Section A

Answer **all** the questions in this section.

1 (a) Ethanoic acid and its salt, sodium ethanoate, is often used as an acid buffer to help extend the shelf-life of food products such as meat, fish and dairy.

A buffer solution of pH 5.5 was prepared by mixing 0.200 mol dm^{-3} of ethanoic acid and 0.200 mol dm^{-3} aqueous sodium ethanoate.

(K_a of ethanoic acid = 1.74×10^{-5} mol dm^{-3})

(i) What do you understand by the term *buffer solution*? [1]

(ii) Calculate the ratio of $\frac{[\text{ethanoate}]}{[\text{ethanoic acid}]}$ required to prepare the above buffer solution.

Hence deduce whether the above buffer is more effective in buffering against added acids or bases.

Write an equation to illustrate your answer. [3]

(iii) Calculate the volume of ethanoic acid and that of aqueous sodium ethanoate required to prepare 60 cm^3 of the above buffer. [1]

(iv) The boiling points of the components in the buffer are as shown.

Ethanoic acid	118 ^oC
Sodium ethanoate	881 ^oC

With reference to the structure and bonding present in the compounds, account for the difference in the boiling points. [3]

(b) The limestone that collects in kettles in hard water areas is mainly calcium carbonate. It can be removed fairly harmlessly by using a warm solution of vinegar, which contains ethanoic acid. The limestone dissolves with fizzing and a solution of calcium ethanoate remains.

(i) Write a balanced equation for the reaction between ethanoic acid and calcium carbonate. [1]

When the solution in **(b)** is evaporated and the resulting solid calcium ethanoate is heated strongly in a test-tube, an organic compound **Q** is formed, which condenses to a colourless liquid. The residue in the tube contains calcium carbonate.

When 0.10 g of compound **Q** was injected into a gas syringe at a temperature of 383 K and a pressure of 101 kPa, 55 cm^3 of vapour were produced.

(ii) Calculate the relative molecular mass of **Q**. [2]

(iii) Compound **Q** is neutral and water-soluble. **Q** does not react with sodium metal nor with Fehling's solution but it does react with alkaline aqueous iodine.

Suggest a structural formula for **Q.** Justify your answer by reference to these properties of **Q**. [4]

(iv) Construct a balanced equation for the formation of **Q** by the action of heat on calcium ethanoate. [1]

(v) The residue calcium carbonate can also undergo thermal decomposition when heated very strongly. Copper(II) carbonate behaves in a similar manner when heated.

State which carbonate, calcium or copper(II) will have a higher decomposition temperature. Explain your answer, with the help of relevant data from the *Data Booklet*. [3]

[Total: 19]

2 (a) In a closed reaction vessel maintained at a high temperature, 1 mol of Al_2Cl_6 dimers dissociate into $AlCl_3$ according to the following equation.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

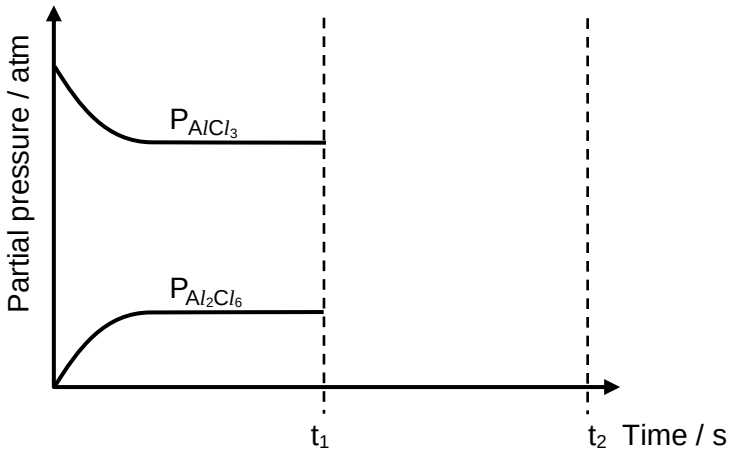
The average M_r of the equilibrium gas mixture is found to be 178.0.

(i) Given that the average M_r of the equilibrium gas mixture is the sum of the mole fractions of each gas, multiplied by the M_r of that gas, calculate the degree of dissociation of Al_2Cl_6, α. [3]

(ii) Write down the expression of K_p for the above equilibrium system. Hence, show that $K_p = K_cRT$. [2]

(iii) An experiment on the dissociation of Al_2Cl_6 was conducted in a closed container of a fixed volume and the partial pressures of all the components were plotted as shown in the figure below.

Copy and complete the diagram to show how the partial pressure of each gas changes when the volume of the container is halved at t_1 until t_2.



[2]

(b) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame and this allows it to be used as a source of redness in fireworks.

Use the data below to answer the questions that follow.

Standard Gibbs free energy change of solution of $SrCl_2(s)$	–41.6 kJ mol^{-1}
Standard enthalpy change of formation of $SrCl_2(s)$	–828.9 kJ mol^{-1}
Standard enthalpy change of formation of $Sr^{2+}(aq)$	–545.8 kJ mol^{-1}
Standard enthalpy change of formation of $Cl^-(aq)$	–167.5 kJ mol^{-1}
Standard enthalpy change of hydration of $Sr^{2+}(g)$	–1446 kJ mol^{-1}
Standard enthalpy change of hydration of $Cl^-(g)$	–378 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation* of strontium chloride. [1]

(ii) Calculate $\Delta H^{\ominus}_{sol}$ and $\Delta S^{\ominus}_{sol}$ of strontium chloride. [4]

(iii) Write an equation to show the relationship between the lattice energy of strontium chloride and $\Delta H^{\ominus}_{sol}$ of strontium chloride. Hence, calculate the lattice energy of strontium chloride. [2]

(iv) Predict with reasoning, how Gibbs free energy change of formation of strontium chloride, ΔG_f will change with increasing temperature. [2]

(c) Using the data given below, draw a labelled energy cycle to calculate the enthalpy change of combustion of solid carbon.

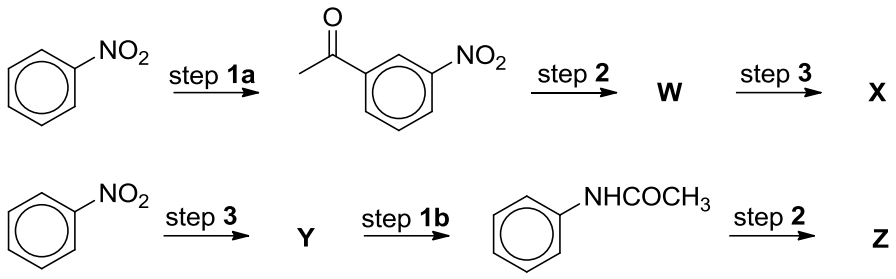
$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184$ kJ mol^{-1}

$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234$ kJ mol^{-1}

$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s) + 3O_2(g)$ $\Delta H = +2440$ kJ mol^{-1} [4]

[Total: 20]

3 (a) Consider the following synthesis pathways starting from nitrobenzene:



(i) Ethanoyl chloride (CH_3COCl) is used as a reactant for step **1a** and step **1b** but under different conditions. State the reaction mechanism that occurred for each step **1a** and **1b** and hence explain the difference in the conditions required. [3]

(ii) Identify the reagents and conditions required for **steps 2** and **3** and hence draw the structures of **W, X, Y** and **Z**.

[Note: **Steps 2** and **3** in both pathways each refers to the same set of reagents and conditions.] [6]

(iii) Compare the relative basicity of **Y** and **Z**. [2]

(b) In an isolated atom, the five d orbitals have the same energy. When a transition element ion is in an octahedral complex, the d orbitals are split into two groups of different energy levels.

(i) Draw an orbital energy diagram to show this, indicating the type of orbitals in each group. [2]

(ii) Use your diagram in **(b)(i)** to explain why transition element complexes like $Co(H_2O)_6^{2+}$ are often colored. [2]

(c) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution which gives the following reactions.

$CoCl_2(aq) \xrightarrow{NaOH(aq)}$ blue ppt. insoluble in excess $\xrightarrow{H_2O_2}$ blue ppt. turned brown

$CoCl_2(aq) \xrightarrow{HCl(aq)}$ no observable change $\xrightarrow{H_2O_2}$ no observable change

(i) By using the data given below and appropriate values from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ and explain the differences in the observations made between **acidic** and **alkaline** medium.

$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^-$ $\quad E^{\ominus} = +0.17$ V

Write equations to account for the observations. [4]

(ii) When brine solution instead of HC*l* was added to $CoCl_2(aq)$, the solution turned from pink to blue. In this reaction, cobalt behaves like a transition element.
Suggest by means of an ionic equation, an explanation for this observation. [2]

[Total: 21]

Section B

Answer **one** question from this section.

4 (a) The kinetics of the acid–catalysed hydrolysis of ethyl ethanoate may be investigated by analysing samples of the reaction mixture at different times.

$$CH_3CO_2CH_2CH_3 + H_2O \overset{H^+ \text{ (catalyst)}}{\rightleftharpoons} CH_3CO_2H + CH_3CH_2OH$$

In one such experiment, the reaction mixture was prepared by mixing solutions of ethyl ethanoate and hydrochloric acid. The concentration of hydrochloric acid, which serves as the catalyst, can be assumed to stay constant throughout the reaction.

At different times, 10.0 cm^3 portions of the reaction mixture were pipetted, quenched and titrated with 0.200 mol dm^{-3} NaOH(aq).

After all necessary samples have been drawn, the remaining reaction mixture is then heated for ½ h to ensure complete reaction. The volume of NaOH required for titrating a 10.0 cm^3 sample of the resulting solution is 30.00 cm^3.

The following experimental data were obtained:

Time / min	Volume of NaOH required for titration, V / cm^3	30.00 – V / cm^3
0	20.00	10.00
10	24.40	5.60
20	26.90	3.10
30	28.20	1.80
40	29.00	1.00
50	29.40	0.60

(i) State how each of the quantities, V and (30 – V), is related to the concentration of the components of the reaction mixture at any point in time. [1]

(ii) Hence, choose appropriate data from the above table to plot a graph that will allow you to determine the order with respect to ethyl ethanoate. [2]

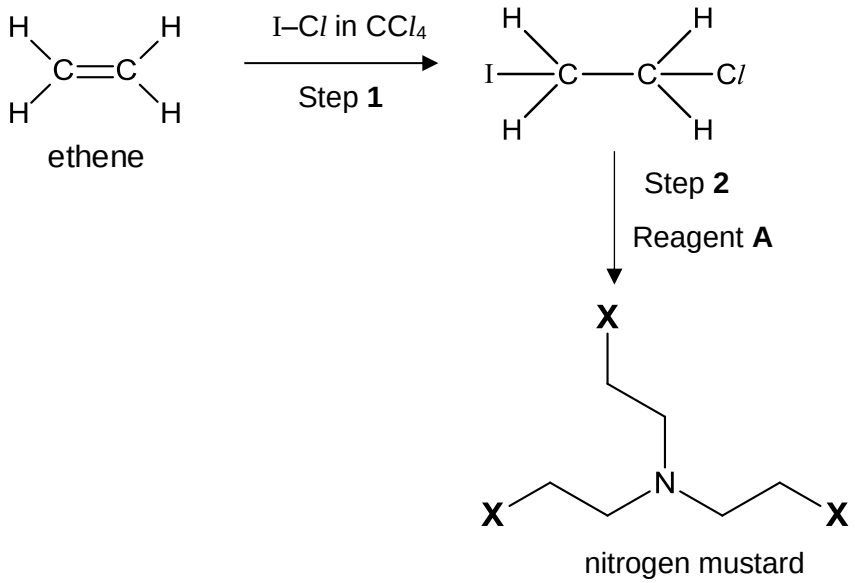
(iii) Deduce the order with respect to ethyl ethanoate, justifying your answer by showing construction lines clearly on your graph. [2]

(iv) Hydrolysis of $CH_3CO_2CH_2CH_3$ can also be catalysed by esterase, an enzyme found in the liver.

Sketch a graph to show how, for a constant [esterase], the rate of hydrolysis varies with [$CH_3CO_2CH_2CH_3$] and explain the shape of the graph. [2]

(b) Nitrogen mustard gas is commonly used in chemotherapy.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:

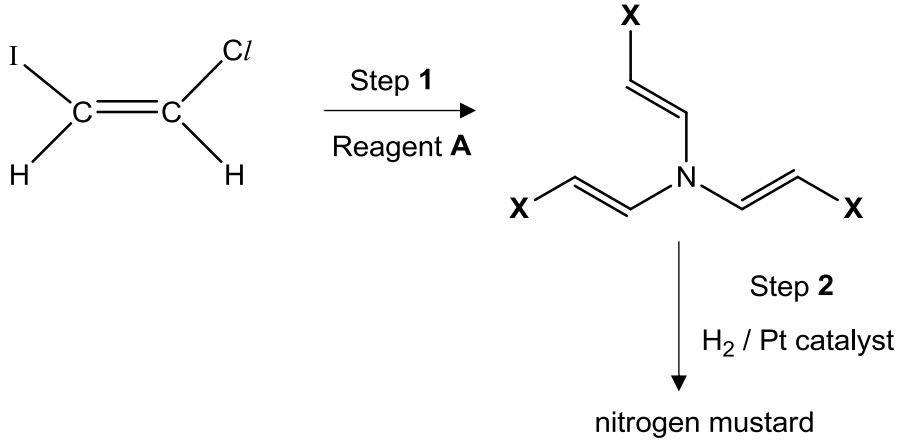


X in nitrogen mustard could be either C*l* or I.

(i) Suggest the identity of reagent **A** and the conditions necessary for an optimal yield in Step **2**. [1]

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [2]

(iii) Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used for the first step:



Explain why this method of synthesis is likely to fail. [2]

(c) Compound **K** is a solid with the formula, $C_4H_9NO_3$. It dissolves in water to form a solution with high electrical conductivity. When **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine. When lithium aluminium hydride was added to **L**, **M**, $C_4H_{10}O_2$, was produced.
M can also be obtained from the oxidation of **N**, C_4H_8 by cold alkaline potassium manganate(VII).

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described. [8]

[Total: 20]

5 (a) The reaction between bromide and bromate(V) ions in acid solution is represented as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The reaction between Br^- and BrO_3^- is relatively fast, with Br_2 produced almost immediately after the reactants are mixed.

To measure the initial rate of the reaction, aqueous Br^- is added to acidified BrO_3^- solution containing a small amount of compound **A** and methyl orange indicator. The initial colour of the methyl orange is pink as the solution is acidic. After some time, the pink colour disappears due to the bleaching action of Br_2 as shown:

$$Br_2 + \underset{\text{pink}}{\text{methyl orange (acid form)}} \rightarrow \underset{\text{colourless}}{\text{bleached methyl orange}} + 2Br^-$$

The time taken for the pink colour to disappear is an indication of the initial rate.

(i) Compound **A** is added to delay the disappearance of the pink colour, which would otherwise take place too quickly for effective measurement of time.

Given that compound **A** is an acidic organic compound containing only **one** functional group, suggest a suitable identity for compound **A**. [1]

(ii) Explain, with the aid of an equation, why the compound mentioned in your answer to **(i)** would be effective in delaying the disappearance of the pink colour. [2]

(iii) To find the order of reaction with respect to H^+, a total of five experiments are conducted.

In all the experiments, 10.0 cm^3 of KBr(aq), 10.0 cm^3 of $KBrO_3$(aq), 5.0 cm^3 of Compound **A** solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and other experimental data for each experiment are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	30.0	900	10.0	0.100
2	25.0	625	14.4	0.069
3	20.0	400	22.5	0.044
4	15.0	225	40.0	0.025
5	10.0	100	90.0	0.011

Choose appropriate data from the table above to plot a graph that will enable you to determine the order of reaction with respect to H^+. [2]

(iv) State, with justification, the order of reaction with respect to H^+. [1]

(b) Champagne is an example of *sparkling wine*, a term referring to wine with significant levels of carbon dioxide in it, making it fizzy. In the traditional method of production, wine is allowed to undergo a natural fermentation after bottling, which involves conversion of the malic acid present into lactic acid:

$$\underset{\text{malic acid}}{HO_2CCH_2CH(OH)CO_2H} \rightarrow \underset{\text{lactic acid}}{CH_3CH(OH)CO_2H} + CO_2$$

(i) A bottle typically has a total capacity of 1.5 dm^3 and contains 1.3 dm^3 of wine with a malic acid concentration of 0.05 mol dm^{-3}.

By means of the ideal gas equation, calculate the pressure exerted inside the air gap of the bottle by the carbon dioxide produced when all the malic acid present undergoes fermentation.

Assume that the temperature inside the bottle is 25°C. [2]

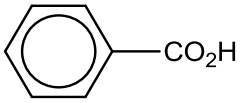
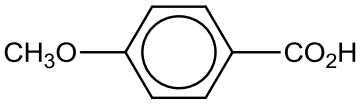
(ii) In fact, the pressure inside the bottle is much less under these conditions. Suggest why the actual pressure differs from the value calculated in **(i)**. [1]

(iii) Besides malic acid, many other organic acids also play an important role in our everyday life. For instance, acrylic acid, with the structure $CH_2=CHCO_2H$, is the starting material for the production of many plastics and adhesives industrially.

State the reagents and conditions that can be used to synthesize acrylic acid from lactic acid in the laboratory. [1]

(iv) Another example of an organic acid is benzoic acid which is commonly used as a food preservative.

The K_a values of benzoic acid and its substituted derivative, 4–methoxybenzoic acid are given below:

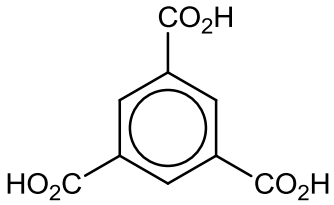
Compound	**K_a / mol dm^{-3}**
 Benzoic acid	6.5×10^{-5}
 4–methoxybenzoic acid	3.5×10^{-5}

Explain the difference in the K_a values of the two acids. [2]

(c) Compound **P** is an aromatic compound with molecular formula $C_{12}H_{15}O_3Cl$. It reacts with exactly 2 mol of PCl_5 to form an organic product **Q**. **P** also gives a brick–red precipitate with Fehling's solution.

Upon heating **P** with alcoholic NaOH, only one of the products formed, **R**, has the molecular formula $C_{12}H_{14}O_3$.

On oxidation with hot acidified potassium manganate(VII) solution, **R** gives **S**, $C_2H_4O_2$, and the following compound:



Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [8]

[Total: 20]