ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme June 2002

GCE

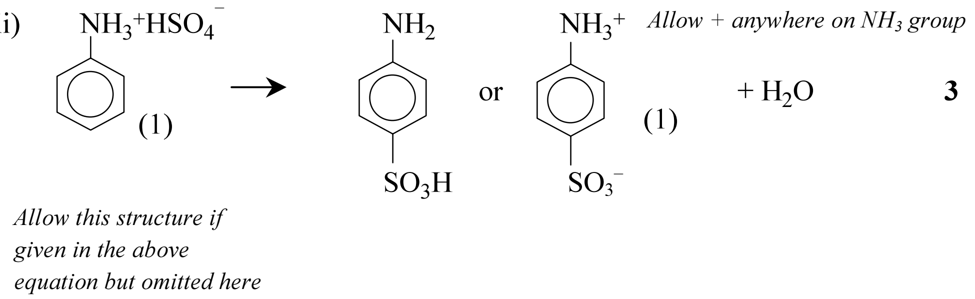
Chemistry

Advanced Extension Award

Question 1

(a) (i) Equation: $C_6H_5NH_2 + H_2SO_4 \longrightarrow C_6H_5NH_4SO_4$ (1)

NB Allow product as $C_6H_5NH_3^+HSO_3^-$ *or* $C_6H_9NSO_4$
NB Ignore state symbols
NB Allow correctly drawn ring but NOT Ph
NB Do not allow if H^+ *in place of* H_2SO_4

(ii) 

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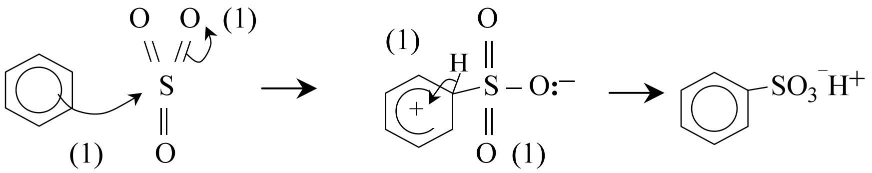
(b) 

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NB Allow mechanisms using Kekule structures
NB Lose first two marks if SO_3 *protonated but allow second two marks consequentially*

(c) Energy barrier(E_1) for formation of isomer 1 is lower than for isomer 2 (E_2) (1)
Fewer molecules exceed E_2 at low temperature than exceed E_1 (1)
Isomer 1 is formed more rapidly than isomer 2 at lower temperature (1)
Sulphonation is reversible (1)
At high temperature many more molecules exceed E_2 (and E_1) (1)
Both isomers are formed (1)
Fall in energy for isomer 2 is more negative than for isomer 1
or ΔH_f larger for isomer 2 or gives out more energy or lower energy state (1)
Isomer 1 will convert to isomer 2 (1)
Isomer 2 is more stable (1) **Max 8**

Question 2

(a)(i) $p_{\mathbf{X}} = \dfrac{xP}{x+y}$ and $p_{\mathbf{Y}} = \dfrac{yP}{x+y}$ (1)

$K_p = \dfrac{p_{\mathbf{Y}}}{p_{\mathbf{X}}^2}$ (1) $= \dfrac{y(x+y)}{x^2P}$ (1)

NB Allow when top and bottom P not cancelled
NB The correct final answer scorse 3 unless [ ] used in K_p expression

As pressure increases y must increase relative to x (1)
in order to keep K_p constant (1)

NB Mark explanations separately and consequentially to above equation
NB Lose both these marks if K_p 'changes with temperature' is stated

Le Chatelier's Principle says, if pressure increases equilibrium moves to side with fewest moles (of gas) or to the right (1) **6**

(ii) If $T_2 > T_1$ then $1/T_2 - 1/T_1$ is negative (1)
Hence the right hand side of the equation is positive (1)
Hence $K_2 > K_1$ (1)

NB These three marks are linked only allow if first statement correct

Le Chatelier's Principle says, if temperature increases the endothermic reaction is favoured or goes to the right. (1) **4**

(b)(i) $N_2(g) + 3H_2(g) = 2NH_3(g)$ (1)

NB If this equation is incorrect lose equation and first 'box' marks then mark consequentially

	N_2	H_2	NH_3	Marks
Moles	(1 – 0.2) = 0.8	(3 – 0.6) = 2.4	(2 – 0.2) = 0.4	1
Mole fraction	0.8 / 3.6 = 2 / 9	2.4 / 3.6 = 2 / 3	0.4 / 3.6 = 1 / 9	1
Partial pressure	2 / 9 × 20 = 40 / 9	2 / 3 × 20 = 40 / 3	1 / 9 × 20 = 20 / 9	1

NB ALL THREE deductions must be correct for each mark
NB Mark mole fraction and partial pressure consequentially to moles

$$K_p = \frac{p_{NH_3}^{\ 2}}{p_{N_2} \times p_{H_2}^{\ 3}} = \frac{\left(20/9\right)^2}{\left(40/9\right)\times\left(40/3\right)^3} = 4.69\times10^{-4}\ \text{MPa}^{-2}$$

(1) or 4.69×10^{-16} Pa^{-2}
(1) (1) **7**

NB Allow 4.4 to 4.7 $\times 10^{-4}$ MPa^{-2}
NB If initial equation is halved the answer is 2.17×10^{-2} MPa^{-2} for full marks
NB Candidates using NH_3 = 0.2 mol score 5 consequentially for an answer of 2.35×10^{-4} MPa^{-2}

(ii)

	N_2	H_2	NH_3	Marks
Moles	(1 – 0.5) = 0.5	(3 – 1.5) = 1.5	(2 × 0.5) = 1.0	1
Mole fraction	0.5 / 3	1.5 / 3	1 / 3	1

$$K_p = 4.69\times10^{-4} = \frac{\left(\frac{1}{3}\times P\right)^2}{\left(\frac{0.5}{3}\times P\right)\left(\frac{1.5}{3}\times P\right)^3}$$ (1)

$$P^2 = \frac{0.11}{0.167\times0.125\times4.69\times10^{-4}}$$ (1)

$$= 1.16\times10^4 \text{ MPa}^2$$ (1)

$P = 106.6$ MPa (allow 106 to 108) (1) **6**

NB Mark (ii) consequentially to answer from (i)
NB Ignore units in (ii)
NB Candidates using NH_3 = 0.5 mol score 4 marks consequentially for an answer of 125.4

(iii) Despite the higher yield, the pressure used is likely to the 20 MPa (1)
because the energy cost for pumping are less or cheaper to produce (1)
and capital costs for pressure resistant plant are less (1)
and the unused N_2 and H_2 are recycled (1) **4**

NB Mark (iii) consequentially to pressure deduced in (ii)
NB Do not allow marks for hazards in the process

(c)(i) $NH_4^+(aq) + H_2O(l)\ (\rightleftharpoons)\ NH_3(aq) + H_3O^+$
or $NH_4^+(aq)\ (\rightleftharpoons)\ NH_3(aq) + H^+$ (1)

NB Ignore NO_3^- ions if given on both sides
NB State symbols not required BUT penalise if wrong

$$K_a = \frac{[NH_3]}{[H_3O^+][NH_4^+]} \quad \text{or} \quad \frac{[NH_3]}{[H^+][NH_4^+]}$$ (1)

Assume $[NH_3] = [H_3O^+]$ or H_3O^+ from water is negligible
or $[NH_4^+]$ = original = 0.01 or little dissociation of $[NH_4^+]$ occurs (1)

NB One of these statements MUST be made

Hence $[H^+]^2 = K_a[NH_4^+]$ (1)

$\therefore [H^+] = \sqrt{0.01\times10^{-9.25}} = 2.37\times10^{-6}$ (1)

pH = 5.6 (1) **6**

NB Score 3 for pH = 5.6 then look back for three additional marks
NB If answer wrong, and not an AE, max 3 for three correct statements

(ii) For the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (1)

$K_w = [H^+][OH^-]$ (1)

Assume $[NH_3] = 0.01$ or little reaction occurs

or $[OH^-] = [NH_4^+]$ or OH^- from water is negligible (1)

NB One of these statements MUST be made

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = [NH_3][H^+] \times \frac{[H^+]}{K_w}$$ (1)

$$[H^+]^2 = K_a \times \frac{K_w}{[NH_3]}$$ (1)

$$= 5.6 \times 10^{-10} \times \frac{10^{-14}}{0.01}$$

$[H^+] = 2.37 \times 10^{-11}\ \text{mol dm}^{-3}$ (1)

pH = 10.6 (1) **7**

NB Score 4 for pH = 5.6 then look back for three additional marks
NB If answer wrong, and not an AE, max 3 for three correct statements

Question 3

(a) The blue solution is $CuSO_4$ (1)

Add $CuSO_4$ to the other three solutions:
A white precipitate formed with $BaCl_2$ (1)
$BaCl_2 + CuSO_4 \longrightarrow BaSO_4 + CuCl_2$ Species (1)
Balanced (1)

A blue or green precipitate formed with Na_2CO_3 (1)
$Na_2CO_3 + CuSO_4 \longrightarrow Na_2SO_4 + CuCO_3$ Species (1)
Balanced (1)

Add Na_2CO_3 to the remaining two solutions:
A white precipitate formed with $BaCl_2$ (1)
$BaCl_2 + Na_2CO_3 \longrightarrow 2NaCl + BaCO_3$ Species (1)
Balanced (1)

A colourless gas evolved with HCl (1)
$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ Species (1)
Balanced (1)

Add HCl to $CuSO_4$;
A yellow-green solution formed (1)
$[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$ Species (1)
Balanced (1) Max 10

Planning (0,1 or 2) **12**

Allow max 10 for answers given ONLY as a table or a list of observations and equations

(b)(i) Oxidising agent MnO_4^- or $KMnO_4$ (1)
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ (1)
$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$ (1)
$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$ (1) **4**

NB Allow any multiple of above equations
NB Ignore additional species as long as they balance out and do not interfere

(ii) Purple colour due to MnO_4^- or name but NOT $KMnO_4$ (1)
$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
Species (1)
Balanced (1) **3**

(c)(i) Empirical formula: Na $\frac{59.0}{23.0} = 2.56$ (1)
O $\frac{41.0}{16.0} = 2.56$

Hence empirical formula is NaO (1)
Molecular formula: $M_r = 78.0$; $M_r = E_r \times n = 39\,n$
Hence molecular formula is Na_2O_2 (1)

NB Allow alternative methods; correct answer scores 3

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$ (1) **4**

(ii)	$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$	Species	(1)	
		Balanced	(1)	
	Na_2O_2 used to remove CO_2, replacing it with O_2		(1)	**3**

NB Allow answers in (ii) consequentially if NaO given as answer to (i)

(iii)	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$	(1)	
	$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	(1)	
	$H_2O_2 + 2Ce^{4+} \longrightarrow O_2 + 2H^+ + 2Ce^{3+}$	(1)	
	moles Ce^{4+} = $mv/1000 = 1.86 \times 10^{-3}$	(1)	
	moles $H_2O_2 = \dfrac{\text{moles } Ce^{4+}}{2}$	(1)	
	$= 9.28 \times 10^{-4}$	(1)	
	(1 mole Na_2O_2 forms 1 mole H_2O_2)		
	mass Na_2O_2 = moles $Na_2O_2 \times M_r$ or M_r used correctly	(1)	
	mass $Na_2O_2 = 9.28 \times 10^{-4} \times 78.0 =$ 0.0724 g (Allow 0.073 g)	(1)	**8**

NB If answer incorrect check back for each correct point made

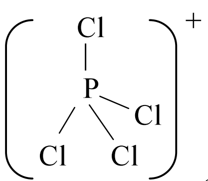
(d)(i)	$5PF_3Cl_2 \longrightarrow 3PF_5 + 2PCl_5$	Species	(1)	
		Balanced	(1)	**2**

(ii)	**C** = PF_6^-	(1)	
	PCl_4^+	(1)	**2**

Allow one mark for <u>two</u> mixed halogen versions

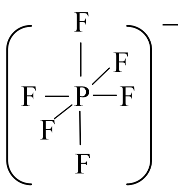
Allow one mark for $P_2F_6Cl_4$

(iii) PCl_4^+



(1)

PF_6^-



(1) **2**

NB Ignore bond angles even if incorrect

NB Charges on ions are not essential

NB Do not allow 'stick' structures

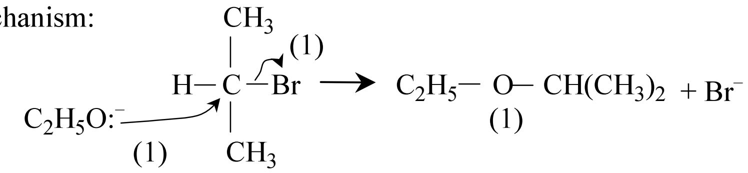
NB Do NOT mark consequentially to wrong answers in (d)(ii)

Question 4

(a)(i) $Na + C_2H_5OH \longrightarrow C_2H_5ONa + {}^1/_2H_2$ (1)
Role of sodium; a reducing agent (1) **2**

(ii) Substitution reaction: ethoxide is a nucleophile or a Lewis base or a lone electron pair donor (1)

Mechanism:



S_N1 mechanism: loss of Br (1); attack by $C_2H_5O^-$ (1); product (1)

NB CE = 0 if a wrong haloalkane used in mechanism but allow in elimination equation below

Elimination reaction; ethoxide is a base (1)
Equation:

$C_2H_5ONa + CH_3CHBrCH_3 \longrightarrow C_2H_5OH + H_2C = CH–CH_3 + NaBr$
or $C_2H_5O^- + CH_3CHBrCH_3 \longrightarrow C_2H_5OH + H_2C = CH–CH_3 + Br^-$ (1) **6**

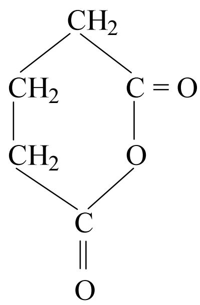
(iii) With primary haloalkane; mainly substitution (1)
With tertiary haloalkane; elimination occurs (1)
Size/steric reasons hinder substitution for tertiary haloalkane (1)
Substitution has a lower E_a, favoured for primary haloalkanes or
elimination has a higher E_a, less likely for primary haloalkanes
or tertiary carbocations more stable than primary carbocations (1) **4**

(b) Deductions:
Structure of **A**: $HO–CH_2CH_2CH_2CH_2–COOH$ (2)
Allow one mark if **A** identified as an acid

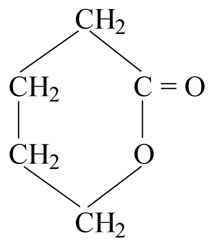
Structure of **B**: $HOOC–CH_2CH_2CH_2–COOH$ (3)

Allow **one** mark for
moles **B** $C_5H_8O_4$ (M_r 132) $= \frac{1.98}{132} = 0.015$ moles **plus** moles NaOH $\frac{0.50 \times 60}{1000} = 0.030$ moles
Allow **one** mark for hence $C_5H_8O_4$ is a dibasic acid

Structure of **C:** (1)



Structure of **D**: (1)



D is an ester (1)

F is a polymer.

Empirical formula: Oxygen content 37.2% (1)

$C, \frac{55.8}{12} = 4.65 : \quad H, = 7.0 : \quad O, \frac{37.2}{16} = 2.325$ (1)

Simplest ratio C : H : O = 2 : 3 : 1

Hence empirical formula = C_2H_3O (1)

Formation of **F**

HO–(- -)–OH + HOOC–$(CH_2)_3$–COOH ⟶ –[–O–(- -)–O–C(=O)–$(CH_2)_3$–C(=O)–]– (1)

Polyester has four oxygens in repeating unit: hence $M_f = (C_8H_{12}O_4)_n$ (1)

Hence diol is C_3 : i.e. HO-$CH_2CH_2CH_2$-OH or given in repeating unit (1)

Hence polymer is

–[–O–$CH_2CH_2CH_2$–O–C(=O)–$CH_2CH_2CH_2$–C(=O)–]$_n$ (1) **15**

NB Correct polymer structure scores 4; if wrong check back for correct separate points
NB Award max one if polymer based on ethan-1,2-diol

(c)(i) Benzene: delocalisation of electrons (1) **1**

(ii) $\Delta H_{hydrog} = -2(-126.9) = -253.8$ kJ mol^{-1}, 15kJ mol^{-1} less than expected

or value for buta-1.3-diene is less than $2\times\Delta H_{hydrog}$ of but-1-ene (1)

i.e. buta-1,3-diene is lower in energy or more stable (1)

due to delocalisation of electrons (1)

Hence C = C – C = C

longer than C = C in but-1-ene(1) shorter than C – C in but-1-ene (1) **5**

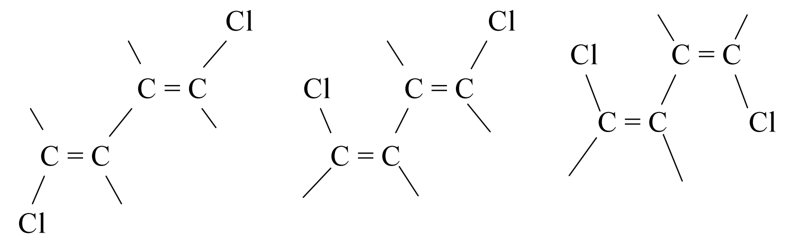
NB Allow max one for 'all carbon to carbon bond are the same length'

(iii) Delocalisation of electrons restricts rotation about C – C (1)

Double bonds further apart in **I** or

interference between H greater in **II** or more steric hindrance (1) **2**

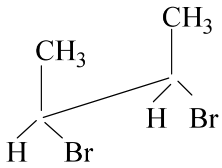
(iv)



trans-trans (1) cis-trans or trans-cis (1) cis-cis (1) **3**

NB Apply 'list principle if more than three answers given
NB Allow carbon skeleton structures
NB Allow if Br given in place of Cl

(v)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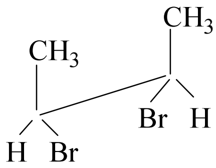
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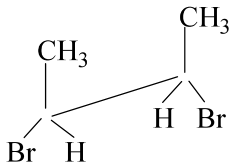
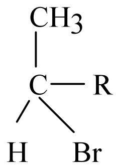

(1)

Max 2

NB Allow 1 for



Question 5(a)

If non-organic compound are given as illustrations, or no illustrations are given, award marks for the points which are indicated by * in the lists below.

1. Non-polar molecules		(1)	
	Hydrocarbons	(1)	
	C and H have similar electronegativities	(1)	
	C-H bonds/molecules not polar	(1)	
	* van der Waals forces between molecules	(1)	
	* Due to induced dipoles	(1)	
	* Linked to molecular size	(1)	
	* Linked to molecular shape/branching	(1)	
	* Forces weak if molecules small	(1)	
	Hence many have low melting/boiling points	(1)	**Max 7**
2. Polar molecules			
	* Dipole–dipole attraction	(1)	
	e.g. haloalkanes, ketones, esters etc.	(1)	
	* Elements with different electronegativities	(1)	
	* Bond polarity	(1)	
	Polar molecules	(1)	
	Structured of example	(1)	
	Boiling points higher (than HC of same M_r)	(1)	**7**
3. Hydrogen bonding *		(1)	
	e.g. Alcohols, acids	(1)	
	* Large dipole when H bonded to O, or N	(1)	
	* Strong dipole–dipole attraction	(1)	
	Structure of example	(1)	
	Intermolecular forces shown	(1)	
	Boiling points high	(1)	**7**
4. Ionic bonding *		(1)	
	e.g. salts, zwitterions	(1)	
	* Strong ion–ion attraction	(1)	
	Solids with high melting points	(1)	
	Protein or salt example	(1)	
	Structure of ions	(1)	**6**

Max 25

Q5(b)

Mark 1: For an identified use, e.g. metal extraction, a cell, a titration, etc

Mark 2: For an example of this use e.g. the extraction of iron, the use of potassium manganate(VII) to estimate, e.g. Fe^{2+}(aq)

Mark 3: A half-equation for an oxidation reaction

Mark 4: A half-equation for a reduction reaction

Note: Whole equations can be accepted if appropriate e.g. the reduction of iron oxides with C or CO or the formation of CO from CO_2 and C.

In the case of organic reactions, accept redox product where appropriate e.g. Tollen's reagent is reduced to silver, but oxidation equations including [O] should be given.

In addition, there is 1 mark for a general explanation of the term redox.

Indicate marks in the margin for each use as:

I = for marks for organic examples.

O = for marks for inorganic examples.

M = for marks for industrial examples (i.e. **M**anufacturing)

G = for a mark for a general statement.

At the bottom of each question give the total marks for the BEST TWO examples in each of the categories I, O, M and G and give the total mark.

e.g. I = 6; O = 5; M = 8; G = 1 Total = 20