Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL

A410U30-1

S18-A410U30-1

CHEMISTRY – A level component 3
Chemistry in Practice

WEDNESDAY, 20 JUNE 2018 – MORNING

1 hour 15 minutes

For Examiner's use only		
Question	**Maximum Mark**	**Mark Awarded**
1.	**6**	
2.	**21**	
3.	**10**	
4.	**8**	
5.	**15**	
Total	**60**	

A410U301
01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 60.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.1**.

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

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

1. Outline **two** simple reactions, including relevant observations, formulae and equations, to show that complexes of copper(II) ions can undergo ligand exchange.

You may choose from the following chemicals **ONLY**, not all of which need to be used.

- aqueous copper(II) sulfate
- aqueous potassium iodide
- aqueous sulfuric acid
- aqueous ammonia
- concentrated hydrochloric acid [6 QER]

Reaction 1: add aqueous ammonia dropwise, then in excess, to pale blue aqueous copper(II) sulfate, which contains the complex ion $[Cu(H_2O)_6]^{2+}$.

A few drops give a pale blue precipitate of copper(II) hydroxide, $Cu(OH)_2$. In excess ammonia this dissolves to give a deep royal blue solution of $[Cu(H_2O)_2(NH_3)_4]^{2+}$ ions, because four NH_3 ligands replace four H_2O ligands:

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 4H_2O(l)$

The complex stays octahedral (coordination number 6) as NH_3 and H_2O are similar in size and both neutral.

Reaction 2: add concentrated hydrochloric acid to pale blue aqueous copper(II) sulfate. A yellow-green solution forms, containing $[CuCl_4]^{2-}$ ions, as Cl^- ligands replace all six H_2O ligands:

$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$

The shape changes from octahedral (6) to tetrahedral (4) as Cl^- ions are larger than H_2O. The reaction is reversible: adding water turns the solution blue again.

In both reactions ligands are replaced by different ligands, changing the colour, so copper(II) complexes undergo ligand exchange.

A410U301 03

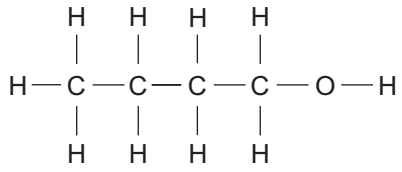
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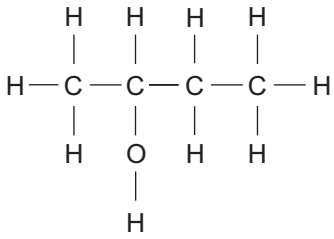
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2. **A**, **B**, **C** and **D** are the four isomeric alcohols of formula $C_4H_{10}O$.

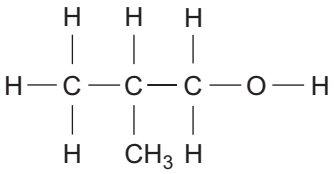
The structural formulae and systematic names of **A**, **B** and **C** are shown below.



A
butan-1-ol

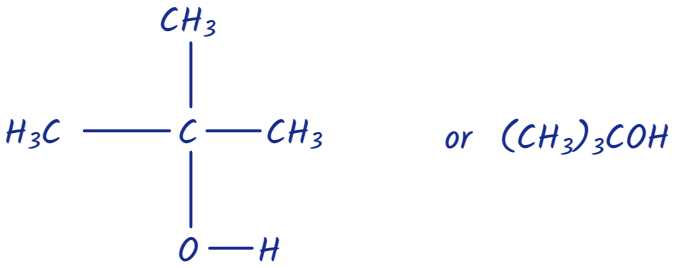


B
butan-2-ol



C
methylpropan-1-ol

(a) Give the structural formula and systematic name of alcohol **D**. [2]



or $(CH_3)_3COH$

methylpropan-2-ol

(b) Describe a test that would give a positive result for butan-2-ol (alcohol **B**) but not for alcohols **A**, **C** and **D**. Give the name of the reagent(s) used and the observation(s) made. [2]

Reagent(s) aqueous iodine and aqueous sodium hydroxide (warm)

Observation(s) yellow crystalline solid (precipitate of CHI_3) forms

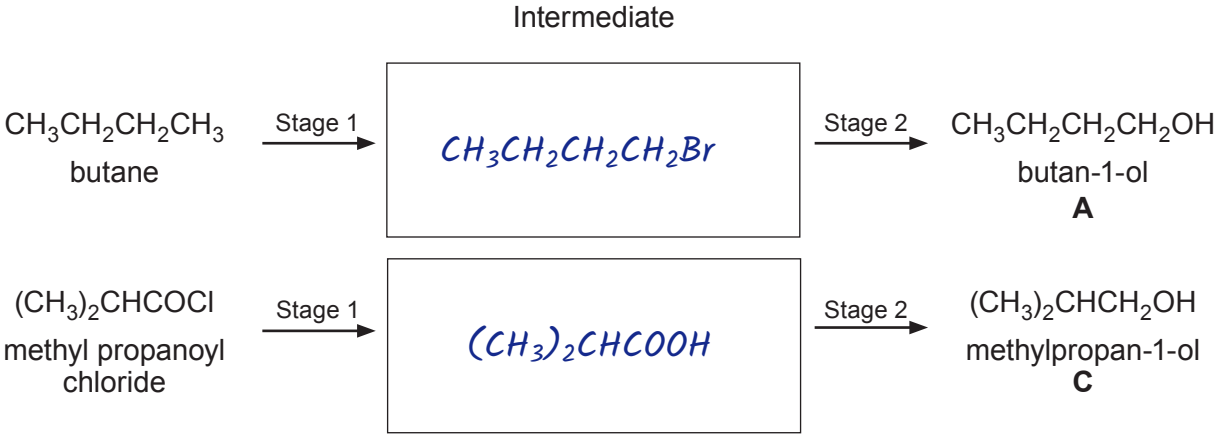
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(c) Two-stage processes for the preparation of alcohols **A** and **C** are shown below. In each case the intermediate compound has been omitted.

Complete the schemes by inserting the shortened structural formula of the intermediate compounds in the spaces provided. [2]



(d) Butan-1-ol can also be prepared directly from 1-aminobutane by reaction with nitric(III) acid (HNO_2). Butan-1-ol is only one of many organic products formed, including butan-2-ol and but-1-ene.

Nitrogen gas, however, is given off in quantities exactly as shown in the equation below. Thus, by measuring the volume of nitrogen gas produced, the exact amount of amine present in the solution can be found.

$$\underset{\text{1-aminobutane}}{CH_3CH_2CH_2CH_2NH_2} + HNO_2 \longrightarrow CH_3CH_2CH_2CH_2OH + N_2 + H_2O$$

Calculate the volume **in cm³** of liquid 1-aminobutane used if 6.60 dm³ of nitrogen gas are produced. Assume that all gas volumes are measured at 298 K and 1 atm pressure. [3]

(density of 1-aminobutane = 0.740 g cm^{-3} at 298 K)

$n(N_2) = 6.60 \div 24.5 = 0.269$ mol

n(1-aminobutane) = 0.269 mol (1 : 1 ratio)

$M_r(C_4H_{11}N) = 73.0$

mass = $0.269 \times 73.0 = 19.7$ g

volume = mass ÷ density = $19.7 \div 0.740 = 26.6$ cm³

Volume = 26.6 cm³

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05

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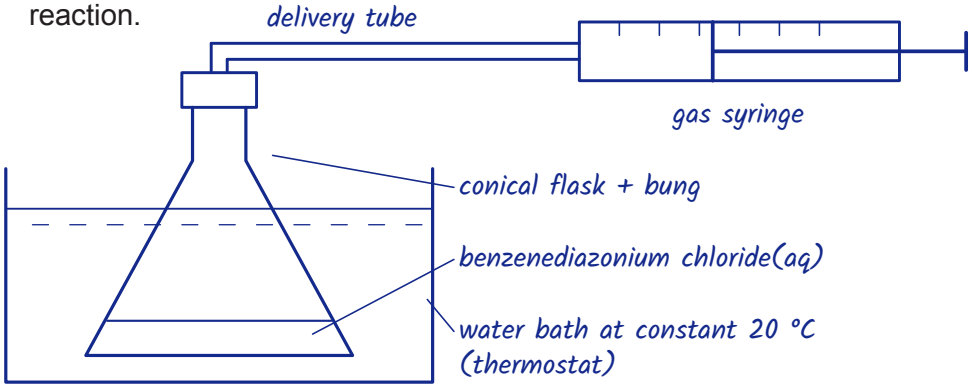
(e) Benzenediazonium chloride, $C_6H_5N_2Cl$, also forms nitrogen gas on decomposition. The reaction is first order with respect to benzenediazonium chloride.

$$C_6H_5N_2Cl(aq) + H_2O(l) \longrightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

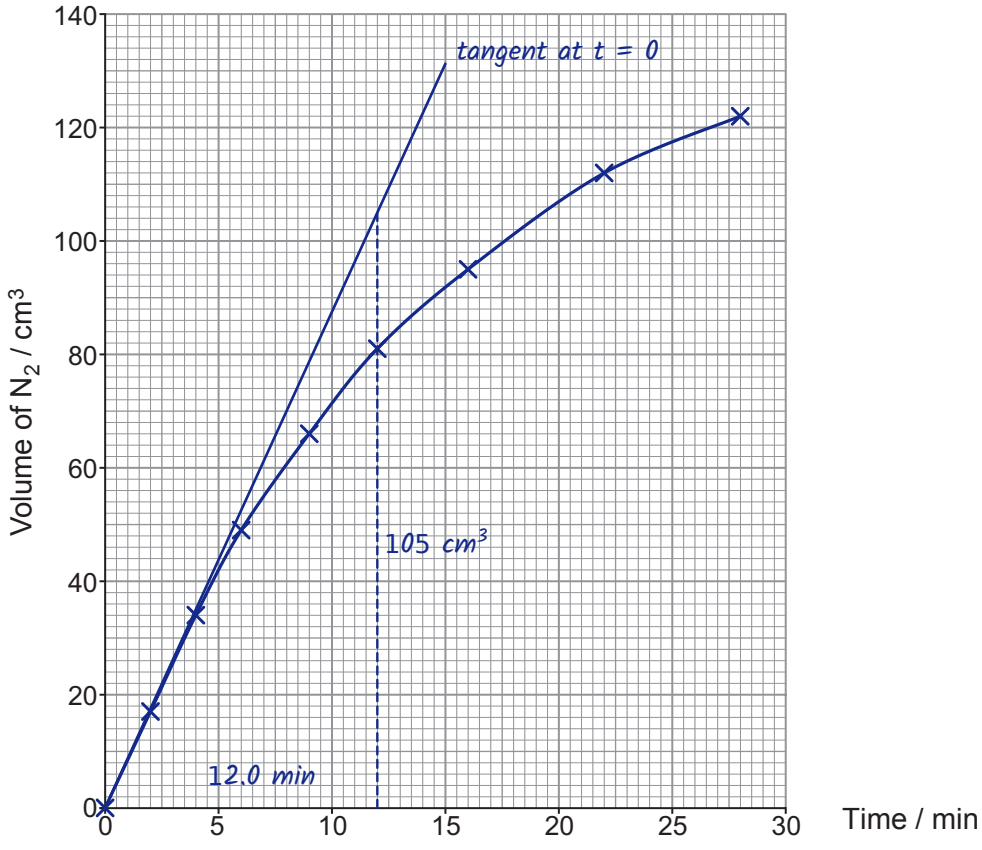
The following table gives the volume of nitrogen gas collected over time in the decomposition of 50 cm^3 of a 0.110 mol dm^{-3} solution of benzenediazonium chloride at 20 °C.

Time / min	0	2.0	4.0	6.0	9.0	12.0	16.0	22.0	28.0
Volume of N_2 / cm^3	0	17	34	49	66	81	95	112	122

(i) Draw a labelled diagram of the apparatus that could be used to follow this reaction. [2]



(ii) Plot the volume of nitrogen gas collected against time on the graph below. [2]



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(iii) Assuming the decomposition of the benzenediazonium chloride is complete, calculate the total volume of nitrogen gas that would be formed at the end of the reaction at 1 atm and 20 °C. [3]

$n(C_6H_5N_2Cl) = 0.110 \times 50/1000 = 0.0055$ mol $= n(N_2)$

$pV = nRT$, so $V = nRT/p = (0.0055 \times 8.31 \times 293) \div 1.01 \times 10^5$

$V = 1.33 \times 10^{-4}\ m^3 = 133\ cm^3$

Volume = 133 cm^3

(iv) I. Use the graph to determine the initial rate of formation of nitrogen gas in **$dm^3\ min^{-1}$**. Give your answer in standard form. [3]

Tangent drawn at $t = 0$ on the graph:

gradient = $105\ cm^3 \div 12.0\ min = 8.75\ cm^3\ min^{-1}$

$= 8.75 \times 10^{-3}\ dm^3\ min^{-1}$

Initial rate = 8.75×10^{-3} $dm^3\ min^{-1}$

A410U301
07

II. Calculate the rate constant for this reaction giving the unit. [2]

rate $= k[C_6H_5N_2Cl]$, so k = rate $\div [C_6H_5N_2Cl]$

$k = 8.75 \times 10^{-3} \div 0.110 = 7.95 \times 10^{-2}$

unit $= dm^3\ min^{-1} \div mol\ dm^{-3}$

Rate constant = 7.95×10^{-2}

Unit = $mol^{-1}\ dm^6\ min^{-1}$

21

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3. A student was asked to identify four inorganic salts, labelled **P**, **Q**, **R** and **S**, by their reaction with aqueous sodium hydroxide and by the interactions between their solutions. The student was told that each solution contains

- a **different cation** and that the cations present are

  Mg^{2+} **Ba^{2+}** **Pb^{2+}** **Fe^{2+}**

- a **different anion** and that the anions present are

  I^- **Cl^-** **NO_3^-** **SO_4^{2-}**

The student tested approximately 2 cm^3 at a time of each solution with NaOH(aq) and then with a few drops of the other solutions in turn.

When no observable reaction happened, "NOR" was recorded in the results table below.

	P	**Q**	**R**	**S**
NaOH(aq)	white precipitate, insoluble in excess NaOH(aq)	white precipitate, soluble in excess NaOH(aq)	green precipitate, insoluble in excess NaOH(aq)	NOR
S	NOR	white precipitate	heavy white precipitate	
R	NOR	white precipitate		
Q	bright yellow precipitate			

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Complete the table below.

- Identify the cation and anion present in each of the four inorganic salts **P**, **Q**, **R** and **S**.
- Give an **ionic** equation to show the formation of **any one** of the precipitates formed. Include state symbols. [10]

Inorganic salt	Cation	Anion
P	Mg^{2+}	I^-
Q	Pb^{2+}	NO_3^-
R	Fe^{2+}	SO_4^{2-}
S	Ba^{2+}	Cl^-

Ionic equation

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

A410U301
09

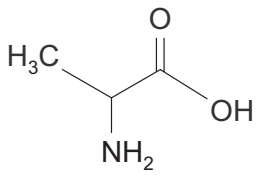
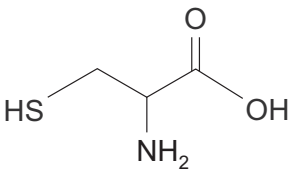
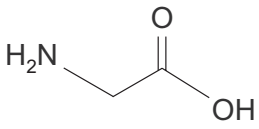
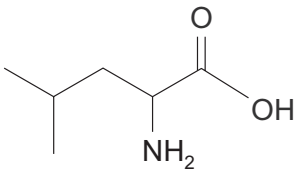
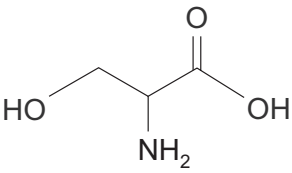
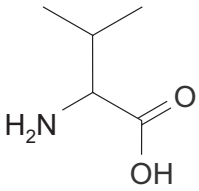
10

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4. A mixture of amino acids produced on hydrolysis of a peptide can be analysed by thin layer chromatography.

R_f values for different amino acids in two different solvents are given in the table below.

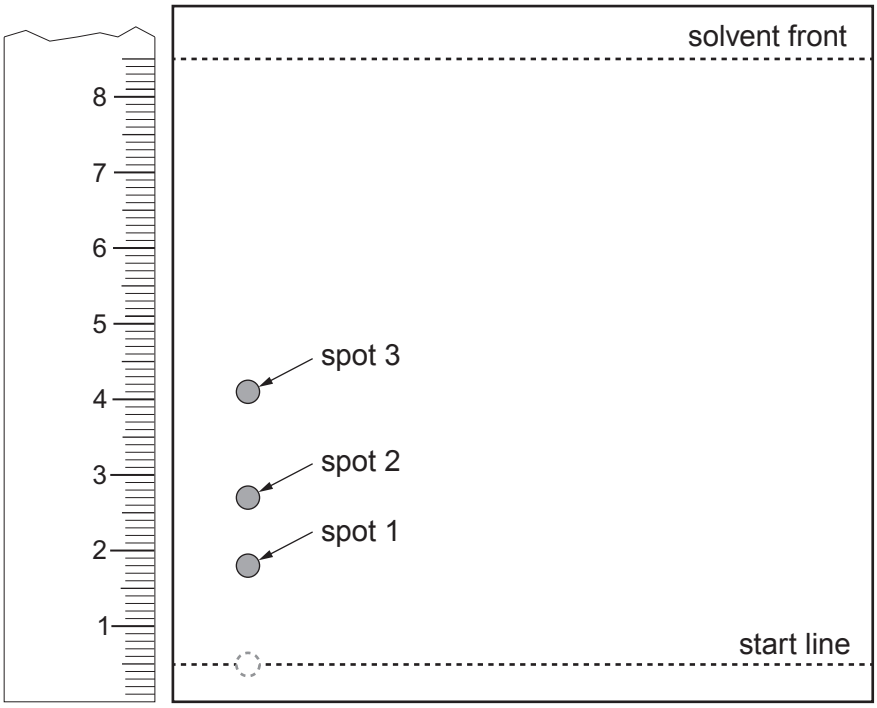
Amino acid		R_f phenol/ammonia solvent	R_f butanol/ethanoic acid solvent
alanine		0.55	
cysteine		0.13	0.05
glycine		0.41	0.17
leucine		0.86	0.61
serine		0.35	0.17
valine		0.76	0.45

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(a) A drop of solution that contains a mixture of **four** amino acids was analysed using thin layer chromatography. The plate was placed in a butanol/ethanoic acid solvent for 30 minutes. It was then dried and sprayed with a developing agent. The following chromatogram was obtained.



Chromatogram 1: butanol/ethanoic acid solvent

(i) Spot 2 on this chromatogram corresponds to alanine. Calculate the R_f value of alanine in this solvent. [2]

distance moved by alanine (spot 2) = 2.2 cm

distance moved by solvent front = 8.0 cm

$R_f = 2.2 \div 8.0 = 0.275$

R_f = 0.275

(ii) Explain, in terms of the data provided, why only three spots are present on this chromatogram even though the solution contains a mixture of four different amino acids. [1]

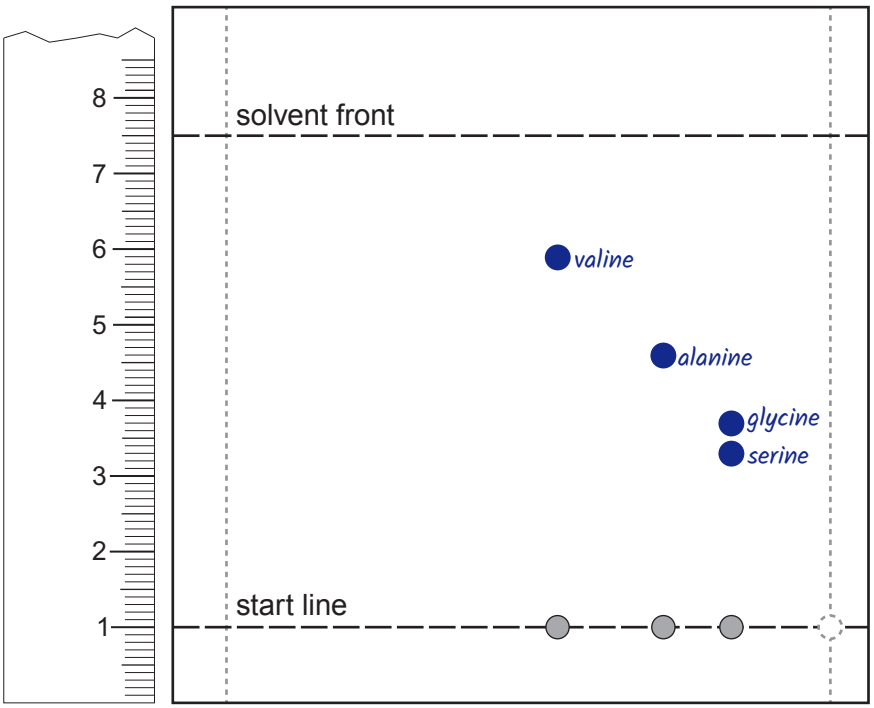
Glycine and serine have the same R_f value (0.17) in this solvent, so both are in spot 1.

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(iii) The plate was rotated through 90° in an anticlockwise direction and then placed in a phenol/ammonia solvent. Complete the diagram below to show the chromatogram you would expect to obtain. [4]



Chromatogram 2: phenol/ammonia solvent

(b) Give the structural formula of **one** of the dipeptides that may be formed from serine and leucine. [1]

$HOCH_2CH(NH_2)CONHCH(COOH)CH_2CH(CH_3)_2$

(dipeptide Ser-Leu)

8

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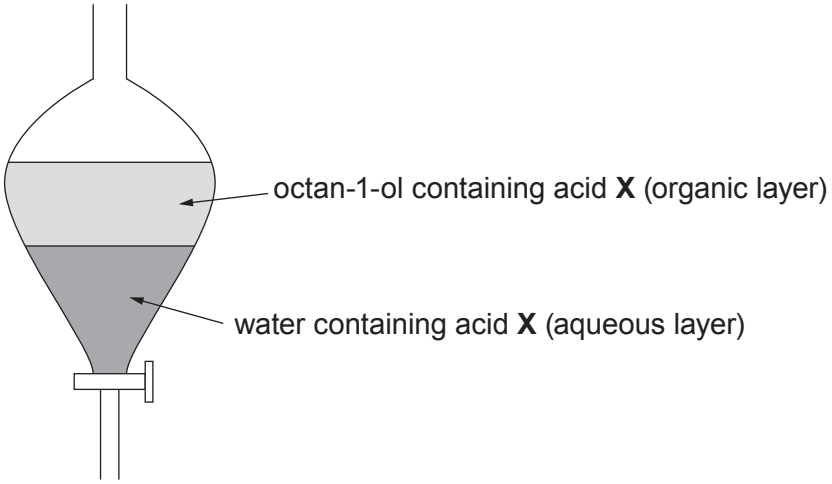
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5. A very weak carboxylic acid **X**, RCOOH, with a molar mass of 116 g mol^{-1} dissolves to some extent in **both** water and the organic solvent octan-1-ol. Water and octan-1-ol **do not mix**.

When a sample of pure **X** is shaken with water and octan-1-ol in a separating funnel and allowed to stand at a constant temperature of 298 K for one week, two layers are formed as shown below.



An equilibrium is established between the amount of **X** in the two solvents.

$$\mathbf{X}\text{(aqueous layer)} \rightleftharpoons \mathbf{X}\text{(organic layer)}$$

Under these conditions at equilibrium the equilibrium constant K is given as

$$K = \frac{[\mathbf{X}\text{(organic layer)}]}{[\mathbf{X}\text{(aqueous layer)}]}$$

In an experiment to find the value for the equilibrium constant K, 15.0 g of pure **X** was shaken with 200 cm^3 of water and 200 cm^3 of octan-1-ol in a separating funnel and left until equilibrium had been established.

After separating the aqueous and organic layers, it was found that 25.0 cm^3 of the aqueous solution of **X** needed 23.50 cm^3 of aqueous sodium hydroxide of concentration 0.0200 mol dm^{-3} to neutralise the acid.

$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$

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(a) (i) The six steps in the calculation to find the value for the equilibrium constant *K* are shown in a random order in the table below.

Number these steps in the correct order. The first step has already been numbered. [1]

Step	Correct order
Calculate the number of moles of **X** in the aqueous layer	3
Calculate the mass of **X** in the organic layer and hence its concentration in mol dm^{-3}	5
Calculate the number of moles of NaOH used in the titration	1
Calculate the value for the equilibrium constant *K* at 298 K	6
Calculate the mass of **X** in the aqueous layer and hence its concentration in mol dm^{-3}	4
Calculate the number of moles of **X** in 25.0 cm^3 of the aqueous layer	2

(ii) Calculate the value of *K*. [5]

$n(NaOH) = 0.0200 \times 23.50/1000 = 4.70 \times 10^{-4}$ mol

$n(X)$ in 25.0 cm^3 aqueous layer = 4.70×10^{-4} mol (1 : 1)

$n(X)$ in 200 cm^3 aqueous layer = $4.70 \times 10^{-4} \times 8 = 0.00376$ mol

mass of X in aqueous layer = $0.00376 \times 116 = 0.436$ g

$[X(aq)] = 0.00376 \div 0.200 = 0.0188$ mol dm^{-3}

mass of X in organic layer = $15.0 - 0.436 = 14.564$ g

$n(X)$ in organic layer = $14.564 \div 116 = 0.1256$ mol

$[X(org)] = 0.1256 \div 0.200 = 0.628$ mol dm^{-3}

$K = [X(org)] \div [X(aq)] = 0.628 \div 0.0188 \ (= 0.1256 \div 0.00376)$

$K = 33.4$

$K =$ 33.4

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(b) Calculate the total maximum percentage error in the volume of sodium hydroxide delivered from the burette, with a maximum error of half a division (±0.05 cm^3). [1]

% error = (2 × 0.05 ÷ 23.50) × 100

(two readings, each ±0.05 cm^3)

Maximum percentage error = 0.43 %

(c) (i) Calculate the pH of the aqueous solution of the weak carboxylic acid **X** at 298 K. [3]

(K_a for carboxylic acid **X** is 1.32 × 10^{-5} mol dm^{-3} at 298 K)

$[HA] = 0.00376 \div 0.200 = 0.0188 \text{ mol dm}^{-3}$

$K_a = [H^+]^2 \div [HA]$, so $[H^+] = \sqrt{(1.32 \times 10^{-5} \times 0.0188)}$

$[H^+] = 4.98 \times 10^{-4} \text{ mol dm}^{-3}$

$pH = -\log(4.98 \times 10^{-4}) = 3.30$

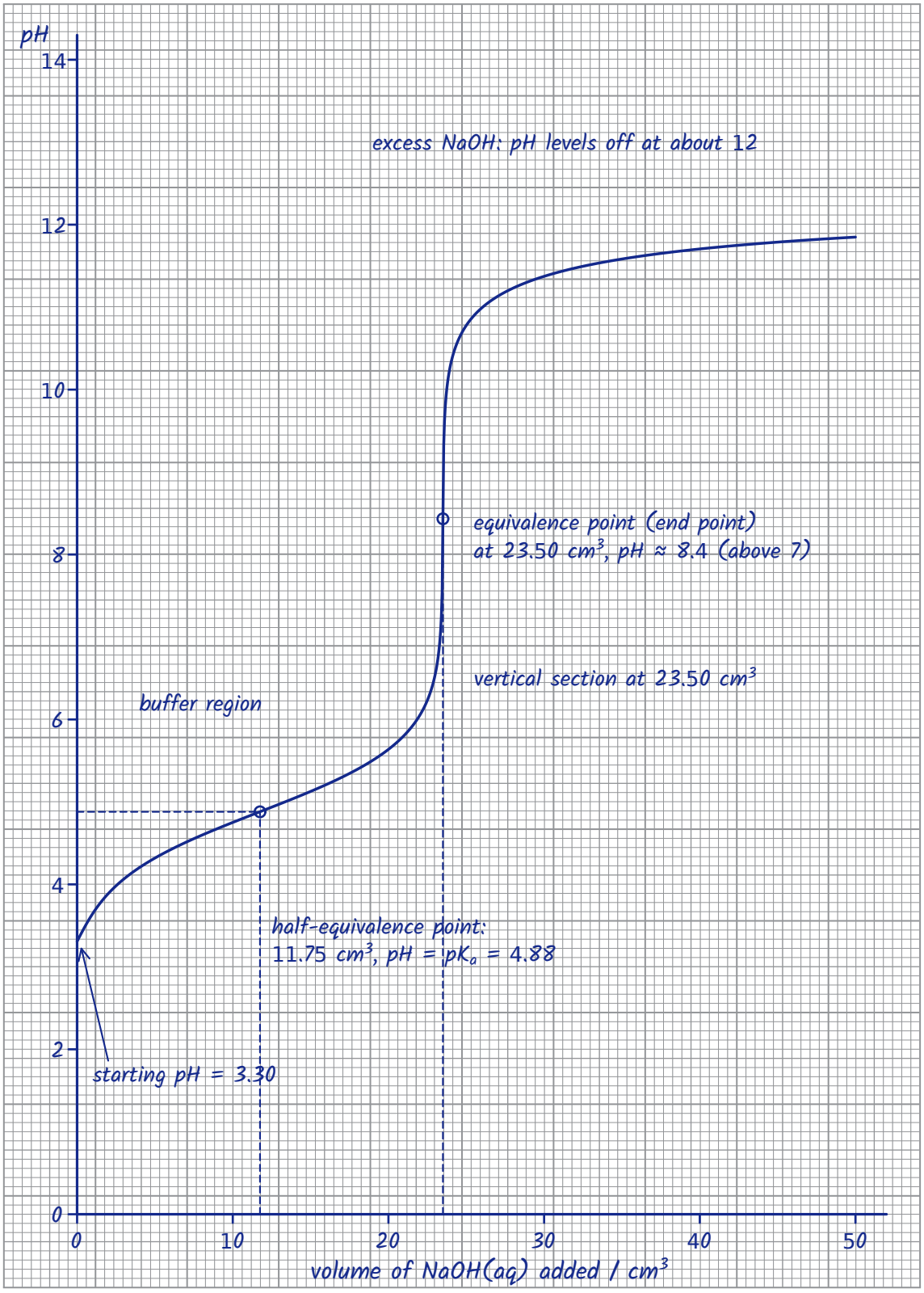
pH = 3.30

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(ii) Sketch a curve to show the variation in pH when 50.0 cm^3 of 0.0200 mol dm^{-3} sodium hydroxide solution is gradually added to 25.0 cm^3 of the solution of carboxylic acid **X**. Label the axes and significant points on the curve. [5]



15

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