}(aq) + H_2O$ $E°_{cell} = 1.00 + 0.26 = +1.26\ V$ 1m for overall balanced equation 1m for correct $E°_{cell}$
		(ii)	Sketch a fully labelled diagram of the above cell, showing the direction of the electron flow.
			 1m for cathode 1m for anode 1m for voltmeter and salt bridge and flow of e
		(iii)	Write the equation for the charging process.
			$VO^{2+}(aq) + V^{3+}(aq) + H_2O \rightleftharpoons VO_2^+(aq) + 2H^+(aq) + V^{2+}(aq)$;
		(iv)	Predict, with reason, the effect of adding water to the half cell containing $V^{2+}(aq)$ and $V^{3+}(aq)$ on the $E°_{cell}$.
			No effect. ; Concentrations of V^{2+} and V^{3+} decrease to the same extent or by the same proportion hence no shift in equilibrium. ;
			[8]
	(b)	Vanadium forms many complexes. The oxidation number of vanadium in a complex was determined as follows:	

A 0.0423 mol sample of the complex cation with an inert anion was dissolved in water and the solution was made up to 250 cm^3. A 25.0 cm^3 portion of this solution reacted exactly with 21.15 cm^3 of 0.0800 mol dm^{-3} aqueous acidified potassium manganate(VII) solution. If the oxidation number of vanadium in the product was +5, calculate the original oxidation number of vanadium in the complex. Need to add this:

Amount of MnO_4^- used = $\frac{0.0800 \times 21.15}{1000}$ = 0.001692 mol

Amount of complex in 25.0 cm^3 = $\frac{0.0423 \times 25}{250}$ = 0.004230 mol

Hence 0.004230 mol complex reacts with 0.001692 of MnO_4^-

MnO_4^- : e: complex = 0.001692 : 0.008460 : 0.004230

1 mol of complex gives out 2 mol of electron

V^{n+} = V^{5+} + 2e , Hence original oxidation state is +3

1m for amount of MnO_4^-

1m for amount of complex

1m for ratio of complex to electron

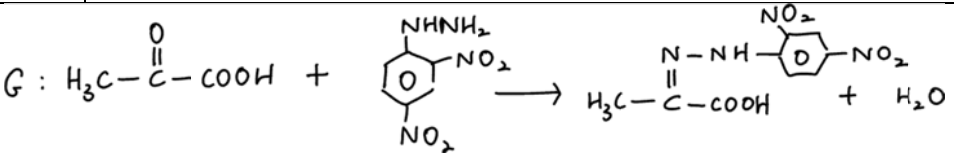
1m for oxidation state

[4]

(c) *α*-Hydroxy acids (AHAs) such as lactic acid, $CH_3CH(OH)COOH$, are naturally occurring carboxylic acids which are well-known for their use in the cosmetic industry.

When orange potassium dichromate(VI) is added to lactic acid, compound **G** is formed and the solution turns green. Compound **H** is formed when **G** is reacted with hydrogen cyanide in the presence of a trace amount of sodium cyanide at 10 – 20 °C.

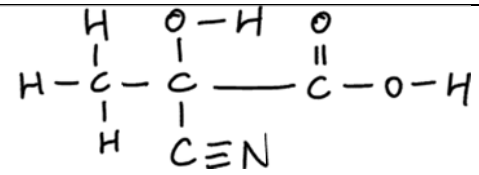
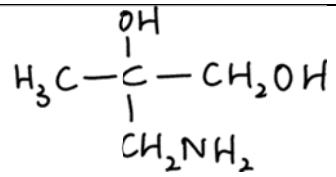
(i) Excess 2,4-dinitrophenylhydrazine was added to compound **G**. Write a balanced equation for this reaction.



1m for equation

(ii) State the type of reaction undergone when **G** reacts to form **H**.

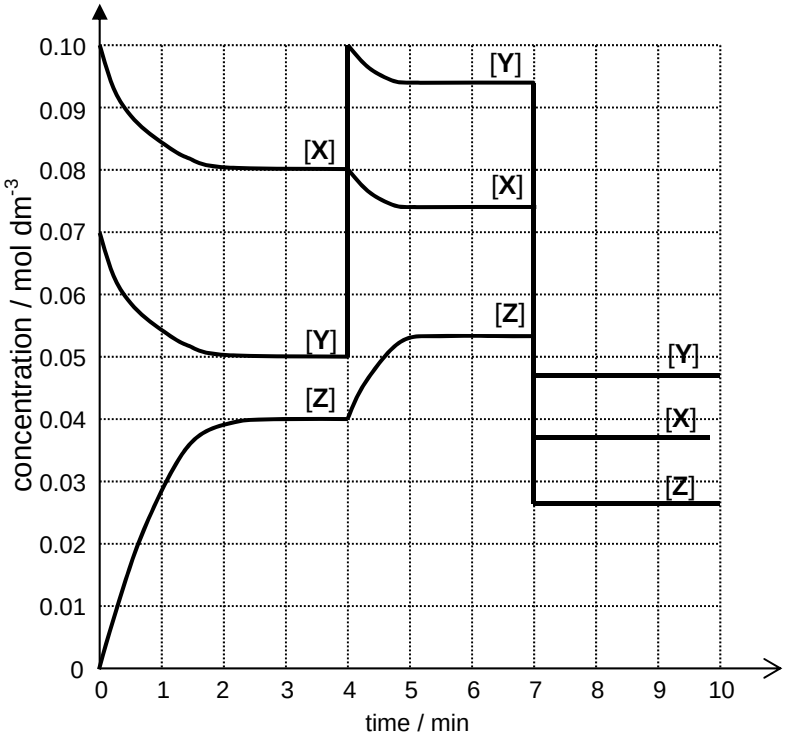
nucleophilic addition ;

		(iii)	Draw the **displayed** formula of compound **H** formed and explain why **H** has no optical activity.
			H :  ; H is a racemic mixture that contains equal proportion of each enantiomer / G is a trigonal planar structure which will have equal attack from the top and bottom. ;
		(iv)	Compound **J** is formed when **H** is treated with lithium aluminium hydride. Deduce the structural formula of compound **J**. Hence, suggest a test that distinguishes **J** and lactic acid.
			J :  ; Reagent/Condition: sodium carbonate Observation: Efferversence that forms a white ppt in limewater for J and no effervescence with white ppt in limewater for lactic acid. OR Reagent/Condition: alkaline aqueous iodine, heat Observation: Lactic acid forms yellow ppt whilst J does not form yellow ppt. Any one test 1m for reagents and conditions 1m for observation of positive test 1m for observation of negative test
			[8]
			[Total: 20]

5. **(a)** **X** and **Y** were mixed in a closed vessel and the whole system was allowed to reach equilibrium, as shown in the following equation:

$$\mathbf{X}\,(g) + \mathbf{Y}\,(g) \rightleftharpoons 2\mathbf{Z}\,(g) \qquad \Delta H < 0$$

The concentrations of all gases were measured at one-minute intervals and the operating conditions were altered at the 4th and the 7th minute. The effects are shown in the graph below.



(i) Write an expression for the equilibrium constant, K_C, and hence calculate its value at the 3rd minute.

$$K_c = \frac{[Z]^2}{[X][Y]} \quad ;$$

$$K_C = \frac{0.04^2}{(0.08)(0.05)} = 0.400 \quad ;$$

(ii) Suggest the change that could have occurred at the:

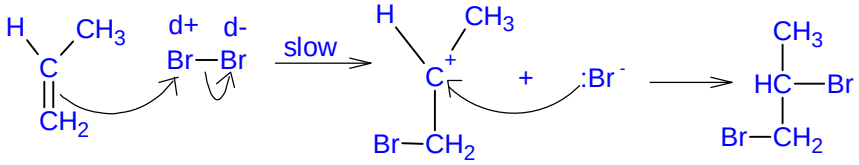
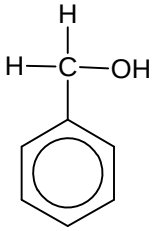
I 4th minute

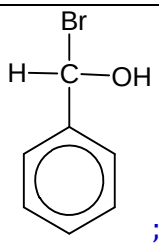
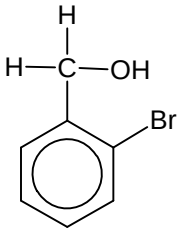
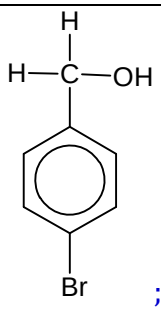
0.05 mol of Y was added ;

II 7th minute

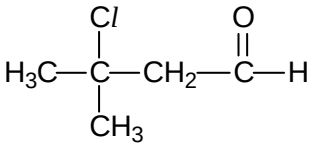
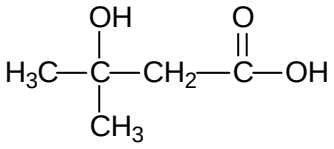
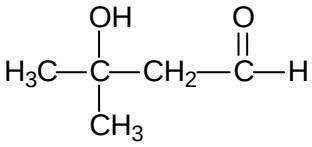
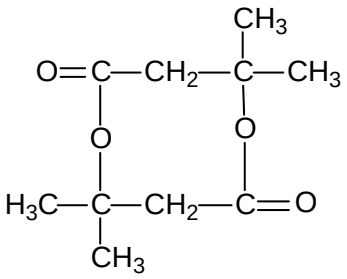
The pressure of the system was halved / The volume of the vessel was doubled. ;

[4]

	(b)	A current of 300 A was passed through molten potassium bromide for 40 min at 450K and 1.21 x 10^5 Pa. A gaseous product was obtained at one of the electrodes.	
		(i)	Write the equations of the reactions occurring at the anode and the cathode.
			anode: $2Br^- \rightarrow Br_2 + 2e$ cathode: $K^+ + e \rightarrow K$ 1m for both equations
		(ii)	Determine the volume of the gas produced.
			Q = 300 x 40 x 60 = 720000 C ; amount of electron = $\frac{720000}{96500}$ = 7.461 mol Amount of Br_2 = 7.461/2 = 3.731 mol ; pV=nRT , 1.21 x 10^5 x V = 3.731 x 8.314 x 450 V = $\frac{3.731 \times 8.314 \times 450}{1.21 \times 10^5}$ = 0.115 m^3 ;
		(iii)	The gas produced was reacted with propene. Outline the mechanism of the reaction.
			 1m for arrows + partial charges 1m for rds + intermediate + product (Markovnikov's rule)
		(iv)	The gas produced also reacts with phenylmethanol under different conditions to yield different products. Phenylmethanol has the following structure.  phenylmethanol Draw the structure of the product when the reaction takes place

			under the following conditions:
			I in the presence of sunlight
			 ;
			II in the presence of iron
			 or  ;
			[8]
	(c)	Compound **C**, C_5H_9OCl, does not react with thionyl chloride but forms an orange precipitate with 2,4-dinitrophenylhydrazine. When refluxed with hot aqueous potassium hydroxide, **C** forms **D**, $C_5H_{10}O_2$. **D** does not form any yellow precipitate with alkaline iodine solution. When treated with acidified potassium dichromate(VI), **D** gives compound **E**. In the presence of hot concentrated sulfuric acid, **E** forms a sweet-smelling liquid, **F**, $C_{10}H_{16}O_4$. Suggest the structural formulae of compounds **C** to **F**, explaining the chemistry involved.
			[8]
			Observations / Deductions • C does not react with thionyl chloride, but forms an orange precipitate with 2,4-DNPH. → • It does not contain an alcohol functional group but contains a carbonyl functional group. • C reacts with KOH (aq) to → • C undergoes nucleophilic

form D.	substitution to form alcohol D.
• D does not undergo positive iodoform test.	• It does not have the $CH_3CH(OH)$- or CH_3CO- structure.
• D reacts with potassium dichromate to give E.	• D is oxidized to form compound E which is likely to be a carboxylic acid.
• E reacts with concentrated sulfuric acid to give F.	• E undergoes esterification /F contains the ester linkage. • This suggests that 1 molecule of E contains –OH alcohol group and –COOH group.
Deductions : 6 marks (max 4m)	
Structures: (1 mark per correct structure)	

C		**E**	
D		**F**	

[Total: 20]