



ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark scheme

June 2002

GCE

Chemistry

Unit CHM5

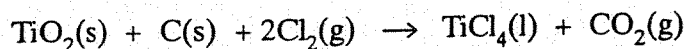
Copyright © 2002 AQA and its licensors. All rights reserved.

The Assessment and Qualifications Alliance (AQA) is a company limited by guarantee registered in England and Wales 3644723 and a registered charity number 1073334
Registered address: Addleshaw Booth & Co., Sovereign House, PO Box 8, Sovereign Street, Leeds LS1 1HQ
Kathleen Tattersall: *Director General*

SECTION A

Answer all the questions in the spaces provided.
You are advised to spend about 1 hour on this section.

- 1 (a) The following reaction occurs in the high-temperature preparation of titanium(IV) chloride.



- (i) Use the data given below to calculate the standard enthalpy change and the standard entropy change for this reaction.

| Substance | TiO ₂ (s) | C(s) | Cl ₂ (g) | TiCl ₄ (l) | CO ₂ (g) |
|---|----------------------|------|---------------------|-----------------------|---------------------|
| $\Delta H_f^\circ / \text{kJ mol}^{-1}$ | -940 | 0 | 0 | -804 | -394 |
| $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$ | 49.9 | 5.7 | 223 | 252 | 214 |

Standard enthalpy change $\Delta H_R = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$ (1)

→ $\Delta H_R = (-804 - 394) - (-940)$ (1)

$= -258 \text{ (kJ mol}^{-1}\text{; ignore units completely)}$ (1)

Allow +258 (2) marks

Standard entropy change $\Delta S = \sum S \text{ products} - \sum S \text{ reactants}$ (1)

→ $\Delta S = (252 + 214) - (49.9 + 5.7 + [2 \times 223])$ (1)

$-35.6 \text{ (J K}^{-1} \text{mol}^{-1}\text{; ignore units completely)}$ (1)

Allow +35.6 (2) marks Mark -36 AE minus one

Allow max one for +187

- (ii) Calculate the temperature at which this reaction ceases to be feasible.

$T = \Delta H / \Delta S$ OR $T = \frac{\Delta H \text{ value from above}}{\Delta S \text{ value from above}}$ (penalise wrong sign) (1)

$T = \frac{-258 \times 1000}{-35.6}$ (1) $= 7245 \text{ to } 7250$ (1)

(Ignore letter after value)

Mark answer conseq. to ΔH and ΔS values from above (9 marks)

If a negative temperature given max 2
If or used incorrectly max 1

If answer wrong this statement is worth (2)

If answer wrong this statement is worth (2)

more >>
if wrong say round

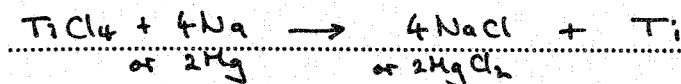
(b) In the industrial extraction of titanium, $TiCl_4$ is reduced to titanium in an inert atmosphere.

Note

CE if
species
incorrect

(i) Write an equation for this reduction process.

Correct species (1)
Balanced (1)



Penalise (aq) by one mark
Ignore other state symbols

(ii) Explain why it is essential to exclude air when this reduction takes place.

Do not allow
hydrolysis

Penalise if
other products
given
eg carbide

Ti reacts with ^(air) oxygen or Ti is oxidised or an oxide formed (1)
or Ti reacts with nitrogen or nitride formed (allow any oxide)
or Na or Mg reacts with oxygen, nitrogen or air (3 marks)

(c) Write an equation for the reaction of $TiCl_4$ with water.



allow $Ti(OH)_4$ when 4 H_2O needed (1 mark)

or $Ti(OH)_4(H_2O)_2$ when 6 H_2O needed

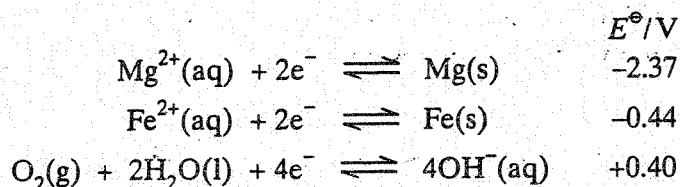
or $TiO_2 \cdot xH_2O$ but must be balanced

and $x = 6$ or less

TURN OVER FOR THE NEXT QUESTION

2 Large blocks of magnesium are bolted onto the hulls of iron ships in an attempt to prevent the iron being converted into iron(II), one of the steps in the rusting process.

Use the data below, where appropriate, to answer the questions which follow.



(a) Calculate the e.m.f. of the cell represented by $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ under standard conditions. Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

Mark on
after an AE

Cell e.m.f. 1.93 (V) CE if a negative value given (1)

Half-equation $Mg \rightarrow Mg^{2+} + 2e^-$ (1)
Ignore state symbols (2 marks)

(b) Deduce how the e.m.f. of the cell $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ changes when the concentration of Mg^{2+} is decreased. Explain your answer.

Mark
separately

Change in e.m.f. Increased (Mark on even if incorrect) (1)

Explanation Cell reaction or overall reaction goes to the right
Equilibrium displaced to Mg^{2+} or to the left (1)

..... (Electrode is more negative or E decreases) (1)
or gives more electrons
or forms more Mg^{2+} ions (3 marks)

(c) Calculate a value for the e.m.f. of the cell represented by $Pt(s)|OH^-(aq)|O_2(g)||Fe^{2+}(aq)|Fe(s)$ and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.

Mark on
after an
AE

Cell e.m.f. -0.84(V) (CE if +ve) (1)

Explanation Fe is giving electrons OR
forms Fe^{2+} OR reaction goes in the
reverse direction (2 marks)

NB In (a) and (c) mark on if no value given but
CE in both (a) and (c) if emf = zero

3 (a) State the origin of the colour of transition-metal complexes.

Donot allow charge transfer

{ Electrons excited
Electron transitions in d shell d-d transition (1)

(Energy in) visible range (Not emits in visible region) (1) (2 marks)

(b) Give three changes to a transition-metal complex which result in a change in colour.

Change 1 (Different) oxidation states (1)

Change 2 (Different) ligands (1)

Change 3 (Different) co-ordination number (1) (3 marks)

Do not allow 'shape' as an answer

(c) You are provided with a 1.00 mol dm^{-3} solution of iron(III) ions and a visible-light spectrophotometer (colorimeter). Outline a plan for experiments using this solution and this apparatus which would enable you to determine the concentration of iron(III) ions in a solution of unknown concentration. [thiocyanate (CNS^-) or bipyridyl]

Add an appropriate (or a given correct) ligand to intensity colour (1)

Make up solutions of known concentration (1)

Measure absorptions or transmission (1)

Plot graph of results or calibration curve (1)

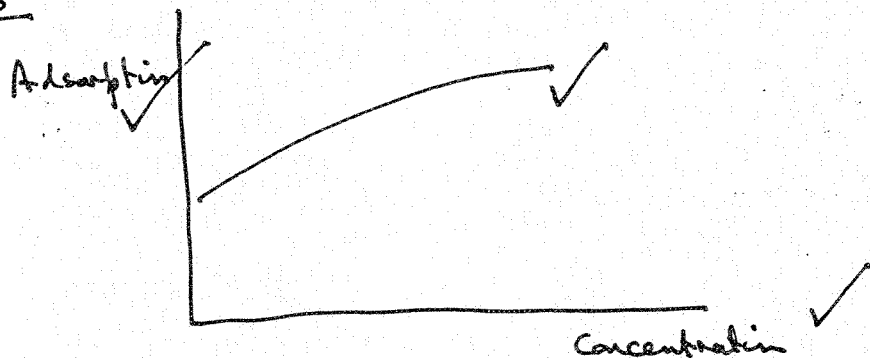
Measure absorption of unknown and compare (1)

NB Allow concentration statement if included in graph statement

Allow adsorption but circle (1)

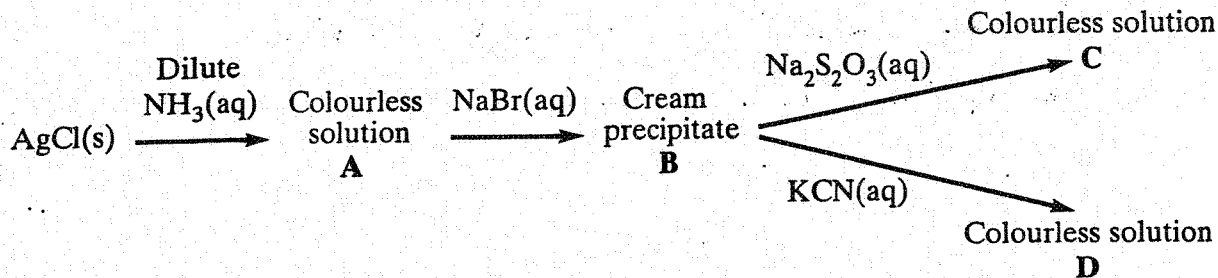
(5 marks)

Also



Scores 3

4 Consider the reaction sequence below.



- (a) Identify the silver-containing species in A, give its shape and state a use for it in organic chemistry.

Mark Species
and Shape
Separately

Species $[\text{Ag}(\text{NH}_3)_2]^+$
 Shape Linear (1)

Mark use
Separately

Use To distinguish between (or identify) aldehydes and ketones OR Tollen's reagent or in 'silver mirror test' (1)
 (3 marks)

- (b) (i) Identify the cream precipitate B and the silver-containing species in C.

Precipitate B AgBr or name (1)

Silver-containing species in C $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ (1)

- (ii) Write an equation for the reaction in which the silver-containing species in C is formed from B and explain the use of this reaction in photographic processing.

Equation $\text{AgBr} + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{Br}^-$ (1)

Explanation Removes AgBr or "fixer" or prevents AgX darkening or reacting with light (1)
 (4 marks)

- (c) Identify the silver-containing species in D, and state one use of solutions containing this species.

Species $[\text{Ag}(\text{CN})_2]^-$ (1)

Use Electroplating (1)
 (2 marks)

- (d) What can be deduced about the outer electronic configuration of silver in each of the species A, C and D from the fact that all the species are colourless?

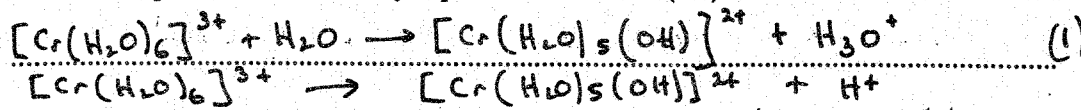
It has a full d shell or does not have a partially filled d shell (1) (1 mark)

Ignore
3 4 3d
stated

Do NOT allow reactions with bases other than water

5 (a) (i) Write an equation to show why aqueous chromium(III) chloride is acidic.

Allow loss of
up to 2H⁺



(ii) Explain why aqueous chromium(III) chloride is more acidic than aqueous chromium(II) chloride.

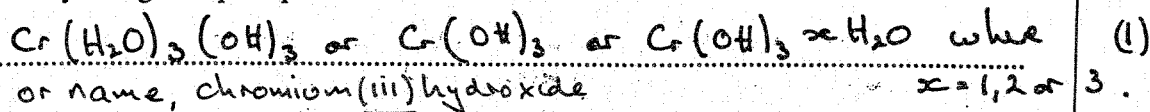
Cr³⁺ is smaller than Cr²⁺

OR Cr³⁺ has a greater charge density or charge to size ratio
 surface density of charge (1)

Cr³⁺ is more polarising⁽¹⁾ or draws electron density from oxygen
 more O-H bonds (break) weakened (3 marks) (1)
 (MAX 2 from 3)

(b) The addition of sodium hydroxide or of sodium carbonate to aqueous chromium(III) chloride results in the formation of the same green precipitate.

(i) Identify this green precipitate.

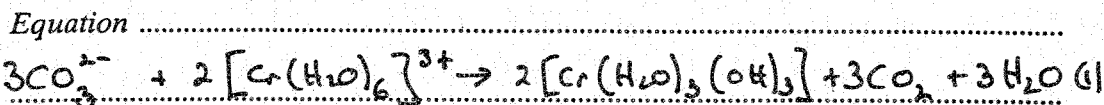


(ii) State the role shown by both sodium hydroxide and sodium carbonate in the formation of this green precipitate.

Base or electron pair donor or proton acceptor (1)
 NOT alkali; ignore nucleophile but penalise 'ligand'

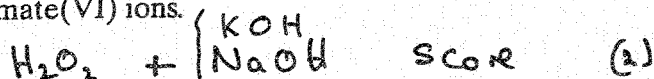
(iii) Identify the gas evolved when carbonate ions react with aqueous chromium(III) ions and write an equation for the reaction occurring.

Gas evolved CO_2 or name (1)



NB If separate equations for CO_3^{2-} and Cr^{3+} given an overall equation must be deduced. (4 marks)

(c) State the reagents which could be used to convert aqueous chromium(III) ions into chromate(VI) ions.



$H_2O_2 +$ anything else or alone scores (1)

$NaOH$ alone score zero. (2 marks)

Na_2O_2 scores (2)

Do not allow 'alkaline', or OH^- or NH_3

6 (a) State what is meant by the term *co-ordinate bond*.

Mark points
separately

A shared electron pair or covalent bond (1)
 Both electrons from one atom (1)
 or when a Lewis base reacts with a Lewis acid (2 marks)

(b) Define the terms *Brønsted-Lowry acid* and *Lewis acid*.

Brønsted-Lowry acid ... A proton or H^+ donor (NOT H_3O^+) (1)
Lewis acid ... A lone or electron pair acceptor (1)
 (2 marks)

(c) State what is meant by the term *bidentate ligand*.

Two atoms or two points of attachment (1)
 Each donating a lone electron pair (1)
 OR forms 2^o co-ordinate bonds (1)
 OR donates two^o pairs of electrons (1)
 (2 marks)

(d) State how the co-ordination number of cobalt(II) ions in aqueous solution changes when an excess of chloride ions is added. Give a reason for the change.

Change in co-ordination number ... 6 to 4 (1)
 Reason for change ... Chloride ligands are larger than water
 ligands or greater repulsion between chloride ligands (1)
 (2 marks)

Do not
allow
chlorine
or Cl

(e) Suggest why the enthalpy change for the following reaction is close to zero.

$[Co(NH_3)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 6NH_3$
 Same number (1) and same type of bonds (1)
 broken and made
 (2 marks)

(f) Deduce the formula of the compound formed when ethane-1,2-diamine is treated with an excess of hydrochloric acid.

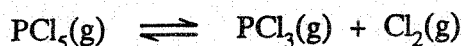
$ClNH_3CH_2CH_2NH_3Cl$ (1)
 or $(NH_3CH_2CH_2NH_3)^{2+} 2Cl^-$ (1 mark)

Allow $C_2H_{10}N_2Cl_2$ and $NH_3ClCH_2CH_2NH_3Cl$

SECTION B

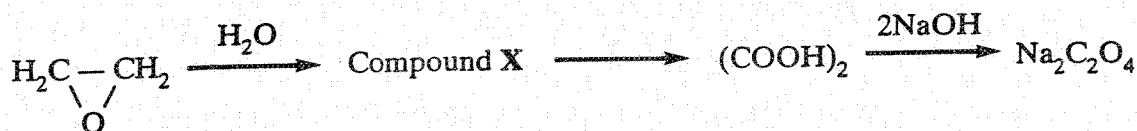
Answer all of the questions below in the space provided on pages 11 to 20 of this booklet.

- 7 A 4.54 g sample of PCl_5 was heated in a sealed flask at 525 K. Partial decomposition occurred as shown by the equation below.



At equilibrium, 45.0% of the PCl_5 had dissociated and the total pressure in the flask was 91.9 kPa.

- (a) Calculate a value for the equilibrium constant K_p of this reaction at 525 K. (9 marks)
- (b) In the gaseous state, both PCl_3 and PCl_5 exist as molecules. In the solid state, PCl_5 is ionic and made up of two species both of which contain phosphorus. Sketch and name the shape of the PCl_3 molecule and that of the PCl_5 molecule. Suggest a formula and a shape for each of the two ionic species present in solid PCl_5 . (6 marks)
- 8 The reaction scheme below shows the conversion of epoxyethane into sodium ethanedioate.



- (a) Identify compound X. State the reagents and conditions required to convert X into ethanedioic acid. Draw the structure of the anion in sodium ethanedioate. (4 marks)
- (b) The addition of sodium ethanedioate to an aqueous solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions results in the formation of a more stable complex ion. Draw the structure of the complex ion formed and explain, in thermodynamic terms, why this substitution reaction occurs. (4 marks)
- (c) (i) Sketch the pH curve for the titration of ethanedioic acid with aqueous sodium hydroxide. Write equations for the reactions which occur during this titration.
- (ii) A 25.0 cm^3 sample of a solution of ethanedioic acid was found to react with exactly 18.2 cm^3 of a $0.145 \text{ mol dm}^{-3}$ solution of sodium hydroxide. Calculate the concentration of the ethanedioic acid solution.

What volume of sodium hydroxide solution would have been required if the solution titrated had been sodium hydrogenethanedioate, NaHC_2O_4 , of the same concentration rather than ethanedioic acid? (7 marks)

- 9 (a) The reaction between aqueous persulphate ions, $S_2O_8^{2-}(aq)$, and iodide ions, $I^-(aq)$, is catalysed by $Fe^{2+}(aq)$ ions. Suggest why this reaction has a high activation energy. Write equations to explain the catalytic action of $Fe^{2+}(aq)$ ions. Suggest why $V^{3+}(aq)$ ions will also act as a catalyst for this reaction but $Mg^{2+}(aq)$ ions will not. (6 marks)
- (b) Outline a mechanism for the reaction between benzene and ethanoyl chloride and explain why $AlCl_3$ acts as a Lewis acid catalyst for this reaction. Predict, with an explanation in each case, the suitability of $FeCl_3$ and of NH_4Cl to act as a catalyst for this reaction. (9 marks)
- 10 (a) **P** and **Q** are oxides of Period 3 elements.
- Oxide **P** is a solid with a high melting point. It does not conduct electricity when solid but does conduct when molten or when dissolved in water. Oxide **P** reacts with water forming a solution with a high pH.
- Oxide **Q** is a colourless gas at room temperature. It dissolves in water to give a solution with a low pH.
- (i) Identify **P**. State the type of bonding present in **P** and explain its electrical conductivity. Write an equation for the reaction of **P** with water.
- (ii) Identify **Q**. State the type of bonding present in **Q** and explain why it is a gas at room temperature. Write an equation for the reaction of **Q** with water. (9 marks)
- (b) **R** is a hydroxide of a Period 3 element. It is insoluble in water but dissolves in both aqueous sodium hydroxide and aqueous sulphuric acid.
- (i) Give the name used to describe this behaviour of the hydroxide.
- (ii) Write equations for the reactions occurring.
- (iii) Suggest why **R** is insoluble in water. (6 marks)

END OF QUESTIONS

Question 7 **NB Mark NOW** awarded for calculating $p\text{PCl}_3$ not $p\text{PCl}_3 = p\text{Cl}_2$

(a)

Initial moles of $\text{PCl}_5 = 4.54/208.5$ (1) = 0.0218 (AE if $M_r \text{PCl}_5$ wrong)

At equilibrium moles $\text{PCl}_5 = 0.0218 \times 55/100$ (1) = 0.01198 (allow 0.012)

NB Award 2 marks if initial moles PCl_5 missing but equilibrium moles PCl_5 correct

Either moles PCl_3 or moles $\text{Cl}_2 = 0.0218 \times 45/100$ (1) = 0.00980

NB This can also be determined by subtraction

NB If mole $\text{PCl}_3 \neq$ Moles Cl_2 award max 4 for the following

Initial moles PCl_5 (1)

Equilibrium moles PCl_5 (1)

Partial pressure = Total pressure \times mole fraction (stated or used correctly) (1)

K_p defined or used correctly (1)

Total moles in system = 0.03158 (Allow 0.032) (1)

NB Mark this consequentially to equilibrium moles of PCl_5 , PCl_3 plus Cl_2

partial pressure = Total pressure \times mole fraction (stated or used correctly) (1)

$p\text{PCl}_5 = 91.9 \times 0.01199/0.03161$ (1) = 34.9 to 34.5

NB Mark consequentially to equilibrium moles PCl_5 and total number of moles

$p\text{PCl}_3 = p\text{Cl}_2 = 91.9 \times 0.00981/0.03161$ (1) = 28.52

$K_p = p\text{PCl}_3 \times p\text{Cl}_2 / p\text{PCl}_5$ (defined or used correctly) (1)

NB Do not allow if [] included here

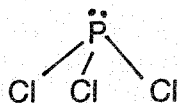
= $28.52^2/34.86 = 23.3$ to 23.9 (kPa) (1)

NB Mark consequentially to partial pressures determined above

NB Ignore units even if incorrect

9

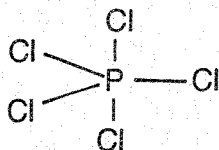
- (b) PCl_3 Pyramidal or Tetrahedral (1)
 Sketch (1)



NB Mark sketch and name separately

NB If clearly pyramidal, allow sketch without lone electron pair

- PCl_5 Trigonal bipyramidal (1)
 Sketch (1)



NB Mark sketch and name separately

- Formulae of ions PCl_4^+ and PCl_6^- (1)
 Shapes Tetrahedral and Octahedral (1)

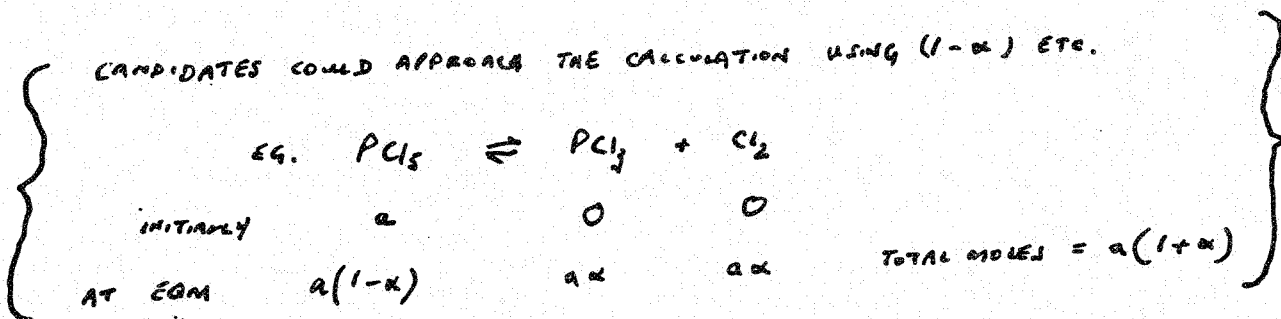
OR PCl_4^+ and stated as tetrahedral (1)

PCl_6^- and stated as octahedral (1)

6

QUESTION 7 : ALTERNATIVE MARK SCHEME.

CANDIDATES COULD APPROACH THE CALCULATION USING $(1-x)$ ETC.



USING THIS METHOD LOOK OUT FOR THE FOLLOWING SCORING POINTS :

$$\left(\frac{1-x}{1+x}\right) \text{ mol fraction } \text{PCl}_5 : x_{\text{PCl}_5} = \boxed{0.3793} \checkmark \quad [2]$$

$$\left(\frac{x}{1+x}\right) \text{ mol fraction } \text{PCl}_3 = \text{mol fraction of } \text{Cl}_2 = \boxed{0.3103} \checkmark \quad [2]$$

$$\boxed{\text{partial pressure} = \text{mol fraction} \times \text{total pressure}} \checkmark \quad [1]$$

$$\left(\frac{1-x}{1+x}\right) P_T \therefore \text{partial pressure of } \text{PCl}_5 = 0.3793 \times 91.9 = \boxed{34.86} \checkmark \quad [1]$$

$$\left(\frac{x}{1+x}\right) P_T \therefore \text{partial pressure of } \text{PCl}_3 = \text{Cl}_2 = 0.3103 \times 91.9 = \boxed{28.52} \checkmark \quad [1]$$

$$\boxed{K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}} \checkmark \quad [1]$$

$$K_p = \frac{\left(\frac{x}{1+x}\right)^2 P_T^2}{\left(\frac{1-x}{1+x}\right) P_T} = \left(\frac{x^2}{1-x^2}\right) P_T$$

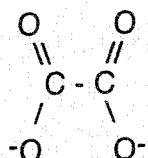
$$= \boxed{23.33} \checkmark \quad (\text{kPa}) \quad [1]$$

9

Question 8

- (a) Identity of **A**;
 ethane-1,2-diol or 1,2 dihydroxyethane or ethylene glycol or formula (1)
 NB Do NOT allow $\text{OHCH}_2\text{CH}_2\text{OH}$ unless a correct name also given
 $\text{K}_2\text{Cr}_2\text{O}_7$ / dilute H_2SO_4 or dilute HCl or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ (1)
 NB Oxidising agent must be a reagent
 NB Do not allow concentrated H_2SO_4
 Reflux (ignore temperature if given) or warm of heat (1)
 NB If a temperature given on its own it must be at or below 200°C

Anion

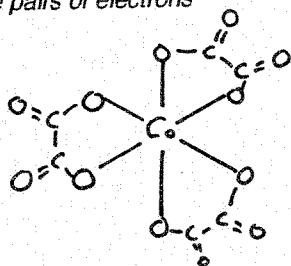


(1) 4

NB Do NOT allow $\text{C}_2\text{O}_4^{2-}$

NB Ignore lone pairs of electrons

- (b) Structure;



correct co-ordination (1)

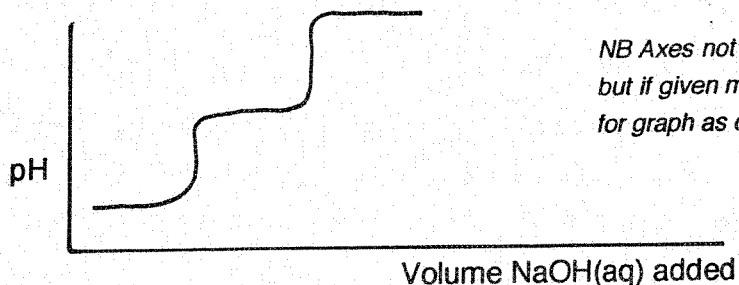
bonding through six
 correct oxygen (1)
 (Score 2 or 0)

NB Not essential to show double bonds i.e. $\text{C}=\text{O}$ in structure

Explanation:

- Substitution produces more molecules or particles or more disorder (1)
 Entropy change is positive (1) 4

- (c)(i) pH curve; two steps shown (1)



NB Axes not essential
 but if given must be correct
 for graph as drawn

- Equations; $\text{H}_2\text{C}_2\text{O}_4 + \text{OH}^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O}$ (1)
 $\text{HC}_2\text{O}_4^- + \text{OH}^- \rightarrow \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O}$ (1)

NB Allow one for $\text{H}_2\text{C}_2\text{O}_4 + 2\text{OH}^- \rightarrow \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O}$

NB Allow 'molecular equations'

- (c)(ii) Moles of NaOH = $0.145 \times 18.2/1000$ (1) = 2.64×10^{-3}
 Moles acid = $(2.64 \times 10^{-3}) \div 2$ (1) = 1.32×10^{-3}

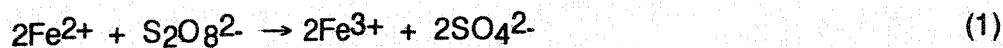
NB Mark CE at this point if moles NaOH not divided by 2

- Concentration of acid = $1.32 \times 10^{-3} \times 1000/25 = 0.0528$ or 0.05278 (1)
 NB Mark concentration consequentially to correct moles acid

- Volume NaOH if NaHC_2O_4 used = $18.2/2 = 9.1$ (1) 7

Question 9

(a) High E_a : $S_2O_8^{2-}$ repels I^- or both ions negative (1)



NB Ignore additional incorrect equations

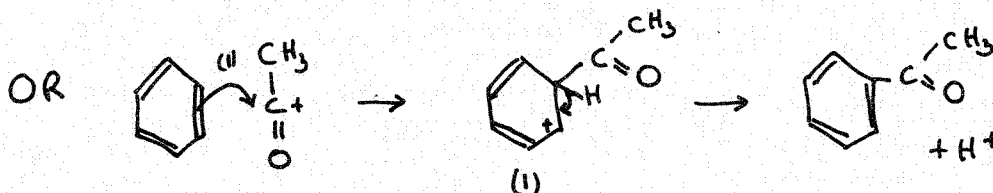
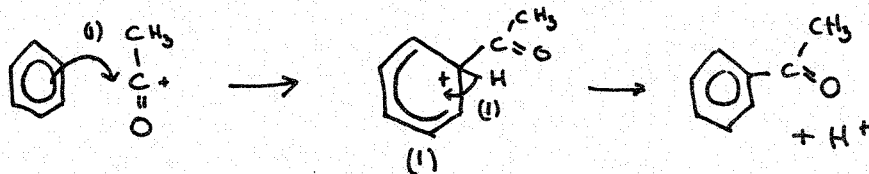
Vanadium is a transition element or Magnesium is not a transition element (1)

Vanadium has variable oxidation states (1)

Magnesium only forms Mg^{2+} , or has only one oxidation state (1) **6**

NB Score two Marks for "Only vanadium has variable oxidation states"

(b) $AlCl_3 + Cl-COCH_3 \rightarrow AlCl_4^- + CH_3CO^+$ (1)



Lewis acid: $AlCl_3$ accepts electron pair (1)

NB Penalise incorrect acyl chloride by one mark

NB Penalise chloroethane by two marks i.e. first equation mark, attack on benzene mark

NH_4Cl : Not a catalyst (1)

$FeCl_3$: A catalyst (1)

has a low energy vacant shell

or has spaces or vacancies in d shell

or has a partially filled d shell

or able to accept an electron pair

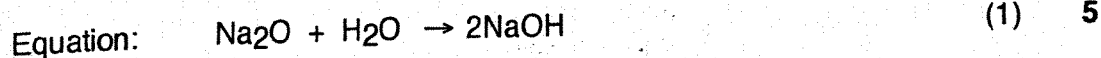
or can form $FeCl_4^-$ (1) **9**

Question 10

(a)(i) Deductions

Ionic (1)
 Ions not free to move in the solid state (1)
 Ions free to move when molten or in aqueous solution (1)

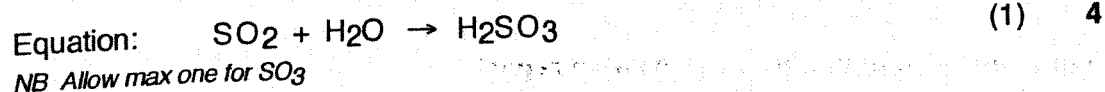
Identity of **P**; Na₂O or sodium oxide (1)
 NB If a formula given this must be correct



(ii) Deductions

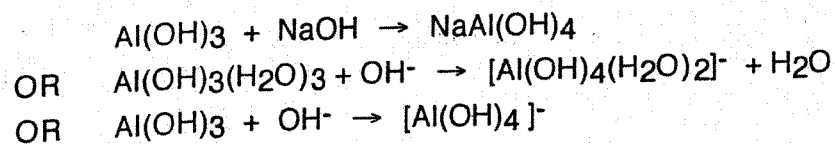
Covalent (1)
 Intermolecular forces are weak or van der Waals forces, or dipole-dipole (1)
 NB Any answer including a reference to hydrogen bonding is incorrect

Identity of **Q**; SO₂ or sulphur dioxide (1)



(b)(i) Amphoteric (1)

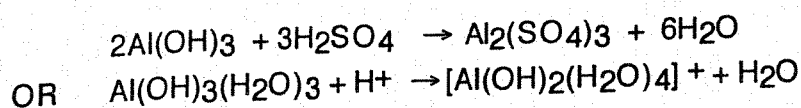
(ii) Equation with NaOH



R identified as Al(OH)₃ or Al(OH)₃(H₂O)₃ (1)
 A balanced equation

(1)
 NB Allow equations with six co-ordinate Aluminium and up to six OH- ligands
 NB Allow equation mark if M(OH)₃ given in a balanced equation

Equation with H₂SO₄



NB Allow equations with six co-ordinate Aluminium and up to six H₂O ligands
 NB Allow equation mark if M(OH)₃ given in a balanced equation

Correct Al species as product (1)
 A balanced equation (1)

(iii)

Large lattice energy
 or strong covalent bonds
 or ΔH_{soln} is very positive
 or ΔG is positive
 or sum of hydration energies less than covalent bond energies (1) 6