1 (a) $\mathbf{H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O}$ [1]

(b) To create a buffer solution so as to keep the $[H^+]$ effectively constant since changes in $[H^+]$, as reaction proceeds, will affect the rate of reaction. [1]

(c) Preparation of stock solution of H_2O_2 [9]

Intended concentration of stock solution of H_2O_2 = **3.0 mol dm^{-3}**

*[In order to ensure that at least one of the experiments would take significantly less than 20 s, the concentration of H_2O_2 to be used for Solution **B** is doubled compared with the info given in the question]*

volume of 7.5 mol dm^{-3} H_2O_2 solution used for dilution

$$= \frac{C_1V_1}{C_o} = \frac{3.0 \times 250}{7.5} = \mathbf{100\ cm^3}$$

Procedure:

1. Using a burette, place 100 cm^3 of the 7.5 mol dm^{-3} H_2O_2 solution into a 250 cm^3 graduated flask.
2. Top up with deionised water to the 250 cm^3 mark. Add dropwise when near to the mark.
3. Shake well to obtain a homogeneous solution.

Iodine clock experiment

*[50 cm^3 of solution **A** and 25 cm^3 of 1.0 mol dm^{-3} ethanoic acid are used in each experiment. The volumes of the H_2O_2 stock solution added are to be varied in each experiment and the total volume is kept constant (100 cm^3) by adding appropriate amounts of deionised water.*
*25 cm^3 of ethanoic acid is used to ensure that the same proportions of solution **A** and aqueous ethanoic acid are used in every experiment.]*

Procedure:

1. Using a burette, transfer 50 cm^3 of solution **A** to a 250 cm^3 conical flask labelled **A**.
2. Fill a 2nd burette with the 3.0 mol dm^{-3} H_2O_2 stock solution prepared and add 25 cm^3 of H_2O_2 into another 250 cm^3 conical flask labelled **B**.
3. Using a 50 cm^3 measuring cylinder, add 25 cm^3 of ethanoic acid to the same conical flask labelled **B** and mix the contents thoroughly by swirling the conical flask.

4. Pour the contents in flask **B** rapidly into flask **A**. Start the stopwatch immediately.
5. Mix the contents thoroughly by swirling the flask.
6. Stop the stopwatch when the solution turns dark blue. Record the time taken.
7. Repeat steps 1 to 6 using different concentrations of H_2O_2 by varying the volume of H_2O_2 stock solution used. The total volume of solutions is kept constant by adding deionised water as required.
8. The results are recorded in the table below.

expt	vol of solution **A** / cm^3	vol of ethanoic acid / cm^3	vol of H_2O_2 / cm^3	vol of deionised water / cm^3	$[H_2O_2]$ in reaction mixture / mol dm^{-3}	time taken, t / s	rate $(\frac{1}{t})$ / s^{-1}
1	50.00	25.0	25.00	0.0	0.750		
2	50.00	25.0	20.00	5.0	0.600		
3	50.00	25.0	15.00	10.0	0.450		
4	50.00	25.0	10.00	15.0	0.300		
5	50.00	25.0	5.00	20.0	0.150		

e.g. $[H_2O_2]$ *in experiment 1* $= \frac{25.00 \times 3.0}{100} = 0.750$ *mol* dm^{-3}

[Some processing of data is required here, by using the example given in question, to check if at least one of the experiments will take significantly less than 20 s.]

$[H_2O_2]$ *in Solution* ***B*** *of example = 0.750 mol* dm^{-3}
(because equal volumes of H_2O_2 *and ethanoic acid were mixed)*

$[H_2O_2]$ *in reaction mixture of example = 0.375 mol* dm^{-3}
(because equal volumes of Solution ***A*** *and* ***B*** *were mixed)*

Hence Experiment 1 will be expected to take significantly less than 20 s since $[H_2O_2]$ *used is twice that of the example. (i.e. It will take about 10 s if the order with respect to* H_2O_2 *is 1)*

Analysis of results

1. For each of the experiments, calculate the reaction rate, where rate is represented by $\frac{1}{\text{time}}$.
2. Plot a graph of the reaction rate against [H_2O_2].
3. For a zero order reaction, the best fit line will be a horizontal straight line.
   For a first order reaction, the best fit line will be a straight line passing through the origin.

[1]: use of appropriate apparatus (e.g. burette, standard / graduated flask)

[1]: essential details (e.g. *250 cm^3* flask, *50 cm^3* measuring cylinder)

[1]: appropriate [H_2O_2] chosen for the stock solution (i.e. *any concentration higher than 1.5 mol dm^{-3}*)

[1]: correct procedure in the preparation of the standard stock solution (including the correct choice of volume of the provided H_2O_2 solution to be used)

[1]: appropriate volumes of H_2O_2 proposed (such that at least one experiment takes less than 20 s and there are sufficient points to draw a best fit line – minimum 3 points for Chemistry)

[1]: maintain proportion of solution **A** and aq. CH_3CO_2H (keeping the total volume constant by adding deionised water)

[1]: start stopwatch at the same time when **A** and **B** are mixed

[1]: graph of rate against [H_2O_2] proposed

[1]: correct interpretation of proposed graph

*Alternatively for the iodine clock experiment, you may prepare 3/5 sets of Solution **B**, each with a different [H_2O_2] and then follow the steps in the given example.*
e.g.
*Solution **B1** – **500 cm^3** of 3.0 mol dm^{-3} stock H_2O_2 prepared + 500 cm^3 of 1.0 mol dm^{-3} ethanoic acid*
*Solution **B2** – **400 cm^3** of 3.0 mol dm^{-3} stock H_2O_2 prepared + **100 cm^3** of deionised water + 500 cm^3 of 1.0 mol dm^{-3} ethanoic acid*
*Solution **B3** – **300 cm^3** of 3.0 mol dm^{-3} stock H_2O_2 prepared + **200 cm^3** of water + 500 cm^3 of 1.0 mol dm^{-3} ethanoic acid*

*Then you mix **50 cm^3** of Solution **A** with **50 cm^3** of Solution **B1/B2/B3** and record the time taken for the mixture to turn dark blue.* (+ the other 2 parts given above)

Comments:

Preparation of stock solution of H_2O_2

Students were expected to state clearly that they intended to dilute the given 7.5 mol dm^{-3} solution of H_2O_2. Descriptions of this procedure must be precise with essential details (e.g. stating the accurate concentration of this solution). Apparatus such as measuring cylinders, beakers and conical flasks used for measuring volumes are inappropriate here.

Iodine clock experiment

*Many students did not realise that [H_2O_2] is the independent variable. They needed to ensure a suitable range of concentrations such that [H_2O_2] was high enough for one experiment to take less than 20 s, and that the proportions of solution **A** and aqueous ethanoic acid should also be the same as described in the example. It is also essential that at the point when solutions **A** and **B** are mixed and swirled the stopwatch is started at the same time.*

Analysis of results

Students had to state clearly what graph they would draw and give a correct interpretation of their proposed graph. They are not to use numerical changes in concentration and time to determine order.

(d) The concentrated hydrogen peroxide solution used is corrosive. Safety goggles and gloves should be worn when handling it. [1]

2 **(a)** **(i)** hydrocarbon [1]

(ii) the <u>high temperature</u> in the internal combustion engine allows the <u>atmospheric nitrogen and oxygen to react</u>. [1]

(iii) <u>protein</u> / <u>amino acid</u> from the fossil remains [1]

(b) **(i)** By Hess' Law,

$\Delta H^{\ominus}_{\text{reaction 1}} = -\Delta H^{\ominus}_{f}(SO_2) + \Delta H^{\ominus}_{f}(SO_3)$

$= -396 - (-297)$ [1]

$= \mathbf{-99.0\ kJ\ mol^{-1}}$ [1]

Note: Drawing of energy cycle is not necessary.

(ii) $\Delta G^{\ominus}_{\text{reaction 1}} = \Delta H^{\ominus}_{\text{reaction 1}} - T\Delta S^{\ominus}_{\text{reaction 1}}$

$= -99.0 - 298(-93.5\ \mathbf{x\ 10^{-3}})$ [1]

$= -71.137\ kJ\ mol^{-1}$

$= \mathbf{-71.1\ kJ\ mol^{-1}}$ [1] ecf

Note: Students are reminded to take note of the difference in magnitude of entropy (J mol K^{-1}) and enthalpy (kJ mol^{-1}) and their respective units.

(c) **(i)** $-71.137\ \mathbf{x\ 10^{3}} = -2.303(8.31)(298)\log_{10}(K_c)$ [1]

$\log_{10}(K_c) = 12.47$

$K_c = 10^{12.47}$

$= \mathbf{2.97\ x\ 10^{12}}\ (mol\ dm^{-3})^{-½}$ [1]

Note: No units are required for this question but students are encouraged to work out the unit of K_c based on the stoichiometry equation.

(ii) The large K_c value calculated in **(i)** suggests that the <u>position of equilibrium lies very much to the right</u> and [1] ecf
the <u>forward</u> reaction is very <u>spontaneous</u> and the reaction would be <u>effectively complete</u>. [1] ecf

(iii) Sulfur undergoes combustion readily in air to form sulfur dioxide. However, further oxidation of the combustion product of sulfur, SO_2 to form SO_3 required <u>very high activation energy</u> and does not proceed. [1]

(iv) The use of V_2O_5 catalyst <u>speeds up the reaction</u> [1]
as it <u>provides an alternative pathway</u> with <u>lower activation energy</u> for the oxidation of SO_2 to SO_3 to take place. [1]

3 (a) (i) $\boldsymbol{K_{sp} = [Pb^{2+}][Cl^{-}]^2}$ [1]

units = $\mathbf{mol^3\ dm^{-9}}$ [1]

(ii) Solubility of $PbCl_2$ = $\dfrac{4.7}{(207.2 + 35.5 \times 2)}$

= 0.0169 mol dm^{-3} [1]

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

K_{sp} = (0.0169)(**2 x 0.0169**)^2 [1]

= $\mathbf{1.9 \times 10^{-5}}$ $mol^3\ dm^{-9}$ *(to 2 s.f.)* [1]

(b) (i) immediately ⇒ <u>white ppt observed</u> [1]

after one hour in daylight ⇒ <u>grey solid observed</u> [1]

(ii) Add <u>dilute $NH_3(aq)$</u> to the white ppt. [1]

The AgCl ppt will <u>dissolve in NH_3</u> to give a <u>colourless solution</u>. [1]

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$ [1]

(iii) $PbCl_2$ forms a <u>soluble complex</u> with concentrated HCl. [1]

$$PbCl_2 + 2Cl^- \rightleftharpoons [PbCl_4]^{2-}$$ [1]

(c) When concentrated HCl is added to an aqueous solution of Cu^{2+}, <u>ligand exchange</u> occurs where Cl^- displaces the H_2O ligands, forming the yellow $[CuCl_4]^{2-}$. [1]

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$ [1]

Addition of water will cause the position of equilibrium to <u>shift to the left</u>, reforming the blue $[Cu(H_2O)_6]^{2+}$. [1]

Note: Addition of water will result in <u>decrease in concentration of the ions</u>. Position of equilibrium will shift to the left as it will result in an <u>increase in no. of ions</u>, reforming the blue $[Cu(H_2O)_6]^{2+}$ as shown by the equation

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

(recall: the effect of decreasing pressure on system will cause P.O.E. to shift to the side with more gaseous particles so as to increase the pressure)

(d) **(i)** In an acidic solution,

$H_2S + aq \rightleftharpoons H^+ + HS^-$ ——— (1)
$HS^- \rightleftharpoons H^+ + S^{2-}$ ——— (2)

the high $[H^+]$ causes the position of equilibriums (1) and (2) to shift to the left, resulting in a low $[S^{2-}]$. [1]

Since the K_{sp} value of CuS is the lowest, the low $[S^{2-}]$ is sufficient for its ionic product > K_{sp}, hence only CuS is precipitated in acidic solution. [1]

(ii) NiS has the highest K_{sp} value, hence a high $[S^{2-}]$ is needed for its precipitation. [1]
(Precipitation of NiS does not occur in neutral or acidic solution as the $[S^{2-}]$ is too low.)
In an alkaline medium, the $[H^+]$ is low, and the position of equilibrium (1) and (2) shifts to the right, resulting in a sufficiently high $[S^{2-}]$ for its ionic product > K_{sp}, hence precipitation occurs. [1]

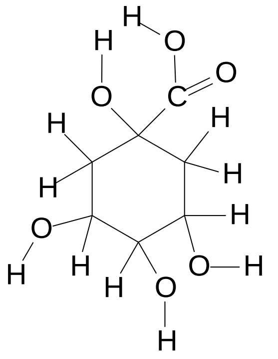
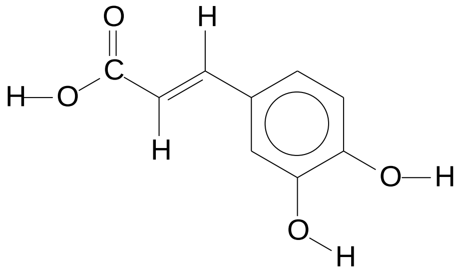
(iii) ZnS has an intermediate K_{sp} value. [1]
In neutral solution, the $[S^{2-}]$ at equilibrium is sufficiently high for precipitation to occur. [1]
In an alkaline solution, the $[H^+]$ is low, and positions of equilibrium for (1) and (2) shift to the right, resulting in a higher $[S^{2-}]$ than in a neutral solution. Hence precipitation of ZnS can also occur in an alkaline solution.

4 **(a)** **(i)** carboxylic acid, [5]
2^{o} alcohol,
3^{o} alcohol,
ester and
phenol

[1] each

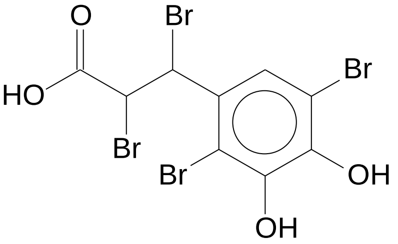
(ii) **4** chiral centres [1]

(b) [2]

	
non–aromatic compound	aromatic compound **R**

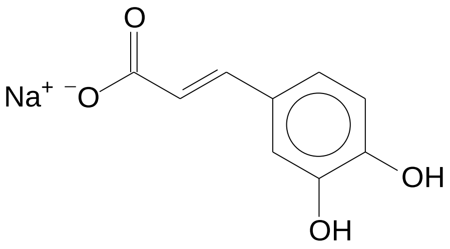
[1] each

(c) [2]



[1] each: electrophilic addition of C=C and electrophilic substitution of benzene

(d) **(i)** [1]



(ii) Carboxylic acid is a <u>stronger acid than H_2CO_3</u>. Hence, it is able to displace out the weaker carbonic acid from $NaHCO_3$. [1]

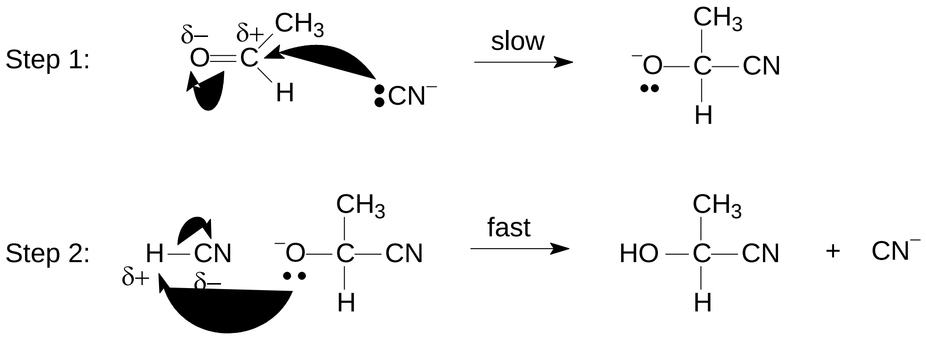
Phenol, which is a <u>weaker acid than H_2CO_3</u>, cannot displace out the H_2CO_3. [1]

5 **(a)** **(i)** Reagent: HCN [1]

Conditions: NaCN as catalyst [1]

Type of reaction: Nucleophilic addition [1]

(ii) [2]



[1]: correct partial charges and arrows
[1]: correct intermediate and labeling of slow/fast step

Note: partial charges, lone pair and negative charge on CN^-, curly arrows and the correct alkoxide intermediate, CN^- ion must be regenerated at the end of the reaction.

(b) **(i)** The presence of a chiral carbon and all the lactic acid molecules present are of the same chirality (or only one enantiomer is present) and hence rotates the plane of polarised light. [1] [1]

(ii) Synthetic lactic acid is formed via nucleophilic addition mechanism and gives an optically inactive racemic mixture. [1]
The CH_3CHO molecule is trigonal planar with respect to the carbonyl carbon atom. Since the molecule is planar, the nucleophile has equal probability of attacking it from either side of the molecule. [1]
This generates equimolar mixture of the enantiomers.

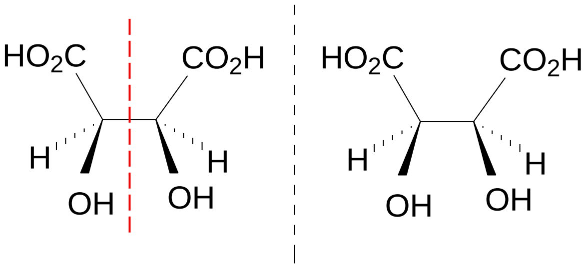
(c) [3]

molecule	explanation
A	The 2 chiral centers on molecule **A** both rotate the plane polarised light to the right. Hence, overall, it is observed that the plane polarised light is rotated to the right.
B	The 2 chiral centers on molecule **B** both rotate the plane polarised light to the left. Hence, overall, it is observed that the plane polarised light is rotated to the left.
C	Molecule **C** is a meso compound that has an internal plane of symmetry. The 2 chiral centers on the tartaric acid molecule rotates plane polarised light in different directions by the same extent and their optical activity are cancelled out. Hence, there is overall no effect on the plane polarised light.

Additional information

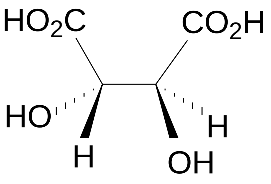
Molecule C

It appears that the 2 molecules below are optical isomers but upon closer inspection, you will notice that there is a plane of symmetry within the molecule. Hence the 2 so called “mirror images” are actually equivalent (i.e. superimposable on one another)



This plane of symmetry is not present in **A** or **B**. Hence **A** and **B** are enantiomers (molecules that are non–superimposable mirror images of each other). They can be distinguished by the direction which each isomer rotates plane polarised light.
e.g. If **A** rotates plane polarised light clockwise by x^{o}, **B** will rotate anti–clockwise by the same magnitude.

Molecule A



Molecule B