RECOGNISING ACHIEVEMENT

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS**

**Advanced GCE**

# CHEMISTRY

# 2816/01

Unifying Concepts in Chemistry

Thursday **24 JUNE 2004** Afternoon 1 hour 15 minutes

Candidates answer on the question paper.
Additional materials:
*Data Sheet for Chemistry*
Scientific calculator

| Candidate Name | Centre Number | Candidate Number |
|---|---|---|
| | | |

**TIME** 1 hour 15 minutes

## INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

## INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

| FOR EXAMINER'S USE | | |
|---|---|---|
| **Qu.** | **Max.** | **Mark** |
| **1** | **14** | |
| **2** | **20** | |
| **3** | **13** | |
| **4** | **13** | |
| **TOTAL** | **60** | |

**This question paper consists of 10 printed pages and 2 blank pages.**

Answer **all** the questions.

1 In an experiment, maltose, $C_{12}H_{22}O_{11}$, was hydrolysed to form glucose, $C_6H_{12}O_6$. The hydrochloric acid behaves as a catalyst for this reaction.

$$\underset{\textbf{maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H^+ \text{ catalyst}} \underset{\textbf{glucose}}{2C_6H_{12}O_6(aq)}$$

This reaction was carried out several times using different concentrations of maltose and of hydrochloric acid. The initial rate of each experimental run was calculated and the results are shown below. In each case, initial concentrations are shown.

| experiment | $[C_{12}H_{22}O_{11}(aq)]$ /mol dm$^{-3}$ | $[HCl(aq)]$ /mol dm$^{-3}$ | initial rate /mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.10 | 0.10 | 0.024 |
| 2 | 0.20 | 0.10 | 0.048 |
| 3 | 0.10 | 0.15 | 0.036 |

**(a) (i)** Suggest what is meant by the *initial* rate of reaction.

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**(ii)** The initial rates measured in each experimental run are for the rate of **disappearance** of maltose.

For experiment 1, deduce the initial rate of **appearance** of glucose, in mol dm$^{-3}$ s$^{-1}$.

..........................................................................................................mol dm$^{-3}$ s$^{-1}$ [1]

**(b) (i)** For each reactant, deduce the order of reaction. Show your reasoning.

$C_{12}H_{22}O_{11}(aq)$ ..........................................................................................

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$HCl(aq)$ ..........................................................................................................

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For Examiner's Use

**(ii)** What is the overall order of this reaction?

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**(iii)** Deduce the rate equation for this reaction.

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**(c)** The experiment was repeated at a higher temperature.

State whether the rate constant would increase, decrease or stay the same.

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**(d)** Experiment 1 was repeated and the concentration of maltose was measured continuously until the reaction was complete.

The half-life of this reaction with respect to maltose was measured as 3 seconds.

**(i)** What is meant by the *half-life* of a reaction?

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**(ii)** Determine the concentrations of maltose and hydrochloric acid in experiment 1 after 3 seconds. In each case, explain how you have arrived at your answer.

$[C_{12}H_{22}O_{11}(aq)]$ ..........................................................................................

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[HC*l*(aq)] ..........................................................................................................

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[Total: 14]

For Examiner's Use

**2** **Equilibrium 1**, shown below, exists between $N_2(g)$, $O_2(g)$ and NO(g).

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \textbf{equilibrium 1}$$

The equilibrium constant $K_c$ for this reaction is $4.8 \times 10^{-31}$ at 25 °C.

**(a)** **(i)** Write the expression for the equilibrium constant, $K_c$, for **equilibrium 1**.

[2]

**(ii)** What does the value of $K_c$ tell you about the equilibrium position in **equilibrium 1** at 25 °C? Explain your reasoning.

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**(iii)** An equilibrium mixture of these three gases had the following equilibrium concentrations: 1.1 mol dm$^{-3}$ $N_2(g)$ and $4.0 \times 10^{-16}$ mol dm$^{-3}$ NO(g).

Calculate the equilibrium concentration of $O_2(g)$.

answer .................................. mol dm$^{-3}$ [3]

**(b)** In a car, nitrogen and oxygen gases in the air are drawn into the engine. The high temperature inside a working car engine increases the value of $K_c$ for **equilibrium 1**.

**(i)** Deduce the sign of the enthalpy change for the forward reaction in **equilibrium 1**. Explain your reasoning.

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**(ii)** Compare the proportion of NO gas inside a working car engine to that at 25 °C. Explain your answer.

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For Examiner's Use

**(iii)** In the absence of a catalytic converter, the NO gas emerges from a car exhaust and then reacts with oxygen in the air. The oxidation number of the nitrogen increases to +4.

Suggest an equation for this reaction

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**(c)** In this question, one mark is available for the quality of written communication.

In industry, NO(g) is used in the manufacture of nitric acid. The production of NO(g) involves the oxidation of ammonia.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -900\,kJ\,mol^{-1}$$

The actual industrial conditions used are a temperature of about 1000 °C, a pressure of 10 atmospheres and a platinum-rhodium catalyst.

Giving reasons,

- predict the conditions required for an optimum equilibrium yield,
- suggest reasons why the actual conditions used may be different from the optimum equilibrium conditions.

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Quality of Written Communication [1]

[Total: 20]



**[Turn over**

For Examiner's Use

**3** A student carried out some practical work on acids and alkalis.

**(a)** He measured the pH of aqueous solutions of two acids. His results are shown in Table 3.1 below.

| acid | concentration/mol $dm^{-3}$ | pH |
|---|---|---|
| HBr | 0.0100 | 2.0 |
| $CH_3COOH$ | 0.0100 | 3.4 |

**Table 3.1**

**(i)** Define pH.

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**(ii)** Compare the concentrations and pH values of the two acids in **Table 3.1**.

Explain what this tells you about the relative strengths of the two acids.

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**(iii)** The student mixed together 10 $cm^3$ of 0.0100 mol $dm^{-3}$ HBr with 90 $cm^3$ of water.

Determine the pH of the diluted acid. Show your working.

[2]

**(b)** The constant $K_w$ has a value of $1.0 \times 10^{-14}$ mol$^2$ dm$^{-6}$.

**(i)** Define $K_w$ by completing the expression below.

$K_w$ = ..................................................................................................[1]

**(ii)** Calculate the pH of 0.020 mol $dm^{-3}$ KOH(aq). Show your working.

[2]

**(c)** The student pipetted 20.0 $cm^3$ of 0.0100 mol $dm^{-3}$ $CH_3COOH(aq)$ into a conical flask.

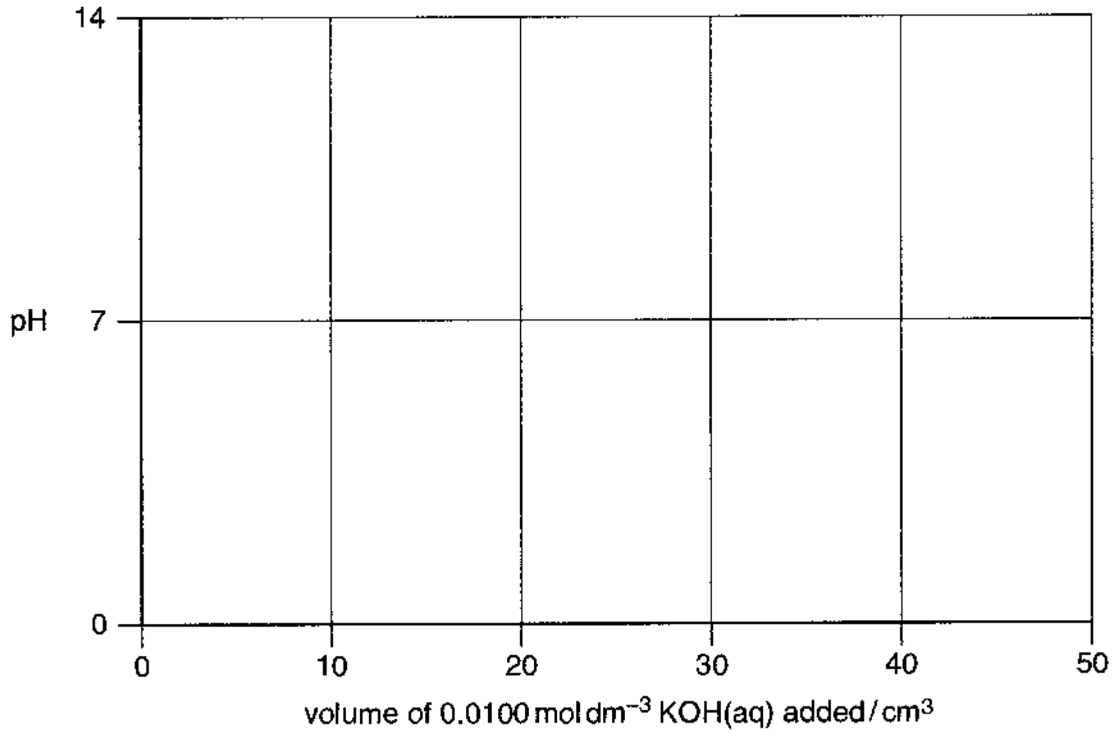
He then slowly added an **excess** of 0.0100 mol $dm^{-3}$ KOH(aq) from a burette. In total, 50.00 $cm^3$ of the alkali were added.

The pH of the resulting solution was measured throughout the experiment with a pH meter.

The equation for the reaction is shown below.

$$CH_3COOH(aq) + KOH(aq) \longrightarrow CH_3COOK(aq) + H_2O(l)$$

**(i)** Sketch the pH curve for this titration on the grid below.




[3]

**(ii)** This titration could be carried out using an indicator. The pH ranges for the pH changes of four indicators are shown below.

| indicator | pH range |
|---|---|
| clayton yellow | 12.2 – 13.2 |
| thymol blue | 8.0 – 9.6 |
| brilliant yellow | 6.6 – 7.8 |
| resazurin | 3.8 – 6.4 |

Explain which of the four indicators is most suitable for this titration.

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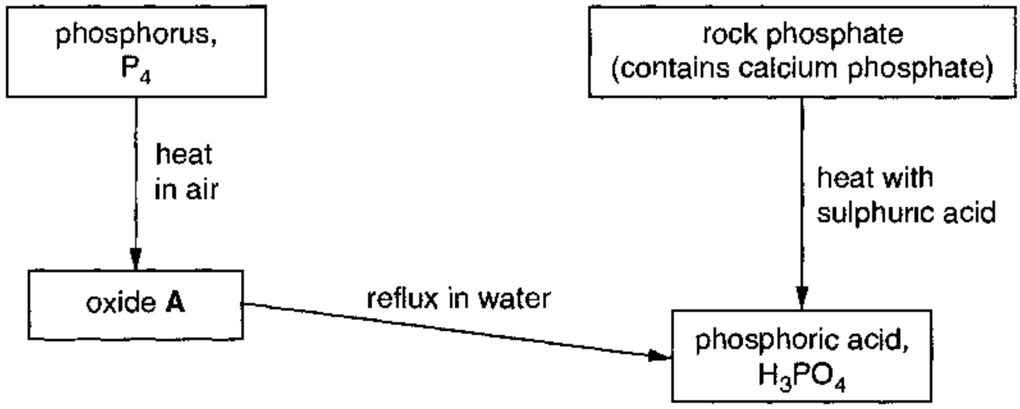
[Total: 13]

4 Phosphoric acid, $H_3PO_4$, is an important chemical used for the manufacture of fertilisers. The acid can be prepared from phosphorus, $P_4$, and from 'rock phosphate' which contains calcium phosphate.

**(a)** The flowchart below summarises the two routes used to make phosphoric acid.




Compound **A** has the percentage composition by mass: P, 43.7%; O, 56.3%. $M_r$ = 284.

Showing **all** your reasoning,

- identify the molecular formula of compound **A**, [3]
- determine the formula of calcium phosphate, [1]
- write equations for the three reactions shown. [3]

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**(b)** In solution, phosphoric acid can donate its three protons in turn.

$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$ $K_a = 7.5 \times 10^{-3}\,mol\,dm^{-3}$

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ $K_a = 6.2 \times 10^{-8}\,mol\,dm^{-3}$

$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$ $K_a = 1.7 \times 10^{-12}\,mol\,dm^{-3}$

**(i)** Compare the relative acidic strengths of $H_3PO_4$, $H_2PO_4^-$ and $HPO_4^{2-}$. Explain how you arrived at your answer.

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**(ii)** Salts of phosphoric acid can be formed by replacing one, two or three protons from $H_3PO_4$.

For example, **two** protons from $\mathbf{H_3}PO_4$ can be replaced to form $Na_2\mathbf{HPO_4}$.

$$H_3PO_4(aq) + 2NaOH(aq) \longrightarrow Na_2HPO_4(aq) + 2H_2O(l)$$

Calculate the volumes of $0.500\,mol\,dm^{-3}$ $H_3PO_4(aq)$ and $0.500\,mol\,dm^{-3}$ NaOH(aq) that you would need to prepare 4.26 g of the salt $Na_2HPO_4$.

[5]

[Total: 13]

**END OF QUESTION PAPER**

RECOGNISING ACHIEVEMENT

**Subject: Unifying Concepts     Code: 2816/1**

**Session: June     Year: 2004**

**FINAL Mark Scheme**

| MAXIMUM MARK | 60 |
|---|---|

## ADVICE TO EXAMINERS ON THE ANNOTATION OF SCRIPTS

1. Please ensure that you use the **final** version of the Mark Scheme.
   You are advised to destroy all draft versions.

2. Please mark all post-standardisation scripts in red ink. A tick (✓) should be used for each answer judged worthy of a mark. Ticks should be placed as close as possible to the point in the answer where the mark has been awarded. The number of ticks should be the same as the number of marks awarded. If two (or more) responses are required for one mark, use only one tick. Half marks (½) should never be used.

3. The following annotations may be used when marking. No comments should be written on scripts unless they relate directly to the mark scheme. Remember that scripts may be returned to Centres.

   x = incorrect response (errors may also be underlined)
   ^ = omission mark
   bod = benefit of the doubt (where professional judgement has been used)
   ecf = error carried forward (in consequential marking)
   con = contradiction (in cases where candidates contradict themselves in the same response)
   sf = error in the number of significant figures

4. The marks awarded for each part question should be indicated in the margin provided on the right hand side of the page. The mark total for each question should be ringed at the end of the question, on the right hand side. These totals should be added up to give the final total on the front of the paper.

5. In cases where candidates are required to give a specific number of answers, (e.g. 'give three reasons'), mark the first answer(s) given up to the total number required. Strike through the remainder. In specific cases where this rule cannot be applied, the exact procedure to be used is given in the mark scheme.

6. Correct answers to calculations should gain full credit even if no working is shown, unless otherwise indicated in the mark scheme. (An instruction on the paper to 'Show your working' is to help candidates, who may then gain partial credit even if their final answer is not correct.)

7. Strike through all blank spaces and/or pages in order to give a clear indication that the whole of the script has been considered.

8. An element of professional judgement is required in the marking of any written paper, and candidates may not use the exact words that appear in the mark scheme. If the science is correct and answers the question, then the mark(s) should normally be credited. If you are in doubt about the validity of any answer, contact your Team Leader/Principal Examiner for guidance.

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|---|---|---|
| **Abbreviations, annotations and conventions used in the Mark Scheme** | / = alternative and acceptable answers for the same marking point<br>; = separates marking points<br>NOT = answers which are not worthy of credit<br>( ) = words which are not essential to gain credit<br>___ = (underlining) key words which **must** be used to gain credit<br>ecf = error carried forward<br>AW = alternative wording<br>ora = or reverse argument | |
| **Question** | **Expected Answers** | **Marks** |
| **1 (a) (i)** | rate at start (of reaction)/ t=0 ✓ | **[1]** |
| **(ii)** | 0.048 (mol $dm^{-3}$ $s^{-1}$) ✓ | **[1]** |
| **(b) (i)** | $C_{12}H_{22}O_{11}$(aq):<br><br>Exp 2 has twice [$C_{12}H_{22}O_{11}$ (aq)] as Exp 1 and rate x 2 ✓,<br>so order = 1 with respect to $C_{12}H_{22}O_{11}$ ✓<br><br>HCl(aq):<br>Exp 3 has 1.5 x [HCl] as Exp 1 and rate increases by 1.5 ✓,<br>so order = 1 with respect to HCl(aq) ✓<br>*ORDER HAS TO BE CORRECT TO GET REASON MARK* | **[4]** |
| **(ii)** | 2/second order ✓<br>This will be dependent on answer to (i) | **[1]** |
| **(iii)** | rate = *k*[$C_{12}H_{22}O_{11}$] [HCl] ✓✓<br>OR<br>rate = 2.4 [$C_{12}H_{22}O_{11}$] [HCl] ✓✓<br><br>*rate = k* [$C_{12}H_{22}O_{11}$] [$H_2O$] scores 1 mark)<br>*rate =* [$C_{12}H_{22}O_{11}$] [HCl] scores 1 mark)<br>*k* [$C_{12}H_{22}O_{11}$] [HCl] scores 1 mark)<br>*k =* [$C_{12}H_{22}O_{11}$] [HCl] scores zero<br>Check for ecf from (i) | **[2]** |
| **(c)** | increases ✓ | **[1]** |
| **(d) (i)** | time for concentration (of a reactant) to fall to half the original value ✓ | **[1]** |
| **(ii)** | $C_{12}H_{22}O_{11}$: 0.05 mol $dm^{-3}$ ✓<br>In one half life, [$C_{12}H_{22}O_{11}$], concentration halves 0.1/2 ✓<br><br>HCl: 0.1 mol $dm^{-3}$ ✓<br>*Assume* mol $dm^{-3}$ unless told otherwise<br>*Assume* 'mol $dm^3$ means mol $dm^{-3}$ but<br>Penalise wrong unit once only | **[3]** |
| | | **Total: 14** |

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|---|---|
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| Question | Expected Answers | Marks |
|---|---|---|
| **2 (a) (i)** | $K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$ ✓✓ *award 1 mark if upside down*<br>*$K_p$ expression worth 1 mark* | **[2]** |
| **(ii)** | Equil ⟶ left because $K_c$ is very small | **[1]** |
| **(iii)** | $[O_2(g)] = \frac{[NO]^2}{[N_2] \times K_c} = \frac{(4.0 \times 10^{-16})^2}{1.1 \times 4.8 \times 10^{-31}}$ ✓<br><br>= 0.30 mol $dm^{-3}$ ✓ (calculator: 0.303030303)<br>answer given to 2 sig figs ✓<br>3.3 ✓✓ (upside down) calc: 3.3<br>$7.6 \times 10^{14}$ ✓✓ (missing out $^2$) calc: 7.5757.....<br>0.37 ✓✓ (1.1 on top) calc: 0.366666..<br>$5.2 \times 10^{-46}$ ✓✓ ('4' values swapped) calc: $5.236363. \times 10^{-46}$ | **[3]** |
| **(b) (i)** | $\Delta H$ is +ve ✓ | |
| **(ii)** | equilibrium moves to the right to compensate for increase in temperature/to lower the temperature / to minimise the change ✓<br><br>increase in proportion of NO ✓<br>because $K_c$ increases<br>*Can be linked to either increased proportion of NO or enthalpy change* ✓ | **[4]** |
| **(iii)** | $2NO + O_2 \longrightarrow 2NO_2$ ✓✓<br>*species correct for 1st mark*<br>*'simplest' balanced equation for 2nd mark*<br>$NO + \frac{1}{2}O_2 \longrightarrow NO_2$ also gets both marks<br>*$N_2O_4$ is fine*<br>*$NO_2$ for 1st mark* | **[2]** |

| | | |
|---|---|---|
| (c) | Optimum Pressure<br>low pressure ✓<br>fewer gaseous moles on left ✓<br>Optimum Temperature<br>optimum: low temperature ✓<br>forward reaction is exothermic ✓<br><br>Reason mark can only be awarded if the condition mark is correct.<br><br>Condition mark is independent<br><br>1000°C used to increase rate with more energetic collisions *OR* so that a greater proportion of molecules exceed activation energy ✓<br><br>10 atm used to increase rate by increasing concentration *OR* increasing collisons ✓<br><br>Catalyst used to increase rate by lowering the activation energy/providing a lower energy route ✓<br>*NOT increase equilibrium yield*<br><br>Quality of written communication:<br>Recognition of a compromise between rate and equilibrium amount ✓ | [7]<br><br>[1] |
| | | Total: 20 |

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|---|---|
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| Question | Expected Answers | Marks |
|---|---|---|
| 3 (a) (i) | pH = –log[$H^+$(aq)] ✓ *state symbols not needed* | [1] |
| (ii) | HBr is stronger than $CH_3COOH$ because pH is lower ✓<br>HBr dissociates more/more $H^-$ ions……. for the same concentration ✓ | [2] |
| (iii) | diluting by a factor of 10/ 10-fold dilution ✓<br><br>pH = 3 ✓<br><br>Credit a calculated pH for ecf from a wrong dilution with working shown | [2] |
| (b) (i) | $K_w$ = [$H^+$(aq)] [$OH^-$(aq)] ✓ *state symbols not needed* | [1] |
| (ii) | $[H^+(aq)] = \frac{K_w}{[OH^-(aq)]} = \frac{1.0 \times 10^{-14}}{0.0200} = 5 \times 10^{-13}$ mol $dm^{-3}$ ✓<br><br>pH = –log (5 x $10^{-13}$) = 12.30 ✓<br>(accept calc value: 12.30103)<br>ecf is possible for pH mark providing that the [$H^+$] value has been derived from $K_w$/[$OH^-$]<br>If pOH method is used, pOH = 1.7 would get 1st mark, pH = 14 – 1.7 = 12.3 gets 2nd mark. | [2] |
| (c) (i) | start at pH=3.4 (approx half way up 0-7 rise) ✓<br>sharp rise at 20 $cm^3$ (must have a vertical part) ✓<br>finish higher above pH 7 than starting pH<br>……………….with line continued to 50 $cm^3$<br>……………….but finish pH is less than 14 ✓<br>NOTE that lines should not loop | [3] |
| (ii) | Indicator that has a pH range coinciding with steepest part of titration curve in (i).<br>Likely to be thymol blue OR brilliant yellow✓<br><br>pH range coincides with ……pH change during sharp rise /equivalence point ✓ | [2] |
| | | **Total: 13** |

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|---|---|---|
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| | | |
| **Question** | **Expected Answers** | **Marks** |
| **4 (a)** | P : O = 43.7/31 : 56.3/16 / 1.41 : 3.52 ✓<br><br>Ratio P:O = 2 : 5 / Empirical formula = $P_2O_5$ ✓<br><br>Molecular formula = $P_4O_{10}$ (from *M*r value) ✓ | **[3]** |
| | $Ca_3(PO_4)_2$ ✓ | **[1]** |
| | Equations:<br>$P_4 + 5O_2 \longrightarrow P_4O_{10}$ ✓<br>(or $P_4 + 5O_2 \longrightarrow 2P_2O_5$)<br><br>$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ ✓<br>(or $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$ )<br><br>$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$ ✓<br><br>*A* candidate who writes an equation forming $P_4O_6$ or $P_2O_3$ can score the equation mark for oxidation of $P_4$. | **[3]** |
| **(b) (i)** | $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$<br>Increased strengths with increasing $K_a$ values ✓ | **[1]** |
| **(ii)** | Molar mass of $Na_2HPO_4$ = 142 g $mol^{-1}$ ✓<br><br>amount of $Na_2HPO_4$ = 4.26/142 = 0.03 mol ✓<br>*e.c.f. mass/molar mass*<br><br>volume of $H_3PO_4$ needed = 0.03 x 1000 / 0.5 = 60 $cm^3$ ✓<br>*e.c.f. moles $Na_2HPO_4$ x 1000/0.5*<br><br>amount of NaOH = 2 x 0.03 = 0.06 mol ✓<br>*e.c.f. 2 x moles $Na_2HPO_4$*<br><br>volume of NaOH needed = 0.06 x 1000 / 0.5 = 120 $cm^3$ ✓<br>*e.c.f. moles NaOH x 1000/0.5*<br><br>Penalise units once. | **[5]** |
| | | **Total: 13** |