



CANDIDATE
NAME

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9701/43

October/November 2023

2 hours

You must answer on the question paper.

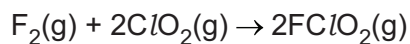
No additional materials are needed.

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **24** pages. Any blank pages are indicated.

- 1 Fluorine reacts with chlorine dioxide, ClO_2 , as shown.



The rate of the reaction is first order with respect to the concentration of F_2 and first order with respect to the concentration of ClO_2 . No catalyst is involved.

- (a) (i) Suggest a two-step mechanism for this reaction.

step 1 $\rightarrow$

step 2 $\rightarrow$

[2]

- (ii) Identify the rate-determining step in this mechanism. Explain your answer.

.....

..... [1]

- (b) When the rate of the reaction is measured in $\text{mol dm}^{-3} \text{s}^{-1}$ the numerical value of the rate constant, k , is 1.22 under certain conditions.

- (i) Complete the rate equation for this reaction, stating the overall order of the reaction.

rate =

overall order of reaction =

[1]

- (ii) Use your rate equation in (i) to calculate the rate of the reaction when the concentrations of F_2 and ClO_2 are both $2.00 \times 10^{-3} \text{ mol dm}^{-3}$.

rate = $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

- (c) Under different conditions, and in the presence of a large excess of ClO_2 , the rate equation is as shown.

$$\text{rate} = k_1[\text{F}_2]$$

The half-life, $t_{1/2}$, of the concentration of F_2 is 4.00 s under these conditions.

- (i) Calculate the numerical value of k_1 , giving its units.

Give your answer to **three** significant figures.

$$k_1 = \dots\dots\dots \text{units} \dots\dots\dots [2]$$

- (ii) An experiment is performed under these conditions in which the starting concentration of F_2 is $0.00200 \text{ mol dm}^{-3}$.

Draw a graph on the grid in Fig. 1.1 to show how the concentration of F_2 changes over the first 12 s of the reaction.

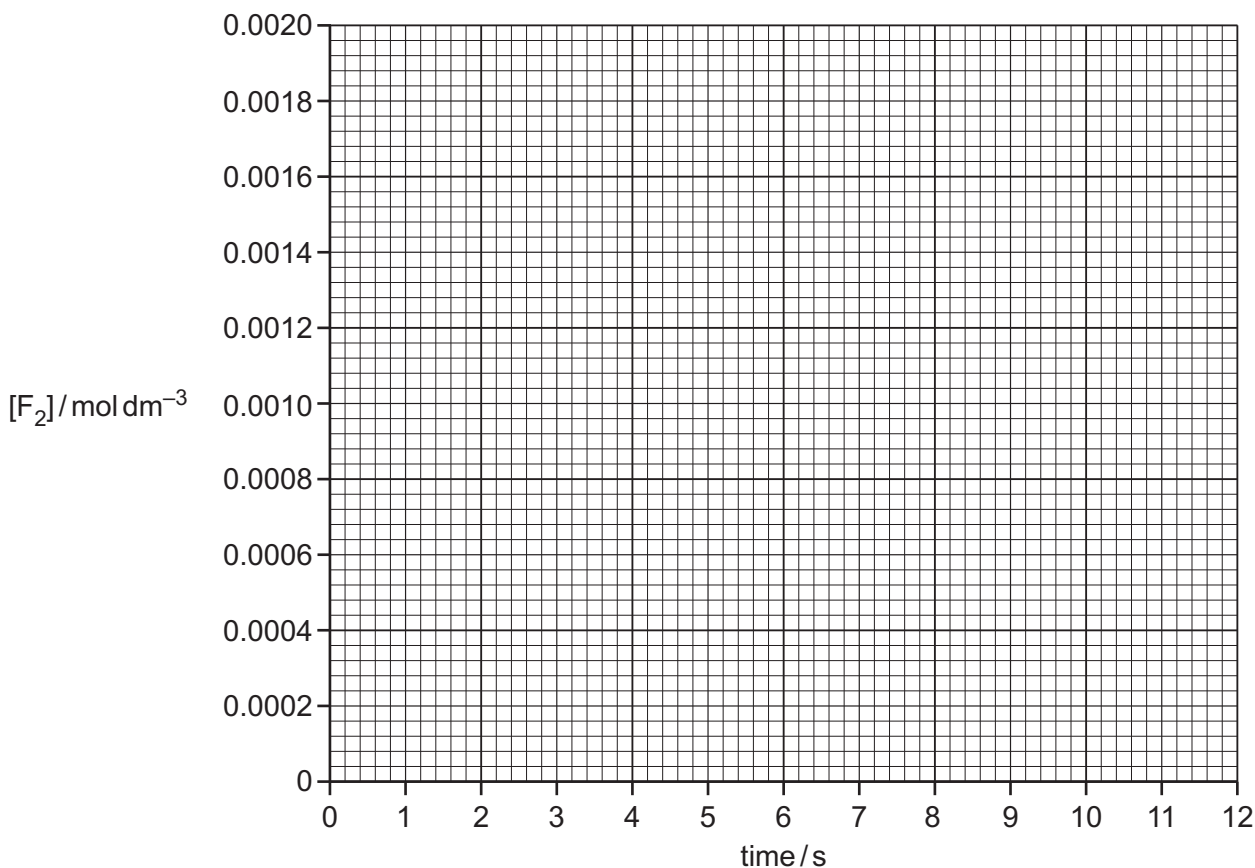


Fig. 1.1

[1]

- (iii) Use your graph in Fig. 1.1 to find the rate of the reaction when the concentration of F_2 is $0.00100 \text{ mol dm}^{-3}$. Show your working on the graph.

$$\text{rate} = \dots\dots\dots \text{mol dm}^{-3} \text{s}^{-1} [1]$$

[Total: 9]

- 2 (a) Define K_w mathematically by completing the expression.

$K_w =$ [1]

- (b) Two solutions, **V** and **W**, are described.

- **V** is $\text{HCl}(\text{aq})$.
- **W** is $\text{NaOH}(\text{aq})$.
- The concentration of HCl in **V** is the same as the concentration of NaOH in **W**.
- The pH values of **V** and **W** differ by exactly 11.00 at 298 K.

- (i) Calculate the concentration of HCl in **V**.

concentration of HCl in **V** = mol dm^{-3} [2]

- (ii) Equal volumes of the two solutions **V** and **W** are mixed, giving solution **X**.

Name solution **X** and state its pH.

solution **X** pH [1]

- (iii) A 1 cm^3 sample of 1.0 mol dm^{-3} HNO_3 is added to 100 cm^3 of solution **X**, forming mixture **Y**.

A 1 cm^3 sample of 1.0 mol dm^{-3} KOH is added to 100 cm^3 of solution **X**, forming mixture **Z**.

Estimate the pH of mixtures **Y** and **Z**. No calculations are required.

mixture **Y** mixture **Z** [1]

- (c) (i) $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CCl}_2\text{COOH}$ and H_2SO_4 are all acidic.

Suggest the trend in the relative acid strength of these three compounds.

Explain your answer.

.....
strongest acid weakest acid

explanation

.....
.....
.....
.....

[3]

- (ii) When concentrated H_2SO_4 is added to water a series of acid-base reactions occurs.

There are three conjugate acid-base pairs that can be identified during this series of reactions.

Write the formulae of these three conjugate acid-base pairs.

conjugate acid 1 conjugate base 1

conjugate acid 2 conjugate base 2

conjugate acid 3 conjugate base 3

[2]

- (d) The partition coefficient, K_{pc} , of a substance, **Q**, between hexane and water is 7.84 at 298 K.

Q is more soluble in hexane than it is in water.

- (i) Define partition coefficient, K_{pc} .

.....

..... [1]

- (ii) 5.00 g of **Q** is shaken with a mixture of 100.0 cm^3 of water and 100.0 cm^3 of hexane at 298 K and left until there is no further change in concentrations.

Calculate the mass of **Q** dissolved in the water.

mass of **Q** = g [1]

- (iii) A sample of **Q** is shaken with a different mixture of water and hexane and left until there is no further change in concentrations.

It is found that the mass of **Q** dissolved in each solvent is the same.

Use the K_{pc} value to suggest possible values for the volume of water used and the volume of hexane used.

volume of water = cm^3

volume of hexane = cm^3
[1]

- (iv) **Q** is more soluble in hexane than it is in water.

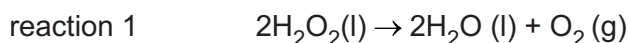
It is suggested that **Q** is one of KCl , $\text{CH}_3(\text{CH}_2)_4\text{OH}$ or HCOOH .

Identify **Q**. Explain your answer.

.....

..... [1]

- 3 Hydrogen peroxide is a liquid at 298K. It is moderately stable under room conditions but will decompose quickly if a catalyst is added.



- (a) (i) Define entropy.

.....
 [1]

- (ii) Predict the sign of the standard entropy change of reaction 1.

Explain your answer.

sign

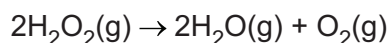
explanation
 [1]

- (b) Some bond energy data are shown in Table 3.1.

Table 3.1

type of bond	bond energy / kJ mol^{-1}
O–O	150
O–H	460
O=O	496

Use the data in Table 3.1 to show that the enthalpy change of the following reaction is -196 kJ mol^{-1} .



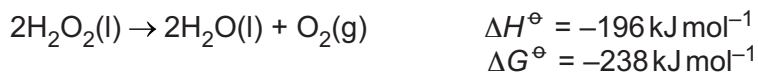
[1]

- (c) Some standard entropies, $S^\ominus$, are shown in Table 3.2.

Table 3.2

substance	$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$
$\text{H}_2\text{O}_2(\text{l})$	+102
$\text{H}_2\text{O}(\text{l})$	+70

The enthalpy change and Gibbs free energy change for the following reaction are shown.



Use the data given to calculate the standard entropy of oxygen, $S^\ominus$, $\text{O}_2(\text{g})$.

$$S^\ominus, \text{O}_2(\text{g}) = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [3]$$

- (d) The decomposition of $\text{H}_2\text{O}_2(\text{aq})$ is catalysed by aqueous iron(III) chloride and by silver metal.

Identify which of these two catalysts is acting as a homogeneous catalyst.

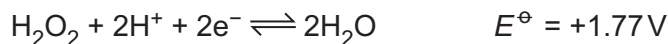
Explain your answer.

homogeneous catalyst

explanation

[1]

(e) The $E^\ominus$ values for two electrode reactions are given.



(i) An electrochemical cell is constructed with the following half-cells (electrodes):

- an acidified solution of H_2O_2 , a platinum wire
- Cr^{2+} mixed with Cr^{3+} , a platinum wire.

Identify the positive half-cell and calculate the standard cell potential, $E_{\text{cell}}^\ominus$.

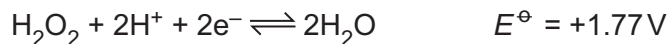
positive half-cell $E_{\text{cell}}^\ominus =$ V

[1]

(ii) Calculate the value of $\Delta G^\ominus$ for the cell reaction that occurs, per mole of H_2O_2 .

$\Delta G^\ominus =$ kJ mol^{-1} [2]

(f) The $E^\ominus$ values for two electrode reactions are given.



An electrochemical cell is constructed with the following half-cells.

half-cell 1 an acidified solution of H_2O_2 under standard conditions, a platinum wire

half-cell 2 a solution containing $0.020\text{ mol dm}^{-3}\text{ Co}^{3+}$ and $2.0\text{ mol dm}^{-3}\text{ Co}^{2+}$, a platinum wire

(i) Use the Nernst equation to calculate the value of E , the electrode potential of half-cell 2 under these conditions.

$E =$ V [2]

(ii) Write an equation for the cell reaction that occurs in this cell under these conditions.

..... [1]

(g) (i) Define enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$.

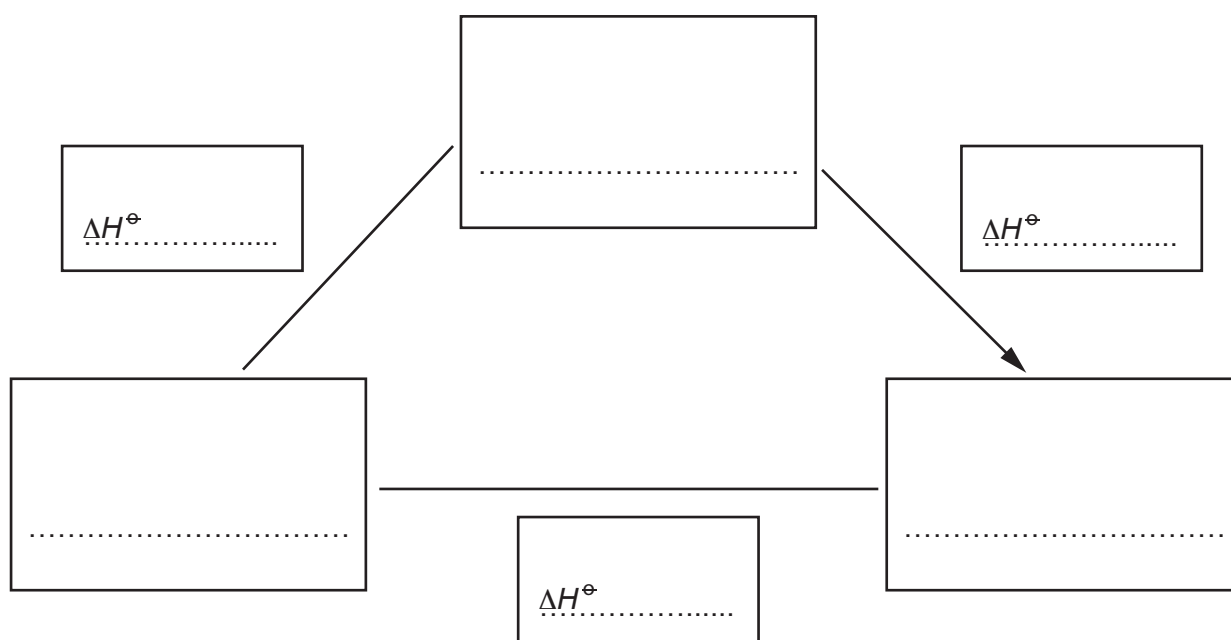
.....
 [1]

(ii) Aluminium fluoride, AlF_3 , is an ionic solid.

Complete and label the energy cycle to show the relationship between:

- the enthalpy change of solution of AlF_3 , $\Delta H_{\text{sol}}^{\ominus}$
- the lattice energy of AlF_3 , $\Delta H_{\text{latt}}^{\ominus}$
- the enthalpy changes of hydration of Al^{3+} and F^- , $\Delta H_{\text{hyd}}^{\ominus}$.

Include state symbols for all substances and ions.



[2]

(iii) Relevant data for this question are given.

$$\Delta H_{\text{sol}}^{\ominus} \text{AlF}_3 = -209 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}^{\ominus} \text{Al}^{3+} = -4690 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}^{\ominus} \text{F}^- = -506 \text{ kJ mol}^{-1}$$

Use these data and your energy cycle in (g)(ii) to calculate the $\Delta H_{\text{latt}}^{\ominus}$ of AlF_3 .

$$\Delta H_{\text{latt}}^{\ominus} \text{ of } \text{AlF}_3 = \dots\dots\dots \text{ kJ mol}^{-1} \quad [1]$$

[Total: 17]

- 4 (a) Cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ions.

- (i) Complete Table 4.1 giving the formula of the cobalt-containing species that is formed in each of the three reactions described.

Table 4.1

reaction	reagent added to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	cobalt-containing species formed
1	$\text{NaOH}(\text{aq})$	
2	an excess of $\text{NH}_3(\text{aq})$	
3	an excess of conc. $\text{HCl}(\text{aq})$	

[2]

- (ii) Describe the colour change seen in reaction 3.

original colour of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$

final colour after addition of an excess of conc. $\text{HCl}(\text{aq})$

[1]

- (b) Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is a white crystalline solid. When heated, it starts to decompose at approximately 500°C .

- (i) Write an equation for the decomposition of $\text{Ca}(\text{NO}_3)_2$.

..... [1]

- (ii) Suggest temperatures at which $\text{Mg}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ start to decompose.

Explain your answer.

temperature at which $\text{Mg}(\text{NO}_3)_2$ starts to decompose $^\circ\text{C}$

temperature at which $\text{Ba}(\text{NO}_3)_2$ starts to decompose $^\circ\text{C}$

explanation

.....

.....

.....

.....

[3]

[Total: 7]

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5 Transition elements behave as catalysts and can form complex ions.

(a) Explain why transition elements behave as catalysts.

.....

.....

..... [2]

(b) Silver forms the linear complex ion $[\text{Ag}(\text{CN})_2]^-$.

Copper forms the tetrahedral complex ion $[\text{Cu}(\text{CN})_4]^{3-}$.

Titanium forms the complex $[\text{TiCl}_4(\text{diars})_2]$, where *diars* is a neutral bidentate ligand.

(i) State the oxidation state and the coordination number of titanium in $[\text{TiCl}_4(\text{diars})_2]$.

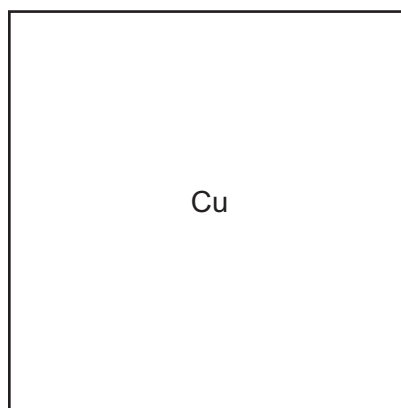
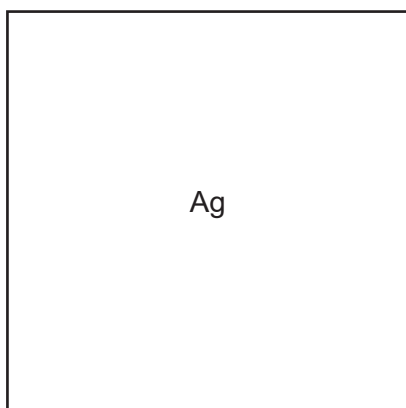
oxidation state

coordination number

[1]

(ii) Draw three-dimensional diagrams to show the shapes of $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Cu}(\text{CN})_4]^{3-}$, in the boxes.

Label one bond angle on each diagram.



[2]

(c) The numerical value of the stability constant, K_{stab} , of the copper(I) complex $[\text{Cu}(\text{CN})_4]^{3-}$ is 2.0×10^{27} .

(i) Write an expression for the K_{stab} of $[\text{Cu}(\text{CN})_4]^{3-}$.

$$K_{\text{stab}} =$$

[1]

- (ii) In a solution the concentrations of CN^- and $[\text{Cu}(\text{CN})_4]^{3-}$ are both $0.0010 \text{ mol dm}^{-3}$.

Use your expression from (c)(i) and the value of K_{stab} to calculate the concentration of $\text{Cu}^+(\text{aq})$ in this solution.

concentration of $\text{Cu}^+(\text{aq}) = \dots\dots\dots \text{mol dm}^{-3}$ [1]

- (d) A piece of a copper-containing alloy has a mass of 0.567 g. It is dissolved in an acid giving 100.0 cm^3 of a blue solution in which all the copper is present as Cu^{2+} ions.

An excess of $\text{KI}(\text{aq})$ is added to a 25.0 cm^3 sample of this solution.

All of the copper is precipitated as white $\text{CuI}(\text{s})$.

Cu^{2+} ions are the only component in the solution that react with $\text{KI}(\text{aq})$. This is reaction 1.



The liberated I_2 is then titrated with $0.0200 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}$. This is reaction 2.



The titration requires 20.10 cm^3 of $0.0200 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}$ to reach the end-point.

- (i) Calculate the number of moles of I_2 that are reduced in this titration.

number of moles of $\text{I}_2 = \dots\dots\dots \text{mol}$ [1]

- (ii) Calculate the number of moles of copper in the original piece of alloy.

number of moles of copper = $\dots\dots\dots \text{mol}$ [1]

- (iii) Calculate the percentage of copper in the alloy.

percentage of copper = $\dots\dots\dots \%$ [1]

- (iv) Suggest why a solution of Cu^{2+} is coloured but solid CuI is white.

.....

 [2]

[Total: 12]

- 6 (a) Five ligands are listed in Table 6.1.

Table 6.1

ligand	type of ligand
NH_3	
EDTA^{4-}	
CN^-	
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	tridentate
$\text{C}_2\text{O}_4^{2-}$	

- (i) Complete Table 6.1 using the words monodentate, bidentate and polydentate only.

Each of these three words may be used once, more than once, or not at all. [2]

- (ii) The molecule $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ is a tridentate ligand.

Suggest the meaning of tridentate ligand.

.....
 [1]

- (iii) Suggest how $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ acts as a tridentate ligand.

.....
 [1]

- (b) Nickel forms the octahedral complex $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$. This complex can exist in three isomeric forms, listed in Table 6.2.

One of these forms is a trans isomer, the other forms are two different cis isomers.

Table 6.2

isomer	polarity
trans isomer	
cis isomer 1	
cis isomer 2	

- (i) Complete Table 6.2 using the terms polar or non-polar.

Each term may be used once, more than once, or not at all. [1]

- (ii) Describe the difference between cis isomer 1 and cis isomer 2.

.....
 [1]

[Total: 6]

- 7 Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules **E** and **G** each contain one $-\text{SO}_3^-$ group. These groups are unchanged in the formation of Sunset Yellow.

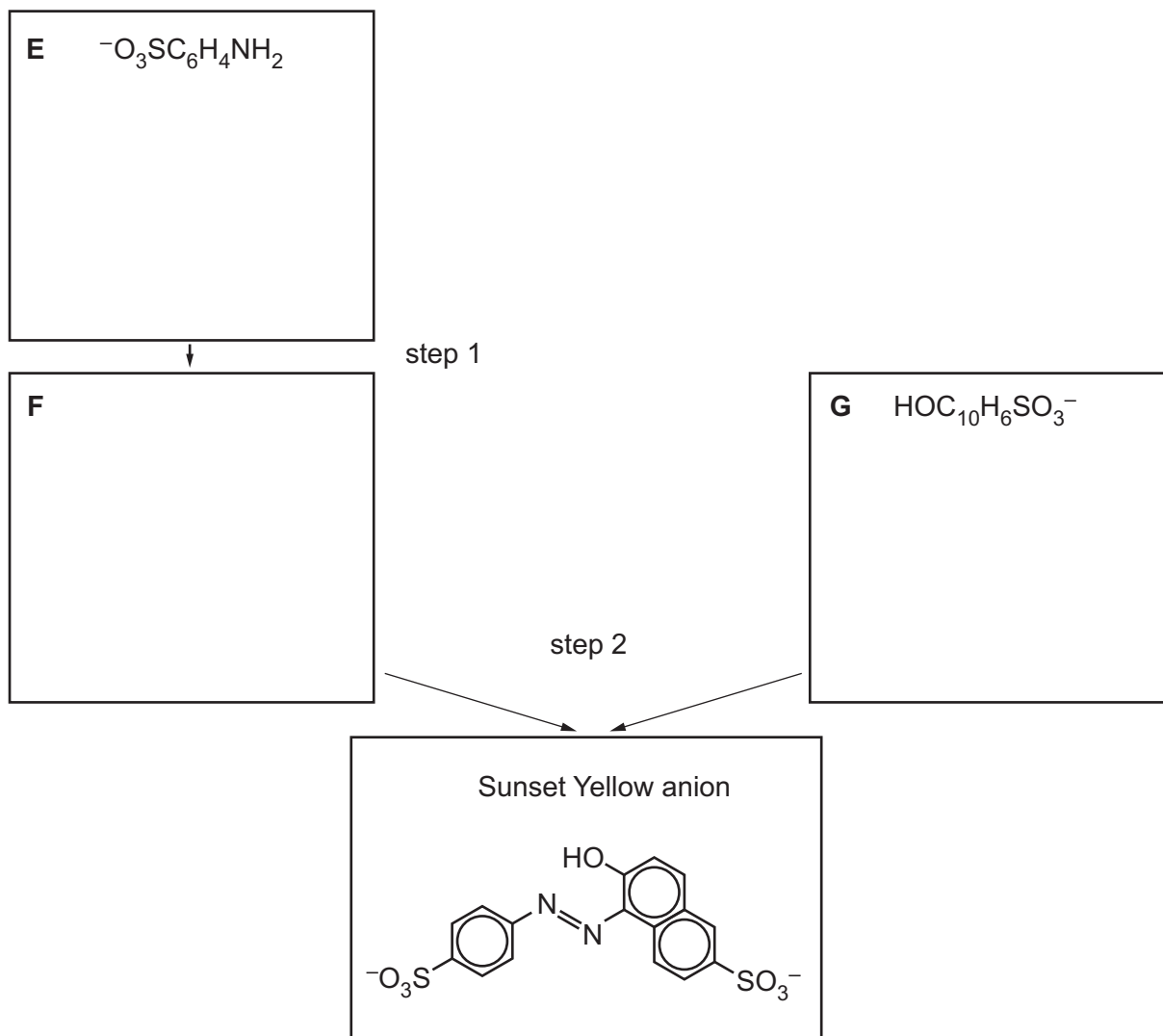
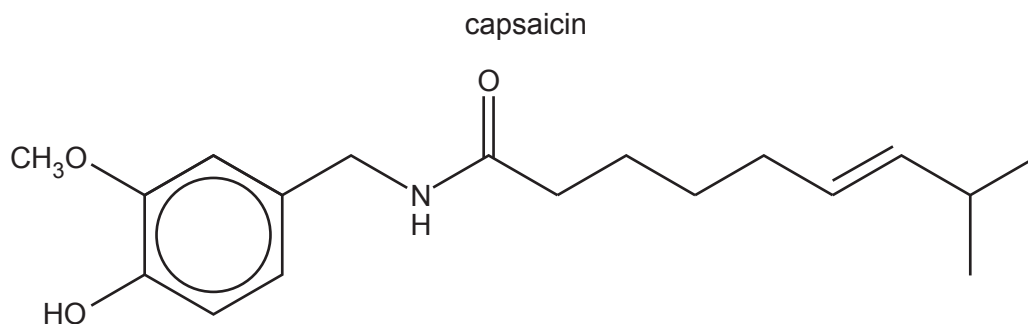


Fig. 7.1

- (a) State the molecular formula of the Sunset Yellow anion.
..... [1]
- (b) Deduce the structures of **E**, **F** and **G** and draw them in the boxes in Fig. 7.1. [3]
- (c) Suggest suitable reagents and conditions for step 1 and 2.
step 1
step 2 [3]
- (d) Predict the number of peaks in the carbon-13 NMR spectrum of the Sunset Yellow anion.
..... [1]

[Total: 8]

- 8 Capsaicin is found in chilli peppers.



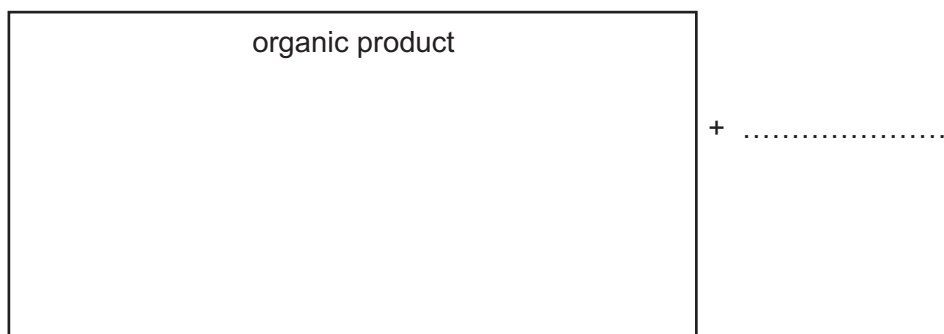
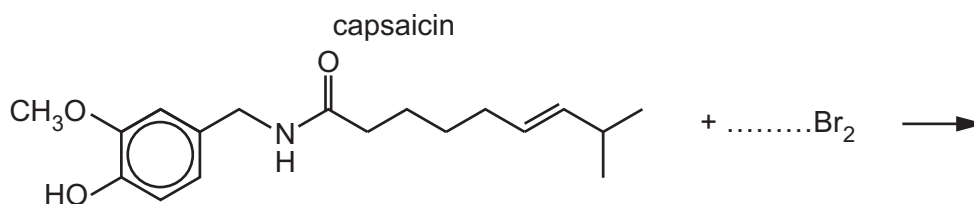
You should assume the CH_3O group is unreactive in the reactions involved in this question.

- (a) Name all the functional groups in capsaicin in addition to the CH_3O group.

..... [1]

- (b) Complete the equation for the reaction of capsaicin with an excess of $\text{Br}_2(\text{aq})$ in the dark.

Draw the structure of the organic product in the labelled box.



[3]

- (c) Capsaicin is heated with an excess of hydrogen gas in the presence of platinum metal.

The six-membered ring reacts in the same way as benzene under these conditions.

Draw the structure of the organic product formed.

[2]

(d) When capsaicin is treated with reagent **J** under suitable conditions one of the products is methylpropanoic acid, $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$.

(i) Identify reagent **J** and any necessary conditions.

..... [1]

(ii) There are three different peaks in the proton (^1H) NMR spectrum of $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$ in CDCl_3 .

Table 8.1

environment of proton	example	chemical shift range δ/ppm
alkane	$-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$	0.9–1.7
alkyl next to $\text{C}=\text{O}$	$\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar , $-\text{CH}_2-\text{Ar}$, $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	CH_3-O , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{Cl}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0

Use Table 8.1 to complete Table 8.2 and state:

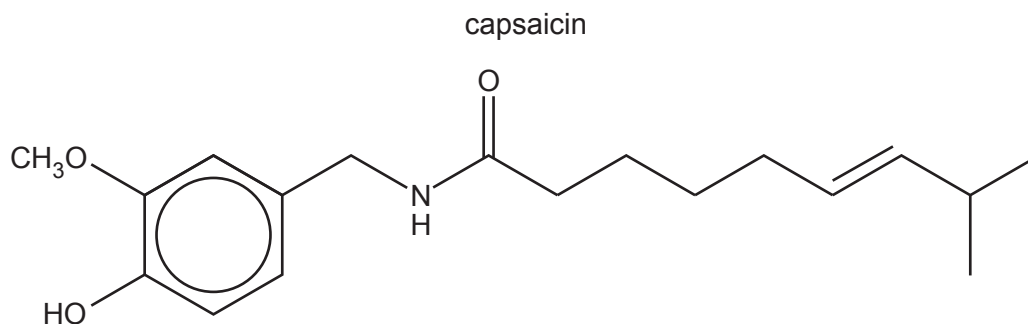
- the typical proton (^1H) chemical shift values (δ) for the protons
- the splitting pattern (singlet, doublet, triplet, quartet or multiplet) shown by each peak
- the explanation for the splitting patterns of the CH_3 protons and the CH proton.

Table 8.2

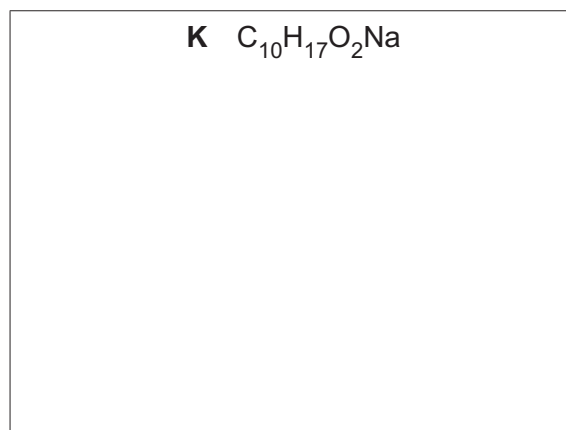
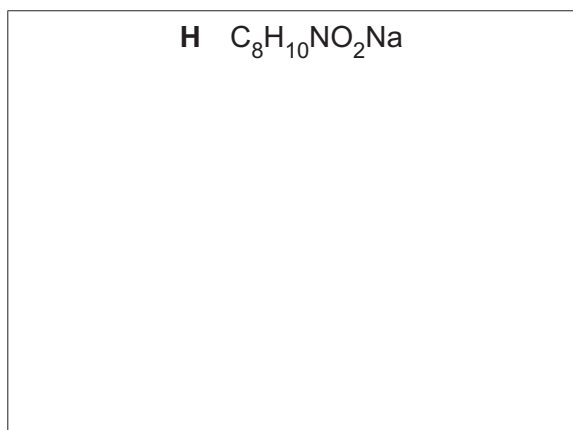
environment	δ/ppm	splitting pattern	explanation for splitting pattern
CH_3			
CH			
COOH			

[3]

- (e) (i) Capsaicin is heated with an excess of hot aqueous NaOH.



Draw the structures of the two organic products **H** and **K**.

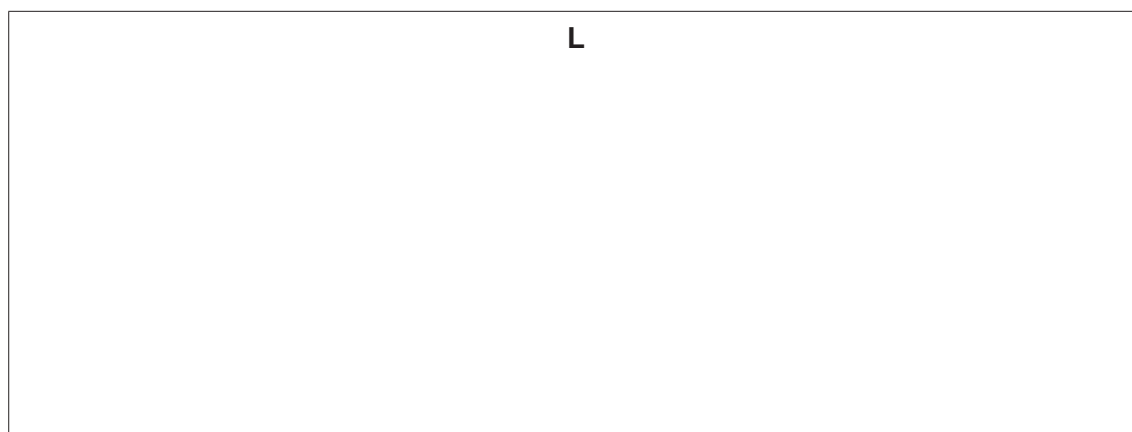


[2]

- (ii) Name the **two** types of reaction occurring in (e)(i).

..... [1]

- (f) Draw the structure of the organic product **L** formed when capsaicin is treated with LiAlH_4 in dry ether.



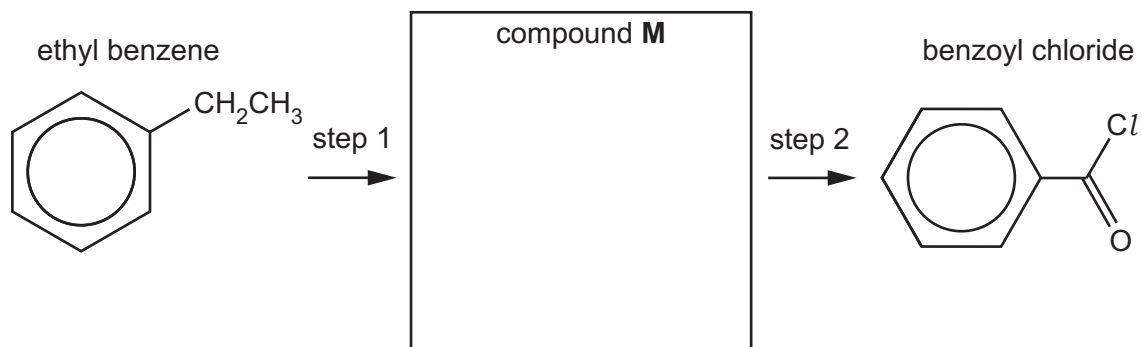
[1]

[Total: 14]

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- 9 (a) Benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, can be made from ethyl benzene in a two-step process.

A reaction scheme is shown.



- (i) Draw the intermediate organic compound **M** in the box. [1]

- (ii) Suggest suitable reagents and conditions for step 1 and step 2.

step 1

step 2 [2]

- (iii) Identify the type of reaction in step 1 and step 2.

step 1

step 2 [2]

(b) $\text{C}_6\text{H}_5\text{COCl}$ reacts with phenol, $\text{C}_6\text{H}_5\text{OH}$, to give the ester phenyl benzoate, $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$.

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.

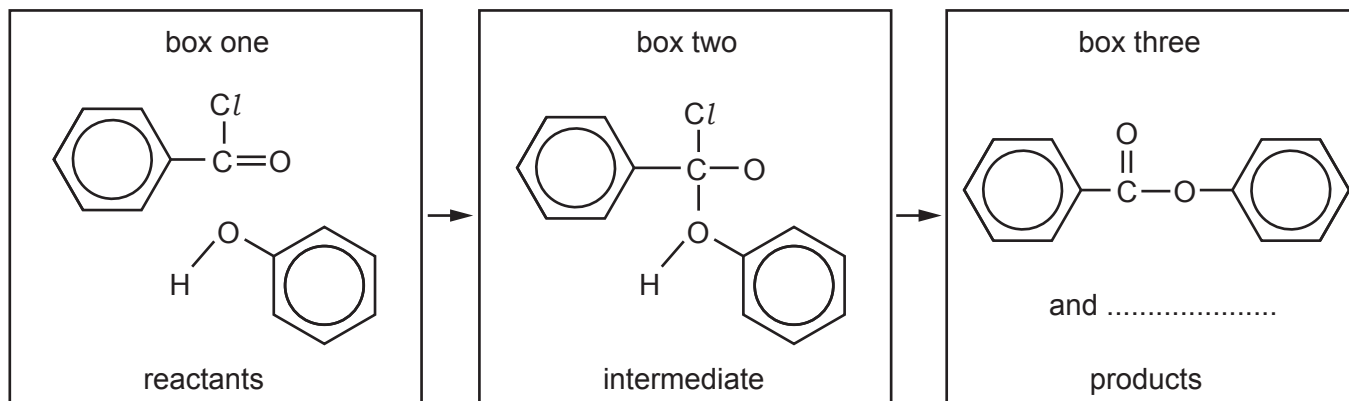


Fig. 9.1

(i) Complete the mechanism in Fig. 9.1 and include:

- all relevant dipoles (δ^+ and δ^-) and full electric charges (+ and -) on the species in box one and in box two
- all relevant lone pairs on the species in box one and in box two
- all relevant curly arrows to show the movement of electron pairs in box one and in box two
- the formula of the second product in box three.

[4]

(ii) Name this mechanism.

..... [1]

(c) Benzoyl chloride, chlorobenzene and chloroethane differ in their rates of hydrolysis when each compound is added separately to water at 25°C .

Suggest the relative ease of hydrolysis of these three compounds.

Explain your answer.

.....
hardest to hydrolyse easiest to hydrolyse

explanation

.....
.....
.....
.....
.....

[3]

[Total: 13]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																			
1	2													13	14	15	16	17	18
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