

VICTORIA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATIONS Higher 2

CHEMISTRY9647/03Paper 3 Free Response17 September 2012Candidates answer on separate paper.2 hoursAdditional Materials:Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.Write in dark blue or black pen on both sides of the paper.You may use a soft pencil for any diagrams, graphs or rough working.Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

You are reminded of the need for good English and clear explanation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **11** printed pages.

Answer any 4 questions.

1 (a) The elements of Group VII are all oxidising agents, but some are more oxidising than others.

Describe and explain, with the aid of equations, the reactions of the elements with the reducing agent, sodium thiosulfate. [3]

Oxidising power of X₂ decreases down the group.

For Cl_2 , Br_2 $4X_2 + S_2O_3^{2^-} + 5H_2O \rightarrow 8X^- + 2SO_4^{2^-}$ O.S. of S increases by 4 units from +2 to +6

For I₂, I₂ + 2S₂O₃²⁻ \rightarrow 2I⁻ + S₄O₆²⁻ O.S. of S increases by 0.5 units from +2 to +2¹/₂ [3.5, max 3]

- (b) Potassium chlorate(V), KClO₃, is one of the products formed during the electrolysis of concentrated aqueous KCl solution.
 - (i) State, with the aid of balanced equations, how KClO₃ is produced in the electrolysis of concentrated aqueous KCl solution.

Electrolysis of KCl solution gives KOH, H₂ and Cl₂ KCl + H₂O \rightarrow KOH + $\frac{1}{2}$ H₂ + $\frac{1}{2}$ Cl₂

 Cl_2 undergoes **disproportionation** and reacts with KOH under **hot conditions** to give KClO₃. $3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O$

(ii) The standard electrode potentials, E^{\ominus} , and standard Gibbs free energy changes, ΔG^{\ominus} , of different chlorine-containing species are tabulated below.

Half-equation	<i>E</i> ^o / V	ΔG^{\ominus} / kJ mol ⁻¹
$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47	-1420
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	-262

Write a half-equation for the conversion of ClO_3^- to Cl^- . Using your knowledge of Hess' Law for ΔG^{\ominus} , calculate ΔG^{\ominus} for this conversion.

 ΔG^{\ominus} and E^{\ominus} are related by the following equation:

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

where ΔG^{\ominus} is the standard Gibbs free energy change in **joules per mole**, *z* is the number of moles of electrons transferred during the redox reaction and *F* is the Faraday constant.

Show that the standard electrode potential of converting ClO_3^- to Cl^- is **not** the summation of +1.47 V and +1.36 V.



Applying Hess Law,

$$\Delta G^{\ominus}$$
 = -1420 + (-262) = -1682 kJ mol⁻¹ OR -841 kJ mol⁻¹

 $E^{\ominus} = -[-1682 \times 10^3 / (12 \times 96500)] = +1.45 \text{ V} \neq 1.47 + 1.36$ OR $E^{\ominus} = -[-841 \times 10^3 / (6 \times 96500)] = +1.45 \text{ V} \neq 1.47 + 1.36$

(iii) One early attempt to make bromic(VII) acid, HBrO₄, was the reaction between bromine water and silver chlorate(VII), AgClO₄. Insoluble silver chloride was formed as a by-product. With the aid of half-equations, construct a full equation for this process.

$$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$$

 $Br_2 + 8H_2O \rightarrow 2HBrO_4 + 14H^+ + 14e^-$
 $7AgClO_4 + 4Br_2 + 4H_2O \rightarrow 7AgCl + 8HBrO_4$
[8]

(c) The identification of the elements in this question is restricted to proton number 1 to 20.

Elements **A** and **B** belong to the same group and element **C** belongs to the same period as **B**.

Elements **A** and **B** have high melting points while element **C** has a low melting point. The various oxides of **A** and **C** exist as simple discrete molecules while the oxide of **B** exists as a giant molecular structure. Both elements **A** and **B** can combine to form a compound with a high melting point.

Both elements **A** and **B** are insoluble in water while **C** readily reacts with water resulting in an acidic solution and the resultant solution gives a white precipitate with aqueous silver nitrate. When elements **A** and **C** react to form a compound **D**, it is inert and does not dissolve in water. When elements **B** and **C** react to form a compound **E**, it is reactive towards water leading to the formation of an acidic solution and fine white solid.

Identify A to E, and explain your reasoning clearly. [9]

Elements **A** and **B** have high melting points, thus they can be <u>metals</u> or <u>non-</u><u>metals with giant molecular structures</u>.

Element **C** has a low melting point means it is a <u>non-metal with simple</u> <u>molecular structure</u>.

The structures of the oxides of A, B and C show that A, B, and C are <u>non-metals</u>.

Hence **B** is **Si** as $\underline{SiO_2}$ has a giant molecular structure.

Since **A** is in the same group as Si, **A** is **C** where the oxides of carbon ($\underline{CO, CO_2}$) exist as simple discrete molecules.

Si and C can form <u>SiC, a giant molecular structure</u> with a high melting point.

Carbon and silicon having giant molecular structures are not soluble in water.

Element C is Cl OR Cl₂.

 Cl_2 reacts with water to produce <u>HCIO and HCI</u> where the presence of CI⁻ ions will give a white ppt of <u>AgCI</u> with AgNO₃.

D is CCl₄

CCl₄ is non-polar so it cannot dissolve in water OR No available energetically accessible d orbitals to undergo hydrolysis.

E is SiCl₄

SiC l_4 reacts with water to give acidic solution of <u>HCl</u> and <u>SiO₂</u>, a fine white solid.

2 Phosphoric acid, H₃PO₄, is a triprotic acid and its structure is given below.



The pK_a values of the three successive dissociations of phosphoric acid at 25 $^{\circ}\!C$ are:

p*K*_{a1} = 2.1; p*K*_{a2} = 7.2, p*K*_{a3} = 12.3

(a) Write three equations to show the stepwise acid dissociation of H_3PO_4 . Determine the p K_b value of $HPO_4^{2^-}$. [2]

 $\begin{array}{rcl} H_{3}PO_{4} + H_{2}O & \longrightarrow & H_{2}PO_{4}^{-} + H_{3}O^{+} \\ H_{2}PO_{4}^{-} + H_{2}O & \longrightarrow & HPO_{4}^{2-} + H_{3}O^{+} \\ HPO_{4}^{2-} + H_{2}O & \longrightarrow & PO_{4}^{3-} + H_{3}O^{+} \\ pK_{b} \text{ of } HPO_{4}^{2-} = 14 - 7.2 \\ & = 6.8 \end{array}$

(b) Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as cola and root beer. A cola having a density of 1.00 g cm⁻³ contains 0.05% by weight of phosphoric acid.

Determine the pH of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid. [3]

No. of moles of H₃PO₄ in 1 cm³ of cola = $\frac{0.05}{100} \times \frac{1}{98}$ = 5.10 x 10⁻⁶ mol cm⁻³

Concentration of $H_3PO_4 = 5.10 \times 10^{-6} \times 1000$ = 5.10 x 10⁻³ mol dm⁻³

$$K_{a} = \frac{[H^{+}][H_{2}PO_{4}^{-}]}{[H_{3}PO_{4}]}$$

$$10^{-2.1} = \frac{[H^{+}]^{2}}{5.10 \times 10^{-3}}$$

$$[H^{+}] = 6.37 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH \text{ of cola} = -lg(6.37 \times 10^{-3})$$

$$= 2.20$$

- (c) A solution of 0.100 mol dm⁻³ H₃PO₄ is titrated with 0.100 mol dm⁻³ NaOH.
 - (i) State the pH that is half-way between the initial point and the first equivalence point.

 $pH = pK_{a1}$ = 2.1

(ii) The pH at the second equivalence point is found to be greater than 7. Explain this observation with the aid of relevant equations.

At the second equivalence point, hydrolysis of HPO_4^{2-} occurs. $HPO_4^{2-} + H_2O \leftrightarrows PO_4^{3-} + H_3O^+$ $pK_a = 12.3$ $HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^- + OH^ pK_b = 6.8$ pK_b is smaller than the pK_a of HPO_4^- . There is an excess of OH^- ions over H_3O^+ ions, making the resultant solution basic i.e. pH > 7.

(iii) State a suitable indicator to determine the first end point of the titration. Explain briefly.

Methyl orange Working range of methyl orange lies in the region of rapid pH change at the first end point.

[5]

- (d) When pure phosphoric acid is heated with POCl₃, another phosphoruscontaining acid, **B**, is produced, along with HC*l*. The addition of aqueous silver nitrate to a solution of acid **B** produces a white precipitate which contains 71.3% by mass of silver and 10.2% by mass of phosphorus, the remainder being oxygen.
 - (i) Determine the identity of the white precipitate. Hence identify acid **B**.

	Ag	Р	0
Mass in 100 g / g	71.3	10.2	√ 18.5
No. of moles / mol	0.660	0.329	1.156
Whole no. ratio	4	2	7

Formula of white precipitate: $Ag_4P_2O_7$. **B** is $H_4P_2O_7$.

(ii) Write an equation for the reaction of acid **B** with silver nitrate.

 $4AgNO_3 + H_4P_2O_7 \rightarrow Ag_4P_2O_7 + 4HNO_3$

(iii) Suggest a structure for the acid **B**, showing the shape clearly.



[5]

(e) William S. Knowles used a rhodium catalyst containing a phosphorus-ligand for the synthesis of L–DOPA which is an important anti-Parkinson drug.



(i) DOPA has two functional groups that exhibit acidic properties. Identify the functional group with the smaller pK_a value. Explain your answer.

The $-CO_2H$ group has a smaller pK_a value than the phenol group. Carboxylate ion is resonance stabilised. Phenoxide ion is also resonance stabilised. Carboxylate ion is stabilised to a greater extent than phenoxide ion. thus making the carboxylic acid the stronger acid.

(ii) Give an equation for the reaction of the functional group identified in (e)(i) to illustrate its behaviour as an acid.

 $\begin{array}{ll} 2RCO_2H + Na_2CO_3 \rightarrow 2RCO_2^-Na^+ + CO_2 + H_2O\\ OR & RCO_2H + NaHCO_3 \rightarrow RCO_2^-Na^+ + CO_2 + H_2O\\ OR & RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O \end{array}$

[3]

(f) Explain the relative basicity of the two nitrogen atoms labelled (a) and (b) in proparacaine.



 $N_{(b)}$ atom in the alkylamine is more basic than $N_{(a)}$ in phenylamine.

This is because the lone pair electrons on the N in the alkylamine is <u>more</u> <u>available</u> due to the <u>electron-donating inductive effect</u> of the alkyl groups.

The lone pair electrons on the N in the phenylamine can be <u>delocalised into</u> <u>benzene ring</u>, thereby making the <u>lone pair less available</u> for donation to an acid.

[2]

3 (a) Glucose exists in two forms, α-glucose and β-glucose. If a solution of α-glucose is left for some time, it will come into dynamic equilibrium with β-glucose.

 α -glucose $\overline{}$ β -glucose

(i) Explain what is meant by *dynamic equilibrium*.

Rate of forward reaction is equal to rate of backward reaction. Concentration of reactants and products remain constant. / No net change in concentrations of reactants and products.

(ii) 1 dm³ of a freshly prepared solution of 1.0 mol dm⁻³ solution of α -glucose is left to stand at 298 K. At equilibrium, concentration of β -glucose is 0.63 mol dm⁻³. Calculate the value of the equilibrium constant, K_c , for the conversion of α -glucose to β -glucose at 298 K.

 $\begin{array}{cccc} \alpha \mbox{-glucose} & & & & & & & & & & & & & \\ \mbox{Initial conc /mol dm}^{-3} & 1 & & & & & & & & & & & \\ \mbox{Eqm conc /mol dm}^{-3} & 1 \mbox{-} 0.63 = 0.37 & & & & & & & & & & \\ \mbox{K_c} & = & [\beta \mbox{-glucose}]/[\alpha \mbox{-glucose}] \\ & = & 0.63/(1 \mbox{-} 0.63) \\ & = & 1.70 \end{array}$

(iii) Each form of glucose will rotate plane-polarised light and the angle of rotation due to each form of glucose is directly proportional to its concentration. The optical rotation of the equilibrium solution is 53°.

The conversion of α -glucose into β -glucose is catalysed by acids. What will be the effect on the final measured rotation if the conversion is now carried out in the presence of dilute sulfuric acid? Explain.

Catalyst increases rate of reaction and has no effect on equilibrium position. Final measured rotation is still 53°.

[4]

(b) In the vapour phase, ethanoic acid associates to form dimers.

 $2CH_3CO_2H(g)$ $(CH_3CO_2H)_2(g)$

At 177 $^{\rm o}C$ and 1.115 x 10 $^{\rm 5}$ Pa, 0.084 g of ethanoic acid vapour occupies 34.3 $\rm cm^3.$

(i) Calculate the average relative molecular mass of the gaseous mixture.

PV = nRT 1.115 x 10⁵ x 34.3 x 10⁻⁶ = $(0.084 \times 8.31 \times 450)/M_r$ Average M_r = 82.1

(ii) Calculate the degree of association of the ethanoic acid, α , using the formula below:

$$\alpha = 2 \left[\frac{\text{average } M_r - M_r(CH_3CO_2H)}{\text{average } M_r} \right]$$

 $\alpha = 2[(82.1-60)/82.1] = 0.54$

(iii) Calculate the value of the equilibrium constant, K_p , for the dimerisation of ethanoic acid at 177 °C. State its units.

 $2CH_{3}CO_{2}H(g) \iff (CH_{3}CO_{2}H)_{2}(g)$ Initial no of moles 1 0 Eqm no of moles 1-0.54 = 0.46 0.27 Total number of moles 0.46 + 0.27 = 0.73 P_{CH3CO2H} = (0.46/0.73) × 1.115 × 10⁵ = 7.03 × 10⁴ Pa P_{(CH3CO2H)2} = (0.27/0.73) × 1.115 × 10⁵ = 4.12 × 10⁴ Pa $K_{p} = 4.12 \times 10^{4}/(7.03 \times 10^{4})^{2}$ = 8.34 × 10⁻⁶ Pa⁻¹ (c) Suggest structures for compounds X and Y in the following multi-step transformations. Indicate the reagents and conditions you would use for each step.

$$(CH_3)_2C=CH_2 \xrightarrow{\text{step 1}} X \xrightarrow{\text{step 2}} Y \xrightarrow{\text{step 3}} CH_3CH=CH_2$$
[5]

<u>Step 1:</u> KMnO₄, H⁺ Heat

<u>Step 2:</u> LiA/H₄ in dry ether followed by hydrolysis room temp

<u>Step 3:</u> Excess conc H₂SO₄ 170 °C

X is $(CH_3)_2C=O$

Y is CH₃CH(OH)CH₃

(d) Primary aryl amines reacts with cold nitrous acid and hydrochloric acid to form relatively stable diazonium salts. This type of reaction is known as diazotisation.

$$\bigvee NH_2 + HNO_2 + HCl \xrightarrow{5^{\circ}C} \bigvee NCl + 2H_2O$$

The diazonium salts obtained can undergo coupling reactions with other organic compounds like phenylamine or phenol to form azo compounds which are useful dyes.



(i) State the mechanism of the coupling reaction between the diazonium salt and phenylamine.

Electrophilic substitution

Methyl orange is made by diazotising 4-aminobenzenesulfonic acid and coupling the product with N,N-dimethylphenylamine.





4-aminobenzenesulfonic acid

N,N-dimethylphenylamine

- (ii) Write balanced equations for
 - (A) the diazotisation of 4-aminobenzenesulfonic acid and



(B) the coupling reaction between one mole of diazonium salt formed in (A) and one mole of N,N-dimethylphenylamine to form methyl orange.



When the diazonium salt obtained in (A) is made to couple with P in a slightly alkaline medium, Sunset Yellow, a food colourant is produced.

(iii) Identify **P** by examining the structural formula of Sunset Yellow below:



(iv) The sodium sulfonate groups have little effect on the colour of Sunset Yellow. Suggest a reason why these groups are needed in the molecule.

The sodium sulfonate groups contain ions.

Ion-dipole interaction between dye and water increases its solubility in water.

[5]

- 4 (a) Selenium, Se, is a Group VI element. In aqueous solution, selenide ions, Se²⁻, and sulfate(IV) ions react spontaneously to form selenium and thiosulfate ion, $S_2O_3^{2-}$. The E_{cell}^{θ} of the reaction is +0.57 V.
 - (i) Write half-equations for the oxidation and reduction processes and hence the balanced equation for the reaction.

 $\begin{array}{rll} Se^{2-}(aq) & \rightarrow & Se(s) \ + \ 2e^{-} \\ 2SO_{3}^{2-}(aq) & + & 3H_{2}O(l) \ + \ 4e^{-} \ \rightarrow 6OH^{-}(aq) \ + \ S_{2}O_{3}^{2-}(aq) \\ 2Se^{2-}(aq) \ + \ 2SO_{3}^{2-}(aq) \ + \ 3H_{2}O(l) \ \rightarrow 2Se(s) \ + \ 6OH^{-}(aq) \ + \ S_{2}O_{3}^{2-}(aq) \end{array}$

(ii) Given E^{θ} (sulfate(IV)/thiosulfate) is -0.35 V, calculate the standard electrode potential for Se/Se²⁻ half-cell.

$$E^{\theta}(\text{Se/Se}^{2-}) = -0.35 - 0.57$$

= -0.92 V

(iii) What happens to the E^{θ}_{cell} of the reaction when pH of the solution is lowered? Explain.

When pH of solution is lowered, [H⁺] increases. Forward reaction is favoured as OH^- is neutralised by H⁺. E^{θ}_{cell} becomes more positive.

(iv) Draw a fully labelled sketch of the electrochemical cell and state the direction of electron flow. Assume that selenium behaves like a metal.



(v) This reaction proceeds at a greater speed when trace amount of Cr^{3+} is added. Explain the observation with the aid of balanced equations.

Cr³⁺ acts as homogeneous catalyst.

 $2Cr^{3+}(aq) + Se^{2-}(aq) \rightarrow 2Cr^{2+}(aq) + Se(s)$ $E^{\theta}_{cell} = -0.41 - (-0.92) = +0.51$ V. Hence reaction is feasible.

 $4Cr^{2+}(aq) + 2SO_3^{2-}(aq) + 3H_2O(I) \rightarrow 4Cr^{3+}(aq) + 6OH^{-}(aq) + S_2O_3^{2-}(aq) E_{cell}^{\theta} = -0.35 - (-0.41) = +0.06 V.$ Hence reaction is feasible.

Each step of catalysed reaction involves ions of opposite charges and hence have lower activation energy.

Uncatalysed reaction that involves two anions will experience repulsion.

[10]

(b) When aqueous zinc sulfate(VI) is electrolysed, the desired half-reaction at the cathode is

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$$

A competing reaction which lowers its yield is the formation of hydrogen gas.

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- aq)$$

(i) If 90% of the current flow results in zinc being deposited with 10% of the current flow producing hydrogen gas, calculate the volume of hydrogen gas produced per gram of zinc deposited at standard temperature and pressure.

Zinc can be extracted from its ores by reduction with carbon at 1100 K.

$$ZnO(s) + C(s) \rightarrow Zn(s) + CO(g)$$

(ii) Given that at 1100 K,

$2C(s) \ + \ O_2(g) \ \rightarrow \ 2CO(g)$	$\Delta G^{\Theta} = -440 \text{ kJ mol}^{-1}$
$2Zn(s) ~+~ O_2(g) ~\rightarrow~ 2ZnO(s)$	$\Delta G^{\theta} = -505 \text{ kJ mol}^{-1}$

Determine the ΔG^{θ} value for the extraction of Zn from ZnO by carbon. By considering both ΔH^{θ} and ΔS^{θ} , explain how ΔG^{θ} varies with temperature for the reaction between zinc and oxygen.

 $\Delta G^{\theta} = (1/2)(-440) - (1/2)(-505)$ = 32.5 kJ mol⁻¹

For reaction between zinc and oxygen, ΔH^{θ} is **negative** as combustion is an exothermic process. ΔS^{θ} is **negative** as 1 volume of gas is converted to solid.

 $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$ Value of $-T\Delta S^{\theta}$ becomes more positive as temperature increases ΔG^{θ} becomes **less negative as temperature increases**.

(iii) Below are some thermodynamic equations involving zinc compounds.

$ZnO(s) + 3C(s) \rightarrow ZnC_2(s) + CO(g)$	$\Delta H^{\theta} = +462 \text{ kJ mol}^{-1}$
$ZnO(s) + H_2O(I) \rightarrow Zn(OH)_2(s)$	$\Delta H^{\theta} = -65 \text{ kJ mol}^{-1}$
$ZnC_2(s) + 2H_2O(g) \rightarrow Zn(OH)_2(s) + C_2H_2(g)$	$\Delta H^{\theta} = -126 \text{ kJ mol}^{-1}$
Using these data together with the following data,	

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
 $\Delta H^{\theta} = -221 \text{kJ mol}^{-1}$

 $2H_2O(I) \rightarrow 2H_2(g) + O_2(g)$ $\Delta H^{\theta} = +572 \text{ kJ mol}^{-1}$

determine the standard heat of formation of $C_2H_2(g)$ with the aid of an energy cycle.

462 $ZnO(s) + 3C(s) + 2H_2O(l)$ $ZnC_2(s) + CO(g) + 2H_2O(I)$ --65 $Zn(OH)_2(s) + 3C(s) + H_2O(I)$ 572/2 -126 $Zn(OH)_2(s) \ + \ 3C(s) + H_2(g) + \frac{1}{2}O_2(g)$ ΔH^{θ} $Zn(OH)_2(s) + C_2H_2(g) + C(s) + \frac{1}{2}O_2(g)$ -221/2 $Zn(OH)_2(s) + C_2H_2(g) + CO(g)$

By Hess' Law,

$$\Delta H^{\theta} = 462 + 65 - 572/2 + 221/2 - 126$$

 $= +225.5 \text{ kJ mol}^{-1}$

[10]

5 (a) Friedel–Crafts alkylation involves the alkylation of an aromatic ring. The general reaction is shown below with anhydrous $FeCl_3$ acting as a Lewis acid catalyst.



(i) Name the mechanism of the reaction and explain the need for $FeCl_3$ to be anhydrous.

Mechanism: electrophilic substitution

FeCl₃ has to be anhydrous so that <u>Fe can accept a lone pair of electron</u> from X⁻ into its empty orbital to form the electrophile R⁺. If water is present, $Fe(H_2O)_6^{3+}(aq)$ complex will be formed and will not be able to do so.

(ii) Trichloromethane reacts with excess benzene in the presence of anhydrous $FeCl_3$ catalyst to give a brightly coloured dye. Suggest the structural formula of the product formed.



[Award ¹/₂ m for mono / di-substitution.]

Friedel–Crafts alkylation can also be achieved using alkenes. An example is shown below.



(iii) With the aid of an equation, propose how $(CH_3)_3C^+$ can be produced. Hence, describe the mechanism of this reaction. Use curly arrows to indicate the movement of electrons.



(iv) Compound L, a structural isomer of compound K, can exhibit stereoisomerism. State the type of stereoisomerism shown by L and draw the stereoisomers.

Optical isomerism



(v) Suggest how you can differentiate between compounds K and L by a chemical test.

Heat both compounds with $H_2SO_4(aq)$ and $KMnO_4$.

L will decolourise purple solution with formation of white ppt (and effervescence of CO_2). No decolourisation of purple KMnO₄ for **K**.

[10]

- (b) Queen substance, **A**, is a naturally occurring compound obtained from honey bees, and has the formula $C_xH_yO_z$.
 - (i) High resolution mass spectrometry shows that the accurate relative molecular mass of compound **A** is 184.11. Three possible molecular formulae for compound **A**, with relative molecular masses close to this value, are $C_9H_{12}O_4$, $C_{10}H_{16}O_3$ and $C_{11}H_{20}O_2$.

Accurate relative isotopic masses for the most abundant isotopes of carbon, hydrogen and oxygen are:

H = 1.008, C = 12.000, O = 15.995

Show how these isotopic masses can be used to determine which of the three possibilities is the molecular formula of compound **A**.

$$\begin{split} M_r(C_9H_{12}O_4) &= 9(12.000) + 12(1.008) + 4(15.995) = 184.076 \\ M_r(C_{10}H_{16}O_3) &= 10(12.000) + 16(1.008) + 3(15.995) = 184.113 \\ M_r(C_{11}H_{20}O_2) &= 11(12.000) + 20(1.008) + 2(15.995) = 184.15 \\ \text{Molecular formula of } \mathbf{A} \text{ is } C_{10}H_{16}O_3. \end{split}$$

(ii) A gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and a yellow precipitate with warm alkaline aqueous iodine.

When **A** is heated under reflux with SOC l_2 , and the product treated with ethanol, it gives **B**, $C_{(x+2)}H_{(y+4)}O_z$.

A decolourises a solution of bromine in an organic solvent. When it is reacted with a methanolic solution of NaBH₄ it gives **C**, $C_xH_{(y+2)}O_z$. Catalytic hydrogenation of **A** gives **D**, $C_xH_{(y+4)}O_z$. When **D** is reacted with alkaline aqueous iodine, it gives the salt of nonanedioic acid, $HO_2C(CH_2)_7CO_2H$.

Oxidation of **A** with hot acidified potassium manganate(VII) gives heptanoic acid, $HO_2C(CH_2)_5CO_2H$.

Using the molecular formula of **A** determined from (**b**)(**i**), suggest structures for **A**, **B**, **C** and **D**. Explain your reasoning clearly.

A is a <u>carbonyl</u> compound as it undergoes <u>condensation</u> reaction with 2,4dinitrophenylhydrazine to form an orange ppt.

A undergoes <u>oxidative cleavage</u> with warm alkaline aqueous iodine to form a yellow ppt, <u>CHI₃</u>.

A has $CH_3CH(OH)$ – or CH_3CO – structure.

A is a <u>carboxylic acid</u> as it reacts with $SOCl_2$ to form <u>acid chloride</u> which then reacts with ethanol to form <u>ester</u>, **B**.

A is an <u>alkene</u> as it decolourises Br₂ in an organic solvent.

<u>Carbonyl</u> group in **A** is <u>reduced</u> by NaBH₄ to give **C** as no. of H atoms increases by 2.

Both <u>alkene</u> and <u>carbonyl</u> group in **A** are reduced by hydrogen to give **D** as no. of H atoms increases by 4.

D contains <u>CH₃CH(OH)</u> structure (not CH₃CO–) as it reacts with alkaline aqueous iodine to give $\underline{-O_2C(CH_2)_7CO_2}$.

A is CH₃COCH=CH(CH₂)₅CO₂H

B is $CH_3COCH=CH(CH_2)_5CO_2CH_2CH_3$

C is $CH_3CH(OH)CH=CH(CH_2)_5CO_2H$

D is $CH_3CH(OH)CH_2CH_2(CH_2)_5CO_2H$

[10]