AQA

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme June 2003

GCE

Chemistry

Unit CHM5

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SECTION A

Answer **all** questions in the spaces provided.

1 Consider the following oxides.

$$Na_2O,\ MgO,\ Al_2O_3,\ SiO_2,\ P_4O_{10},\ SO_3$$

(a) Identify one of the oxides from the above which

Penalise any wrong answer to zero

(i) can form a solution with a pH less than 3 ..... P_4O_{10} or SO_3 ..... (1)

(ii) can form a solution with a pH greater than 12 ..... Na_2O ..... (1)

(2 marks)

(b) Write an equation for the reaction between

(i) MgO and HNO_3

ie $MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$

$MgO + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2O$ or an ionic equation (1)

(not $O^{2-} + 2H^+ \rightarrow H_2O$)

(ii) SiO_2 and NaOH

ie $SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O$

$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$ or ionic equation (1)

(iii) Na_2O and H_3PO_4

ie $Na_2O + 2H^+ \rightarrow 2Na^+ + H_2O$ or an ionic equation

$3Na_2O + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3H_2O$ etc (1)

(3 marks)

(c) Explain, in terms of their type of structure and bonding, why P_4O_{10} can be vaporised by gentle heat but SiO_2 cannot.

P_4O_{10} is a molecular (structure) or simple covalent (1)

Weak intermolecular forces or van der Waals forces (between molecules) (1)

SiO_2 is macromolecule / giant covalent / giant molecule (Not giant-lattice) (1)

(Strong) covalent bonds (between atoms) must be broken (1)

(4 marks)

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2 (a) Identify a reagent, or mixture of reagents, necessary to carry out each of the following conversions.

Alkaline H_2O_2 scores (1)

(i) $[Cr(H_2O)_6]^{3+}(aq) \rightarrow CrO_4^{2-}(aq)$

H_2O_2 (1) plus NaOH (1) (Na_2O_2 scores (2))

only allow if H_2O_2 given

(ii) $VO_2^+(aq) \rightarrow [V(H_2O)_6]^{2+}(aq)$

Zn (1) plus HCl / H_2SO_4 (1) Ignore conc Not HNO_3

Only allow if Zn given

(iii) $[Ag(NH_3)_2]^+(aq) \rightarrow Ag(s)$

A named aldehyde or a correct formula clearly with an aldehyde group (1)

Or Cu → Mg *(5 marks)*

(b) In an acidic solution, hydrogen peroxide, H_2O_2, is oxidised to oxygen by manganate(VII) ions, which are reduced to Mn^{2+} ions.

(i) Write half-equations for the reactions occurring and use these to deduce the overall equation for this reaction.

Half-equation for the oxidation of H_2O_2

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (or multiple) (1)

Half-equation for the reduction of manganate(VII) ions

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (or multiple) (1)

Overall equation

Only allow $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ (or multiple) (1)

(ii) 20.0 cm^3 of an acidified solution of H_2O_2 was found to react with exactly 15.7 cm^3 of a 0.0180 mol dm^{-3} solution of potassium manganate(VII).
Calculate the concentration, in g dm^{-3}, of the solution of hydrogen peroxide.
(If you have been unable to complete the overall equation in part (b)(i), assume that the mole ratio of manganate(VII) to H_2O_2 is 3:5. This is not the correct ratio.)

Moles MnO_4^- = mv/1000 = $(2.82 \text{ to } 2.83) \times 10^{-4}$ (1)

Mark conseq to equation in b(i)

Moles H_2O_2 = $2.826 \times 10^{-4} \times 5/2$ (1) = $(7.06 \text{ to } 7.08) \times 10^{-4}$

$[H_2O_2] = 7.065 \times 10^{-4} \times 1000/20$ (1) = $(3.53 \text{ to } 3.54) \times 10^{-2}$

Mass = moles × Mr = $3.53 \times 10^{-2} \times 34$

= 1.2(0) (Ignore units) (1)

Max 3 if ratio 2/5 used. (Final answer 0.19)

(7 marks)

NB Using 3:5 ratio

Moles MnO_4^- = $(2.82 \text{ to } 2.83) \times 10^{-4}$ (1)

Moles H_2O_2 = $2.826 \times 10^{-4} \times 5/3$ (1) = $(4.70 \text{ to } 4.72) \times 10^{-4}$

$[H_2O_2] = 4.71 \times 10^{-4} \times 1000/20$ (1) = $(2.35 \text{ to } 2.36) \times 10^{-2}$

Mass = 0.8(0) (1) (ie 2 sig fig required)

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TURN OVER FOR THE NEXT QUESTION

3 (a) The ion $C_2O_4^{2-}$ can act as a bidentate ligand.

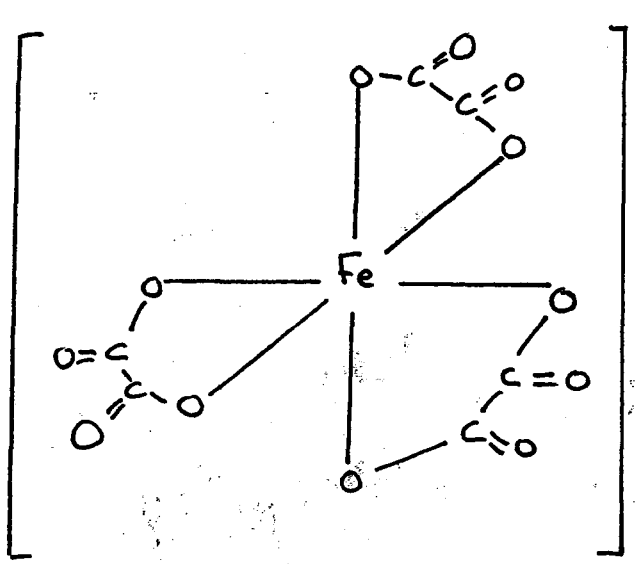
(i) Explain the meaning of the term *bidentate ligand.*

Two (1) lone pair donor / electron pair donor (1) atoms

Allow :- forms two co-ordinate bonds (1)

NOT atom with two lone pairs (0)

(ii) Sketch the structure of the octahedral complex ion formed by Fe^{3+} ions which contains $C_2O_4^{2-}$ as the only ligand. Include the overall charge on the complex ion.



Correct ligand structure (1) (if not essential)
(Penalise any error)

Six correct O-Fe bonds (1)

Correct charge (1)

NB Penalise the second mark if arrow from Fe shown

NB Ignore charges on atoms

(5 marks)

(b) Explain the meaning of the term *chelate effect.*

(Substitution of a monodentate ligand by a) bi or multidentate ligand (1) giving a { more stable complex or with an increase in entropy/disorder or forming a ring / cage complex/structure (crab like) } (1) *(2 marks)*

(c) The chloride ion can act as a monodentate ligand.

(i) Deduce the formula of the linear complex formed when an excess of concentrated hydrochloric acid is added to silver chloride.

$[AgCl_2]^-$ or $AgCl_2^-$ (1)

(ii) Explain why metal(II) ions do not usually form octahedral complexes when chloride ions are the only ligands.

Chloride or Cl^- big or large or repel (1)

NOT Cl_2 or Cl^+ or Cl

Allow 'chlorine ion'

(2 marks)

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(d) The concentration of $C_2O_4^{2-}$ ions can be determined by titration in acidic solution using a standard solution of potassium manganate(VII). At room temperature, the reaction proceeds very slowly at first but becomes faster after some of the manganate(VII) ions have reacted.

(i) Suggest why this reaction is very slow at first.

(Both) ions are negative or ions repel or High E_a (1)

(ii) This is an example of an autocatalytic reaction. State the meaning of the term *autocatalytic* and identify the catalyst.

Meaning of the term autocatalytic A product of the reaction acts as a catalyst (1) NOT A self-catalysing reaction (0)

Catalyst Mn^{2+} or Mn^{3+} (1)

(iii) Suggest how this catalyst might be involved in the reaction. (Allow n 3 to 6)

Mn^{2+} converted into Mn^{n+} or Mn^{2+} oxidised (1)

Mn^{n+}/oxidised species then oxidises/reacts with $C_2O_4^{2-}$ (1)

(5 marks)

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TURN OVER FOR THE NEXT QUESTION

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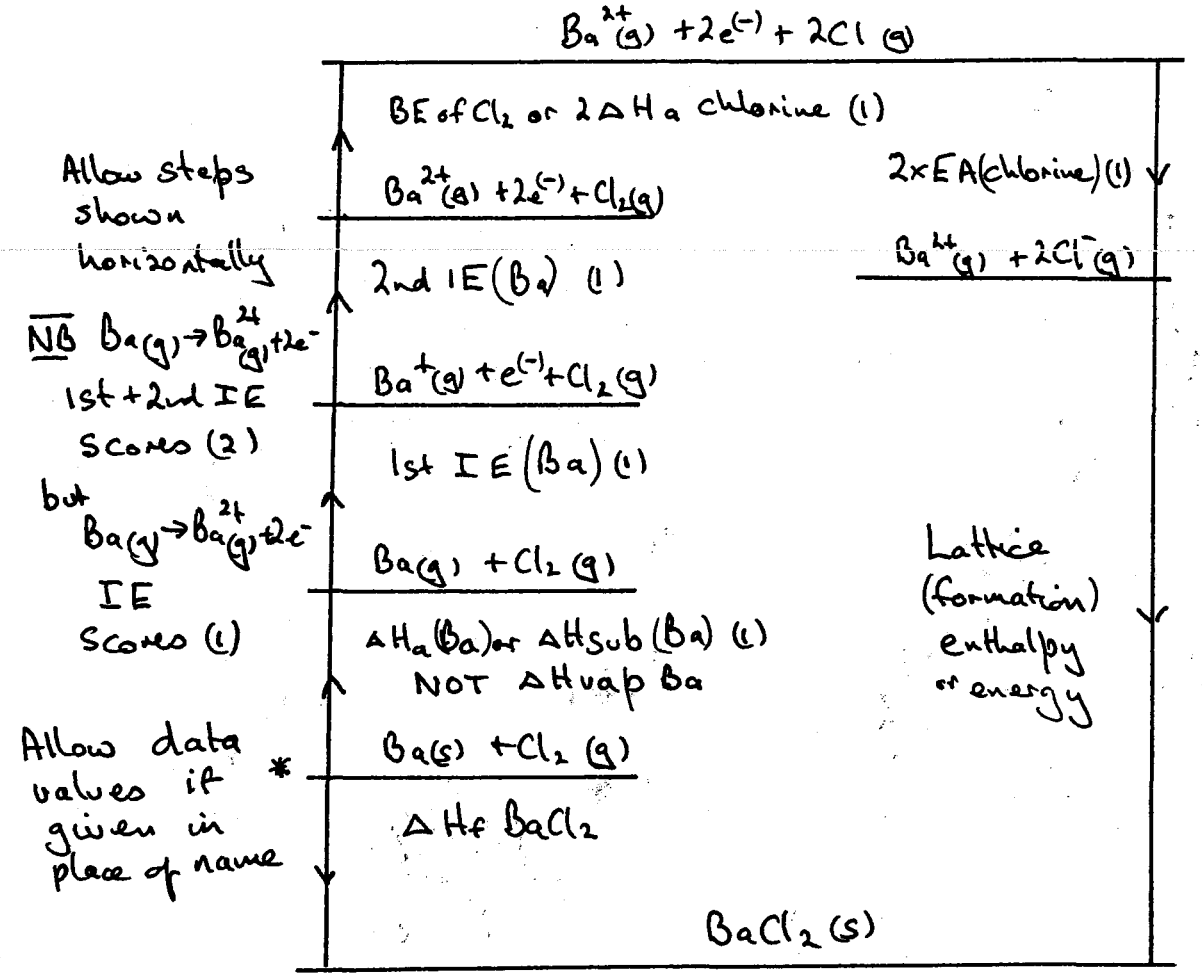
4 (a) (i) Draw a fully-labelled Born–Haber cycle for the formation of solid barium chloride, $BaCl_2$, from its elements. Include state symbols for all species involved.



ONLY consider species involved in the step marked

(ii) Use your Born–Haber cycle and the standard enthalpy data given below to calculate a value for the electron affinity of chlorine.

Enthalpy of atomisation of barium	+180 kJ mol^{-1}
Enthalpy of atomisation of chlorine	+122 kJ mol^{-1}
Enthalpy of formation of barium chloride	–859 kJ mol^{-1}
First ionisation enthalpy of barium	+503 kJ mol^{-1}
Second ionisation enthalpy of barium	+965 kJ mol^{-1}
Lattice formation enthalpy of barium chloride	–2056 kJ mol^{-1}

Calculation −1 for each error

Cycling clockwise about * (CE if a Step missing)

$\Delta H_a Ba + 1st\ IE\ Ba + 2nd\ IE\ Ba + 2\Delta H_a Cl + 2EA Cl + LE - \Delta H_f BaCl_2 = 0$ (1)

Mark conseq.

$+180 + 503 + 965 + 2 \times 122 + 2EA - 2056 + 859 = 0$ (1)

$EA = -695/2 = -(347 \text{ to } 348)$ (1) Ignore units

NOTES
−695 scores (2)
+(347 to 348) scores (2)
−(286 to 287) scores (2)
+(286 to 287) scores (1)
−573 scores (1)
+573 scores (0)

(9 marks)

(b) Use data from part (a)(ii) and the entropy data given below to calculate the lowest temperature at which the following reaction becomes feasible.

$$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$$

	$BaCl_2(s)$	Ba(s)	$Cl_2(g)$
$S^{\ominus}/JK^{-1}mol^{-1}$	124	63	223

$\Delta S = \Sigma S_{products} - \Sigma S_{reactants}$

$= (63 + 223) - 124 = 162$ (1)

$\Delta G = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$ or $T = \Delta H/\Delta S$ or used correctly (1)

$\Delta H = 859 \times 10^3$ (1) $= T \times 162$

$T = (5\,300$ to $5304)$ K (1)

Penalise if units °C

−1 for each error + mark conseq.

(4 marks)

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TURN OVER FOR THE NEXT QUESTION

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5 Ethane, from North Sea gas, can be cracked to form ethene and hydrogen. In practice, the cracking reaction is incomplete and a mixture of ethane, ethene and hydrogen is obtained.

(a) Write an equation for this cracking reaction.

$C_2H_6 \rightarrow C_2H_4 + H_2$ (1)

(1 mark)

(b) Calculate the total number of moles of gas in a 25.0 cm^3 sample of the gaseous mixture after cracking, measured at a temperature of 332 K and a pressure of 110 kPa.
($R = 8.31\ J\ K^{-1}\ mol^{-1}$)

-1 for each error

$PV = nRT$; or $n = PV/RT$ (1)

$n = 110{,}000 \times 25 \times 10^{-6} / 8.31 \times 332$ (1)

$= (10 \text{ to } 9.968) \times 10^{-4}$ (moles) (1)

(3 marks)

(c) The 25.0 cm^3 sample of the gaseous mixture from part (b) was treated with 75.0 cm^3 of gaseous bromine, also measured at 332 K and 110 kPa.

(i) Calculate the number of moles of bromine added to the gaseous mixture and write an equation for the reaction between ethene and bromine.

Calculation $3 \times^{(1)} (1.0 \text{ to } 9.968) \times 10^{-4}$

$= (3.0 \text{ to } 2.99) \times 10^{-3}$

Allow consequential on 3× answer to (b)

Equation $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ (1)

Penalise if an incorrect structural formula given

After the reaction between ethene in the gaseous mixture and bromine was complete, the unreacted bromine was treated with an excess of aqueous potassium iodide. Iodine was formed.

(ii) Write an equation for the reaction between aqueous potassium iodide and bromine.

$2KI + Br_2 \rightarrow 2KBr + I_2$ or an ionic equation (1)

Iodine reacts with aqueous sodium thiosulphate according to the following equation.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The iodine formed reacted with 22.1 cm^3 of a 0.250 mol dm^{-3} solution of sodium thiosulphate.

(iii) Calculate the number of moles of iodine formed. Hence, calculate the number of moles of bromine which reacted with the ethene present in the 25.0 cm^3 sample of the gaseous mixture.

Number of moles of iodine formed

Moles thio = $22.1 \times 0.250/1000$ = $(5.52 \text{ to } 5.53) \times 10^{-3}$ (1)

Moles I_2 = Moles thio / 2 (1)

= $(2.76 \text{ to } 2.77) \times 10^{-3}$

Number of moles of bromine which reacted with ethene

$2.99 \times 10^{-3} - 2.76 \times 10^{-3} = (2.25 \text{ to } 2.41) \times 10^{-4}$ (1)

Mark conseq even if answer is negative

(iv) Use these results to calculate the percentage by moles of ethene present in the gaseous mixture.

% Ethene = (moles ethene / total moles gas) × 100 (1)

= $(2.25 \text{ to } 2.41) \times 100 / (1.0 \text{ to } 9.966) \times 10^{-4}$

= (22.4 to 24.2) % (1) *(8 marks)*

Mark conseq as C(iii) × 100 / (b)

Notes Correct answer scores (5)

If there is no subtraction in b(ii) part two score max(3) two in c (iii) part are plus one in c (iv) for first point

Answer in b(iv) must be a %

TURN OVER FOR THE NEXT QUESTION

Negative final % or answers over 100% lose the last mark.

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SECTION B

Answer **all** of the questions below in the space provided on pages 16 to 20 of this booklet.

6 (a) State what is observed when aqueous ammonia is added dropwise, until present in excess, to a solution of cobalt(II) chloride, and the mixture obtained is then left to stand in air.
Give the formula of each cobalt-containing species formed. Explain the change which occurs when the mixture is left to stand in air. *(8 marks)*

(b) Explain why separate solutions of iron(II) sulphate and iron(III) sulphate of equal concentration have different pH values.
State what is observed when sodium carbonate is added separately to solutions of these two compounds. Give the formula of each iron-containing species formed.
(9 marks)

7 Concentrated sulphuric acid is a useful laboratory reagent. Choosing appropriate examples, illustrate this statement by considering how you would use concentrated sulphuric acid

(a) to distinguish between solid samples of two sodium halides, *(6 marks)*

(b) to prepare isomeric alkenes from an alcohol, *(5 marks)*

(c) to prepare an aromatic nitro-compound. *(4 marks)*

Write equations for the reactions occurring and state the role(s) of sulphuric acid in each reaction.

Question 6 Answers

(a) Forms blue or pink or blue/green precipitate (Not green) (1)

of $Co(H_2O)_4(OH)_2$ etc (1)

(Precipitate) dissolves or forms a solution (in excess ammonia) (1)

Forms yellow or pale brown or 'straw' (coloured solution) (1)

containing $[Co(NH_3)_6]^{2+}$ (1)

Darkens or goes brown on standing in air (1)

as $[Co(NH_3)_6]^{3+}$ formed (1)

Due to oxidation (by O_2 in air) or by reaction with oxygen (Q of L) (1) **8**

(b) Fe^{3+} has a large charge (1)

and smaller size than Fe^{2+} (1)

NB Fe^{3+} has a higher charge size ratio or higher surface density of charge or higher charge density, scores (2)

NB Lose these two marks if candidates refers to either atoms or molecules

Greater polarisation (of water) by Fe^{3+} or more hydrolysis occurs or Fe^{3+} weakens the O-H bond more (Allow converse statements) (1)

Fe^{2+} higher pH than Fe^{3+} or Fe^{3+} more acidic or solution of Fe^{3+} contains more H^+ (1) **4**

NB Allow marks for correct hydrolysis equations i.e.

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$$

if accompanied by a statement that this equilibrium lies further to the right for Fe3+ than for Fe^{2+} (1) and more H^+ produced/pH lower (1). (Allow converse statements)

Fe^{2+} with Na_2CO_3 ; green precipitate (1)

of $FeCO_3$ (1)

Fe^{3+} with Na_2CO_3 ;(rust)/brown or red/brown precipitate (Not red) (1)

of $[Fe(H_2O)_3(OH)_3]$ etc (Allow $Fe_2O_3.xH2O$ but not Fe_2O_3) (1)

and (carbon dioxide) gas evolved (1) **5**

Question 7 Answers

(a) Any **two** correct NaX reactions. If more than two given allow **best** scores.

NB *Apply list principle if additional incorrect **observation** given*
If NaX dissolved in water awarded Max 2 for equations
Allow molecular or ionic equations but not single half-equations

NaF: Colourless gas or steamy fumes (1)
H_2SO_4 acts as an acid (1)
$NaF + H_2SO_4 \rightarrow NaHSO_4 + HF$ etc (1)

NaCl; Colourless gas or steamy fumes (of HCl) (1)
H_2SO_4 acts as an acid (1)
$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ etc. (1)
NB If NaF and NaCl chosen allow Max 3 unless HF stated to etch glass

NaBr; Brown, yellow,orange or red/brown (fumes) (not red) (of bromine) (1)
NB Not SO_2 as HBr would also react with reagents used to test for it.
H_2SO_4 acts as an oxidising agent (1)
$2NaBr + 2H_2SO_4 \rightarrow Na_2SO_4 + Br_2 + SO_2 + 2H_2O$ (1)
NB A correct redox equation required for this mark

NaI; Yellow solid(S) or Bad egg smell(H_2S) or Purple fumes or
black solid (I_2) (Allow correct observation and ignore product identity) (1)
H_2SO_4 acts as an oxidising agent (1)
One correct redox equation (1) **6**

(b) A correct alcohol (1)

2 isomeric alkenes (2)
NB (Allow cis/trans isomers; ignore names unless no structure given

Equation (Ignore additional incorrect equations) (1)

H_2SO_4 acts as an acid or as a dehydrating agent or a catalyst (Q of L so MUST be stated in words) (1) **5**

NB Max 2 if alcohol incorrect
Penalise stick structures once only unless isomer correctly named

(c) Conc. HNO_3 (1)

Product (Allow in an equation or mechanism) (1)

Equation (Any) (Ignore additional incorrect equations) (1)

H_2SO_4 acts as an acid or as a catalyst. (Allow adds protons) (1) **4**

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8 (a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.110 mol of ethanol was maintained at 25 °C until the following equilibrium had been established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The ethanoic acid present at equilibrium required 72.5 cm^3 of a 1.50 $mol \cdot dm^{-3}$ solution of sodium hydroxide for complete reaction.

(i) Calculate the value of the equilibrium constant, K_c, for this reaction at 25 °C.

(ii) The enthalpy change for this reaction is quite small. By reference to the number and type of bonds broken and made, explain how this might have been predicted.
(9 marks)

(b) Aspirin can be prepared by acylation using either ethanoyl chloride or ethanoic anhydride, as represented by the equations shown below.

$$CH_3COCl + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + HCl$$

$$(CH_3CO)_2O + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + CH_3COOH$$

(i) By a consideration of the intermolecular forces involved, explain why the product HCl is a gas but the product CH_3COOH is a liquid at room temperature.

(ii) Give **two** industrial advantages of using ethanoic anhydride rather than ethanoyl chloride in the manufacture of aspirin. *(4 marks)*

9 You are required to plan an experiment to determine the percentage by mass of sulphate ions in some solid waste made up of the three compounds silicon dioxide, sodium carbonate and magnesium sulphate.

You are provided with dilute hydrochloric acid, a solution of barium chloride and simple laboratory equipment. (Hydrochloric acid reacts with carbonate ions and prevents the precipitation of barium and magnesium carbonates.)

(a) Outline how you would extract the sulphate ions from the solid waste and convert the extracted sulphate ions into a precipitate of barium sulphate.
Write equations for the reactions which occur. *(8 marks)*

(b) Describe how you would separate pure barium sulphate from other reaction products and how you would determine its mass.
Hence, explain how the percentage by mass of sulphate ions in the solid waste would be calculated. *(7 marks)*

END OF QUESTIONS

Question 8 Answers

(a) (i) Moles NaOH = mv/1000 = 1.50 × 72.5/1000 = 0.108 to 0.11 (1)

Moles of ethanoic acid at equilibrium = moles sodium hydroxide (1)

Moles ester = moles water (= moles acid reacted) (1)

= 0.200 - 0.108 = 0.090 to 0.092 (1)

Moles ethanol = 0.110 - 0.091 = 0.018 to 0.020 (1)

K_C = [Ester][Water]/[Acid][Alcohol] (Allow if used correctly) (1)

= $(0.091)^2$/ 0.109 × 0.019 = 3.7 to 4.9 (Ignore units) (1) **7**

NB *Allow the answer 4 one mark as correct knowledge*

(ii) Similar (types) of bond broken and made (1)
Same number of the bonds broken and made (any number if equal) (1) **2**

NB *If a list given then the total number of each type of bond broken and made must be the same*

(b)(i) (Weak) dipole-dipole attraction between HCl molecules (1)

(Strong) hydrogen bonds between CH_3COOH molecules (1) **2**

NB *Ignore van der Waals forces*

(b)(ii) Ethanoic anhydride is

cheap compared to ethanoyl chloride (1)

less corrosive than ethanoyl chloride or HCl evolved (1)

reaction less violent or vigorous or exothermic or dangerous or safer to use (1)

less vulnerable to hydrolysis (1)

reaction more easily controlled (1) Max **2**

Question 9 Answers

(a)

Weigh out a sample (Must be stated)	(1)	
Add hydrochloric nitric acid to the sample	(1)	
Until fizzing stops or excess acid added	(1)	
Filter off SiO_2 (Allow sand)	(1)	
Add barium chloride(solution)	(1)	
Until no more precipitation occurs or excess added	(1)	
$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$ (or ionic)	(1)	
$MgSO_4 + BaCl_2 \rightarrow MgCl_2 + BaSO_4$ (or ionic)	(1)	**8**

NB *Max 4 if H_2SO_4 added rather than HCl*
i.e. Weigh sample (1), Filter SiO_2 (1) Two equations (2)

(b)

Filter off the barium sulphate	(1)	
Wash to remove other reagents	(1)	
Dry	(1)	
Weigh	(1)	
Mole $BaSO_4$ = Mass $BaSO_4$/M_r $BaSO_4$ (or 233.4)	(1)	
Mass SO_4^{2-} = Mole $BaSO_4$ × M_r SO_4^{2-} (or 96.1)	(1)	
Percentage SO_4^{2-} = Mass SO_4^{2-} / Mass sample × 100	(1)	**7**