



ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark scheme June 2002

GCE

Chemistry

Unit CHM5

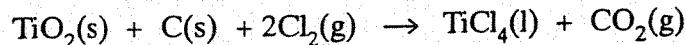
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Kathleen Tattersall: Director General

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	$\text{TiO}_2(\text{s})$	$\text{C}(\text{s})$	$\text{Cl}_2(\text{g})$	$\text{TiCl}_4(\text{l})$	$\text{CO}_2(\text{g})$
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	-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)

If answer strong this statement is worth (2) $\rightarrow \Delta H_R = (-804 - 394) - (-940)$ (1)
 $= -258 \text{ (kJ mol}^{-1}\text{; ignore units completely)}$ (1)

Allow + 258 (2) marks

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

If answer strong this statement is worth (2) $\rightarrow \Delta S = (252 + 214) - (49.9 + 5.7 + [2 \times 223])$ (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)

$$T = \frac{-258 \times 1000}{-35.6} = 7245 \text{ to } 7250 \quad (\text{Ignore letter after value})$$

Mark answer conseq to all and AS values from above (9 marks)

If a negative temperature given max 2 }*

If °C used incorrectly max 2 }

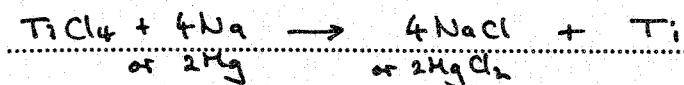
* R. + n.l. penalise no. of these errors

- Note
CE if species incorrect
- (b) In the industrial extraction of titanium, $TiCl_4$ is reduced to titanium in an inert atmosphere.

Correct species (1)
Balanced (1)

Penalise (aq) by one mark
Ignore other state symbols

- (i) Write an equation for this reduction process.



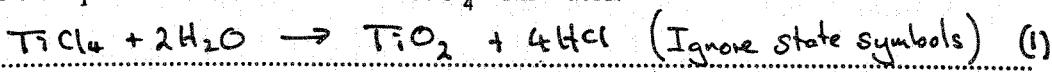
Do not allow hydrolysis

Penalise if other products given eg carbide

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

Ti reacts with $\{Oxygen$ or Ti is oxidised or an oxide formed (air)
or Ti reacts with nitrogen or nitride formed or formula of any nitride
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 $TiO_2 \propto H_2O$ but must be balanced
and $\propto = 6$ or less

13

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.

	E^\ominus/V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40

- (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)
 or \Rightarrow
 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. Increases (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 (1)
 (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.

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

Don't allow
charge
transfer

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

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

Change 1 (Different) oxidation states (1)

Do not
allow
'shape'
as an
answer

Change 2 (Different) ligands (1)

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

(3 marks)

- (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 absorption or transmission (1)

Plot graph of results or calibration curve (1)

Measure absorption of unknown and

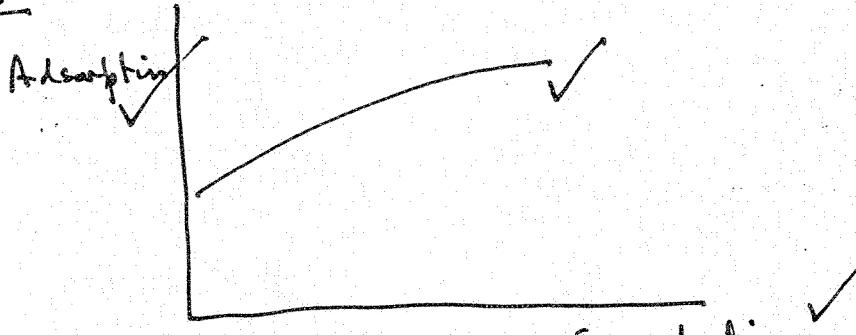
compare (1)

NB Allow concentration statement if included in graph statement

Allow absorption but circle (1)

(5 marks)

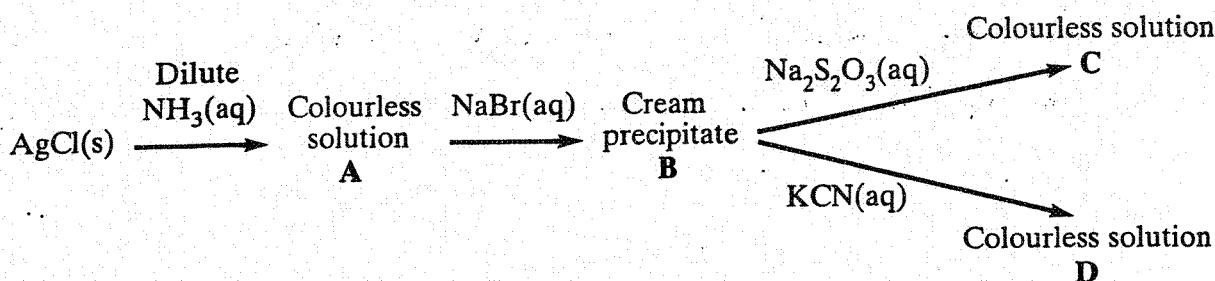
Also



Score 3

10

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

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 Ag^+ 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)

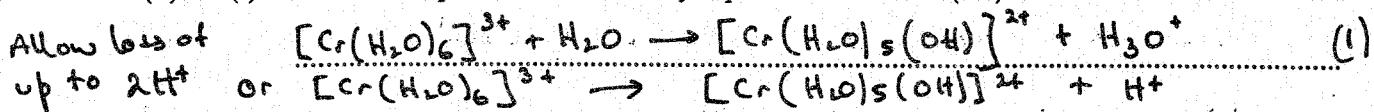
- (d) What can be deduced about the outer electronic configuration of silver in each of the species A, C and D from the fact that all the species are colourless?

Ignore 3 if 3d stated
 It has a full d shell or does not have a partially filled d shell (1) (1 mark)

NOT 'it has a full ⁶⁰ outer shell'

Do NOT allow reactions with bases other than water

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



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

Cr^{3+} is smaller than Cr^{2+}

OA Cr^{3+} has a greater charge density or charge-to-size ratio
surface density of charge (1)

Cr^{3+} is more polarising (1). $\text{H}-\text{O}$ bonds break
or draws electron density from oxygen (3 marks)
weakened (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.

$\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$ or $\text{Cr}(\text{OH})_3$ or $\text{Cr}(\text{OH})_3 \approx \text{H}_2\text{O}$ where $x = 1, 2$ or 3.
or name, chromium(III) hydroxide (1)

- (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.

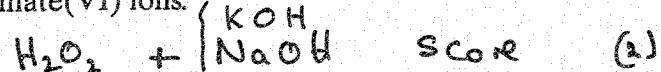
Gas evolved CO_2 or name (1)

Equation



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 scores zero.

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
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 2⁰ co-ordinate bonds (1)
OR donates two 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)

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

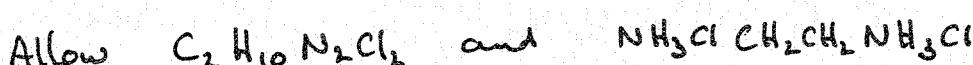
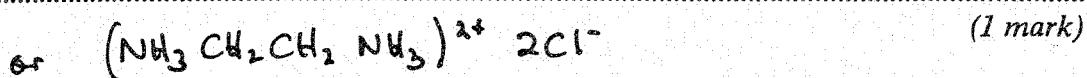


Same number (1) and same type of bonds (1)

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.



SECTION B

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

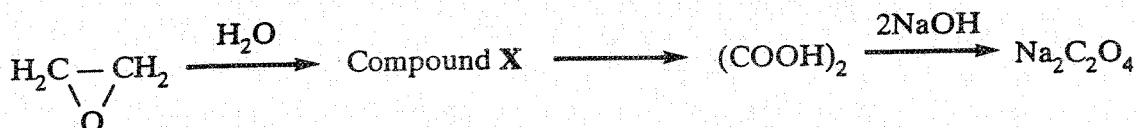
- 7 A 4.54 g sample of PCl_5 was heated in a sealed flask at 525 K. Partial decomposition occurred as shown by the equation below.



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)

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

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

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

$$\text{Either moles } \text{PCl}_3 \text{ or moles } \text{Cl}_2 = 0.0218 \times 45/100 \quad (1) = 0.00980$$

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)

$$\text{Total moles in system} = 0.03158 \quad (\text{Allow 0.032}) \quad (1)$$

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)

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

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

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

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

NB Do not allow if [] included here

$$= 28.52^2/34.86 = 23.3 \text{ to } 23.9 \quad (\text{kPa}) \quad (1)$$

NB Mark consequentially to partial pressures determined above

NB Ignore units even if incorrect

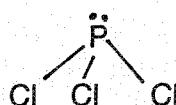
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(b)

PCl_3 Pyramidal or Tetrahedral Sketch

(1)

(1)



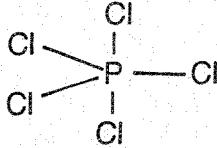
NB Mark sketch and name separately

NB If clearly pyramidal, allow sketch without lone electron pair

PCl_5 Trigonal bipyramidal Sketch

(1)

(1)



NB Mark sketch and name separately

Formulae of ions PCl_4^+ and PCl_6^-

(1)

Shapes Tetrahedral and Octahedral

(1)

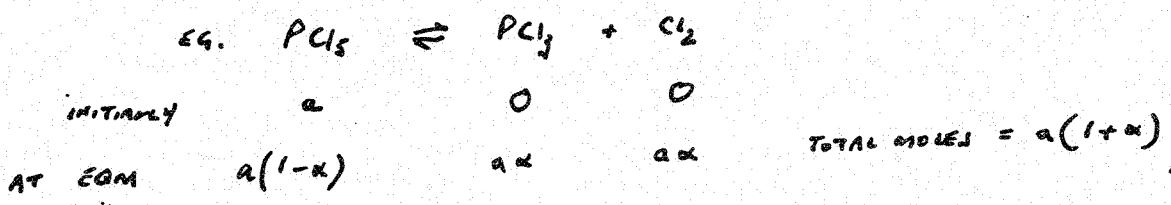
OR PCl_4^+ and stated as tetrahedral (1)

PCl_6^- and stated as octahedral (1)

6

QUESTION 7 : ALTERNATIVE MARK SCHEME.

CANDIDATES COULD APPROXIMATE THE CALCULATION USING $(1-\alpha)$ ETC.



USING THIS METHOD LOOK OUT FOR THE FOLLOWING SCORING POINTS :

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

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

: partial pressure = mol fraction \times total pressure $\checkmark \quad [1]$

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

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

$$K_p = \frac{P_{\text{Cl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

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

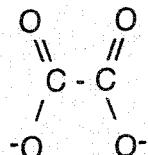
$$= 23.33 \quad \checkmark \quad (\text{kPa}) \quad [1]$$

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 OHCH₂CH₂OH unless a correct name also given
- K₂Cr₂O₇/ dilute H₂SO₄ or dilute HCl or K₂Cr₂O₇/H⁺ (1)
- NB Oxidising agent must be a reagent*
NB Do not allow concentrated H₂SO₄
- 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

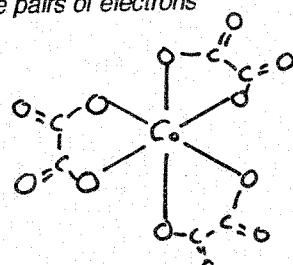
Anion



NB Do NOT allow C₂O₄²⁻

NB Ignore lone pairs of electrons

(b) Structure;



correct co-ordination (1)

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

NB Not essential to show double bonds i.e. C=O in structure

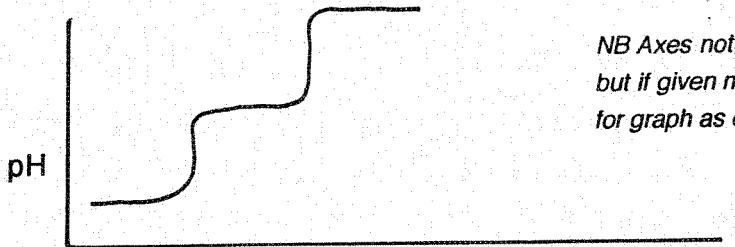
Explanation:

Substitution produces more molecules or particles or more disorder (1)

Entropy change is positive (1)

4

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



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

Equations; H₂C₂O₄ + OH⁻ → HC₂O₄⁻ + H₂O (1)

HC₂O₄⁻ + OH⁻ → C₂O₄²⁻ + H₂O (1)

NB Allow one for H₂C₂O₄ + 2OH⁻ → C₂O₄²⁻ + 2H₂O

NB Allow 'molecular equations'

(c)(ii) Moles of NaOH = 0.145 × 18.2/1000 (1) = 2.64 × 10⁻³
Moles acid = (2.64 × 10⁻³) ÷ 2 (1) = 1.32 × 10⁻³

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

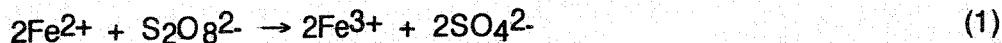
Concentration of acid = 1.32 × 10⁻³ × 1000/25 = 0.0528 or 0.05278 (1)

NB Mark concentration consequentially to correct moles acid

Volume NaOH if NaHC₂O₄ 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

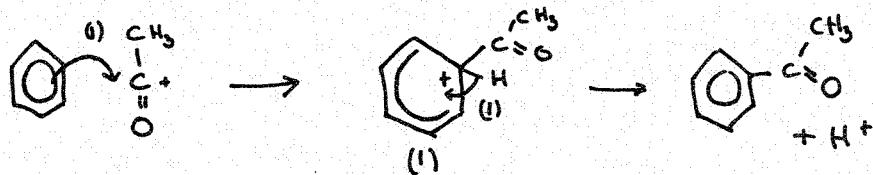
Vanadium is a transition element or Magnesium is not a transition element (1)

Vanadium has variable oxidation states (1)

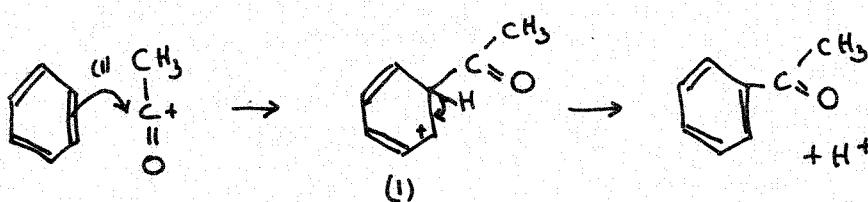
Magnesium only forms Mg^{2+} , or has only one oxidation state (1) 6

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

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



OR



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

Ions not free to move in the solid state
Ions free to move when molten or in aqueous solution

(1)

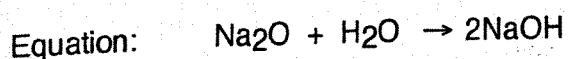
(1)

(1)

(1)

Identity of P; Na_2O or sodium oxide

NB If a formula given this must be correct



(1)

5

(ii) Deductions

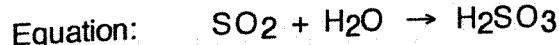
Covalent

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

(1)

(1)

Identity of Q; SO_2 or sulphur dioxide



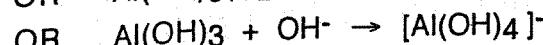
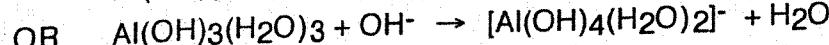
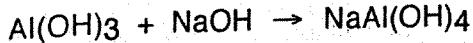
(1)

4

NB Allow max one for SO_3

(b)(i) Amphoteric

(ii) Equation with NaOH



(1)

(1)

R identified as $\text{Al}(\text{OH})_3$ or $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$

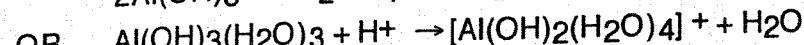
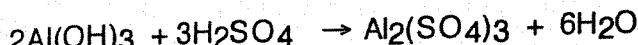
A balanced equation

(1)

NB Allow equations with six co-ordinate Aluminium and up to six OH- ligands

NB Allow equation mark if $\text{M}(\text{OH})_3$ given in a balanced equation

Equation with H_2SO_4



NB Allow equations with six co-ordinate Aluminium and up to six H₂O ligands

NB Allow equation mark if $\text{M}(\text{OH})_3$ 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