2.2.2 Expected answers, marking scheme and observations and conclusions related to paper II

Ú The observations related to the answers for Paper II have been presented by the graphs 2, 3, 4.1, 4.2 and 4.3.

PART A — STRUCTURED ESSAY

*Answer **all four** questions on this paper itself. (Each question carries **10 marks.**)*

1. (*a*) Answer the questions given below in the space provided.

(i) Of the three isolated ions Fe^{3+}, Cr^{3+} and Co^{2+}, which one has **three** unpaired electrons? .....

(ii) Of the three 3*d* block elements Ti, V and Cr, which one has a maximum of **five** electrons that can participate in bonding? .....

(iii) Of the three elements C, N and Si, which one has the **lowest** electronegativity? .....

(iv) Of the three elements Na, Mg and Al, which one has the **highest** first ionization energy? .....

(v) Of the three isoelectronic anions N^{3-}, O^{2-} and F^{-}, which one has the **largest** ionic radius? .....

(vi) Of the three cations Na^{+}, Ca^{2+} and Al^{3+}, which one has the **smallest** ionic radius? .....

(3.0 *marks*

(*b*) Peroxonitrous acid (HOONO) is formed as an intermediate during the oxidation of acidified aqueous solutions of nitrites to nitrates using H_2O_2. Answer the Parts (i) to (vii) which are based on the peroxonitrite ion, $[OONO]^{-}$. Its skeleton is given below:

O—O—N—O

(i) Draw the **most** acceptable Lewis structure for this ion.

(ii) Draw resonance structures for this ion. Giving reason/s comment on their relative stabilities.

(iii) Deduce the shapes around the following atoms using the VSEPR theory.

I. **N** .....

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II. **O** attached to both **N** and **O**

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(iv) State the following:

I. electron pair geometry (arrangement of electron pairs) around the atoms

II. hybridization of the atoms

given in the table below.

		N	**O** attached to both **N** and **O**
I.	electron pair geometry		
II.	hybridization		

(v) Sketch the shape of the Lewis structure drawn in Part (i) above showing approximate bond angles.

(vi) Identify the atomic/hybrid orbitals involved in the formation of the following bonds in the Lewis structure drawn in Part (i) above. Oxygen atoms are labelled 1, 2 and 3 as given below:

$O^1—O^2—N—O^3$

I. O^1 and O^2 .....

II. O^2 and N .....

(vii) Give an isomer of peroxonitrous acid.

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(*c*) (i) Select **two** polar species from the list given below.

H_2CO (formaldehyde), SF_6, COS, ICl_4^-, $SiCl_4$ ..... and .....

(ii) State the type(s) of intermolecular forces that exist between the molecules in each of the following pairs.

I. HBr(g) and H_2S(g) .....

II. Cl_2(g) and CCl_4(g) .....

III. CH_3OH(l) and H_2O(l) .....

2. (*a*) (i) Give the formulae of the oxides with the highest oxidation state formed by the elements in the third period. Comment on their acidic / amphoteric / basic nature using the following list.

very strongly acidic, strongly acidic, weakly acidic, very weakly acidic, weakly basic, basic, strongly basic, amphoteric, neutral

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(ii) State how the electronegativity, atomic radius and first ionization energy vary from left to right across the third period.

electronegativity .....

atomic radius .....

first ionization energy .....

(iii) Give the general reaction to show the thermal decomposition of Group II nitrates using **M** as the metal.

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(iv) Arrange the Group II nitrates in the order of **increasing** thermal stability (use the notation <). Explain your answer based on polarization of ions.

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(*b*) The following questions are based on the transition metal, Mn and its compounds.

(i) Give the electronic configuration of Mn.

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(ii) State the common oxidation states of Mn.

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(iii) Give the chemical formulae of the oxides formed by Mn in these common oxidation states. Indicate whether each of these oxides is acidic, amphoteric or basic.

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(iv) Give the IUPAC name of $KMnO_4$.

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(v) Mn has the lowest melting point and lowest boiling point among the 3*d* transition elements. Explain why this is so.

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(vi) What would you expect to observe when a dilute ammonia solution is added to an aqueous solution of Mn^{2+} and then left exposed to the air?

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(vii) An aqueous solution of $KMnO_4$ turns green upon addition of conc. KOH. On diluting the green solution with water or acid, a purple solution and a blackish brown precipitate are obtained. Write balanced chemical equations to explain these observations.

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(viii) Give **one** important use of each of the following.

I. $KMnO_4$ (other than as an oxidizing agent)

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II. Mn metal

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(ix) Give half reactions to show how $KMnO_4$ behaves as an oxidizing agent in acidic and basic media.

acidic medium : .....

basic medium : .....

(x) Indicate **two** problems you may expect when using $KMnO_4$ as an oxidizing agent.

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3. (*a*) At pressure P and temperature T, a mixture of $O_2(g)$ and $O_3(g)$ exists at equilibrium in a closed rigid container of volume V.

(i) Express the density of the gas mixture (d), in terms of n_1, n_2, M_1, M_2 and V, where

n_1 = number of moles of O_2 $\quad$ n_2 = number of moles of O_3

M_1 = molar mass of O_2 $\quad$ M_2 = molar mass of O_3

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(ii) Express the above relationship in terms of X_1, X_2, M_1, M_2, V and n, where,

X_1 = mole fraction of O_2 $\quad$ X_2 = mole fraction of O_3

n = total number of moles of both gases

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(iii) Hence show that, $X_1 = \left(3 - \frac{dRT}{16P}\right)$,

where R is the universal gas constant. (relative atomic mass of O = 16)

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(iv) State the assumption/s you made in the above steps.

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(*b*) (i) Consider the following standard reduction potentials:

$$E^{\ominus}\left[Br_2(l)/Br^-(aq)\right] = 1.07\ V$$

$$E^{\ominus}\left[I_2(s)/I^-(aq)\right] = 0.54\ V$$

I. What reaction would you expect to take place when liquid bromine is added to an aqueous solution of 1.0 mol dm^{-3} KI?

II. Write the colour changes you would expect in the above experiment.

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(ii) Consider the following electrochemical reaction:

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

I. Write the cathodic reaction of the Galvanic cell consistent with the above reaction.

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II. Write the conventional notation for representing the above cell, which includes a salt bridge.

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III. Does the entropy increase, decrease or remain constant when the above cell reaction proceeds?

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Briefly explain your answer.

IV. What should be the relationship between enthalpy change (ΔH) and entropy change (ΔS) for the above reaction to be spontaneous at temperature T?

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4. (*a*) **A**, **B** and **C** are three isomeric hydrocarbons with the molecular formula C_7H_{14}. Compound **A** shows geometrical isomerism while compounds **B** and **C** do not. All three compounds exhibit optical isomerism. On catalytic hydrogenation, all three compounds yield compound **D** (C_7H_{16}). Compound **D** also shows optical isomerism. Give the structures of **A**, **B**, **C** and **D**. (It is **not** necessary to draw the stereoisomeric forms.)

A	**B**	**C**	**D**

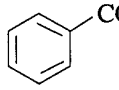
On treatment with bromine followed by dehydrobromination with alcoholic KOH, **A** forms two compounds **E** and **F**, while **B** forms compound **G**, and **C** forms compound **H**. All four compounds **E**, **F**, **G** and **H** have the same molecular formula of C_7H_{12}. Compound **E** shows geometrical isomerism, while **F**, **G** and **H** do not. Give the structures of **E**, **F**, **G** and **H**.

E	**F**	**G**	**H**

Give **one** chemical test to distinguish between **F** and **G**.

(*b*) The reactant and reagent in each of the reactions 1 - 5 are given in the table below.

For each reaction, write the reaction type [Nucleophilic addition (A_N), Electrophilic addition (A_E), Nucleophilic substitution (S_N), Electrophilic substitution (S_E), Elimination (E)] and the major product in the relevant boxes.

	Reactant	Reagent	Reaction type	Major product
1		conc. HNO_3/conc. H_2SO_4		
2	$CH_3CH{=}CH_2$	HBr		
3	CH_3CHO	H^+/KCN		
4	$CH_3CH_2CHBrCH_3$	alcoholic KOH		
5	CH_3CH_2I	aq. KCN		

PART B — ESSAY

Answer two questions only. (*Each question carries* **15** ***marks.***)

Universal gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$, Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$

5. (*a*) Consider the following equilibria exhibited by gas **A**, contained in a closed rigid vessel.

(i) At a temperature T (in Kelvin), **A** undergoes the reaction,

$$2A(g) \rightleftharpoons B(g) \qquad (1)$$

After equilibrium is reached, it has been found that 40% of the initial amount of **A** has been converted to **B**, and that the total pressure of the system is $4 \times 10^5\ N\ m^{-2}$. Calculate the equilibrium constant K_p at temperature T for this equilibrium.

(ii) When the temperature of the system is increased to $2T$ (in Kelvin), in addition to the above reaction, **A** undergoes another reaction as shown below.

$$2A(g) \rightleftharpoons C(g) + D(g) \qquad (2)$$

After the system reaches equilibrium at $2T$, it has been found that 20% of the initial amount of **A** has been converted to **C** and **D**, and that 20% of the initial amount of **A** remains.

I. Calculate separately, the number of moles of **A**, **B**, **C** and **D** at this equilibrium if the initial number of moles of **A** was a.

II. Calculate the equilibrium constant K_p for equilibrium (2) at $2T$.

III. Calculate the equilibrium constant K_p for equilibrium (1) at $2T$.

(8.5 ***marks)***

(*b*) A student used the following procedure to determine the distribution coefficient of acetic acid between water and *n*-butanol phases at a constant temperature.
Different volumes of *n*-butanol, 1.0 mol dm^{-3} aqueous acetic acid and water were added to numbered reagent bottles 1 and 2 as shown in the table below.

Reagent bottle	Volume of *n*-butanol/cm^3	Volume of aqueous acetic acid/cm^3	Volume of water/cm^3
1	20.00	40.00	0.00
2	20.00	30.00	10.00

The bottles were shaken well and then, each system was allowed to reach equilibrium. After the layers were separated, 10.00 cm^3 each from the aqueous layer and the butanol layer were withdrawn and titrated with a standard NaOH solution of concentration 0.500 mol dm^{-3}. The reading obtained at the end point on titrating the aqueous layer taken from bottle (1) is given in the table below.

Reagent bottle	Volume of NaOH required for 10.00 cm^3 of aqueous layer / cm^3	Volume of NaOH required for 10.00 cm^3 of *n*-butanol layer / cm^3
1	16.00	x
2	y	z

(i) Calculate the end point x that would have been obtained for the *n*-butanol layer of bottle (1).

(ii) Calculate the distribution coefficient of acetic acid between water and *n*-butanol using the system in bottle (1).

(iii) Calculate the volumes y and z that would have been obtained for the system in bottle (2).

(iv) State the assumptions you made in the above calculations.

(v) Name an indicator that could be used for these titrations.

(vi) State whether the pH of the aqueous layer would change during the period when the bottles were being shaken. Explain your answer.

(6.5 ***marks)***

6. (*a*) (i) Derive an expression for the pH of an aqueous CH_3COOH solution of concentration c mol dm^{-3}, in terms of the acid dissociation constant K_a and c.

(ii) Write the assumptions you made in the above derivation.

(iii) A 100.0 cm^3 sample of the above acid solution was diluted to 1.00 dm^3 by adding distilled water. Write an expression for the pH of this acid solution with the help of the expression obtained in Part (i) above.

(iv) Using the answers obtained in Parts (i) and (iii) above, show that the difference in pH values of the two acid solutions is 0.5 pH units.

(v) Calculate the pH of the solution prepared by mixing 220.0 cm^3 of the acid solution in Part (i) above and 20.0 cm^3 of NaOH solution of concentration c mol dm^{-3}.

(7.5 *marks*)

(*b*) (i) The solubility product of $BaSO_4$ is 1.0×10^{-10} mol^2 dm^{-6} at 25 °C. Calculate the Ba^{2+} concentration in a saturated aqueous solution of $BaSO_4$ at this temperature.

(ii) Calculate the mass of pure solid Na_2SO_4 that should be added to 1.0 dm^3 of the solution in Part (i) above to halve the concentration of Ba^{2+} at 25 °C. (O = 16, Na = 23, S = 32)

State assumptions, if any, you made in this calculation.

(iii) The solubility product of $PbSO_4$ is 1.6×10^{-8} mol^2 dm^{-6} at 25 °C. Calculate the concentrations of Ba^{2+} and Pb^{2+} separately in an aqueous solution saturated with both $BaSO_4$ and $PbSO_4$ at this temperature.

(7.5 *marks*)

7. (*a*) Grignard reagents are prepared by reacting alkyl or aryl halides with Mg in dry ether. However, the Grignard reagent given below **cannot** be prepared using the following reaction. Explain why it cannot be.

$$HOCH_2CH_2CH_2Br \xrightarrow{Mg\,/\,dry\ ether} HOCH_2CH_2CH_2MgBr$$

(2.0 *marks*)

(*b*) Provide a mechanism for chlorination of benzene in the presence of $FeCl_3$.

(3.0 *marks*)

(*c*) Using **only** the chemicals given in the list, show how you would carry out the following conversion.

$$(CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C-\overset{\overset{O}{\|}}{C}-OC(CH_3)_3$$

List of chemicals
conc. H_2SO_4, dil. H_2SO_4, PCl_5,
Mg, Ether, HCHO, $K_2Cr_2O_7$

(5.0 *marks*)

(*d*) Show how you would synthesize the following compound using propanal as the **only** organic starting material.

$$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—NH—CH_2—CH_2—CH_3$$

(5.0 *marks*)

PART C — ESSAY

*Answer **two** questions only. (Each question carries **15** **marks**.)*

8. (*a*) (i) A solid mixture contains only **two** of the following:

$Ba(NO_3)_2$ $Zn(NO_3)_2$ $AgNO_3$ $CaCO_3$ NaOH

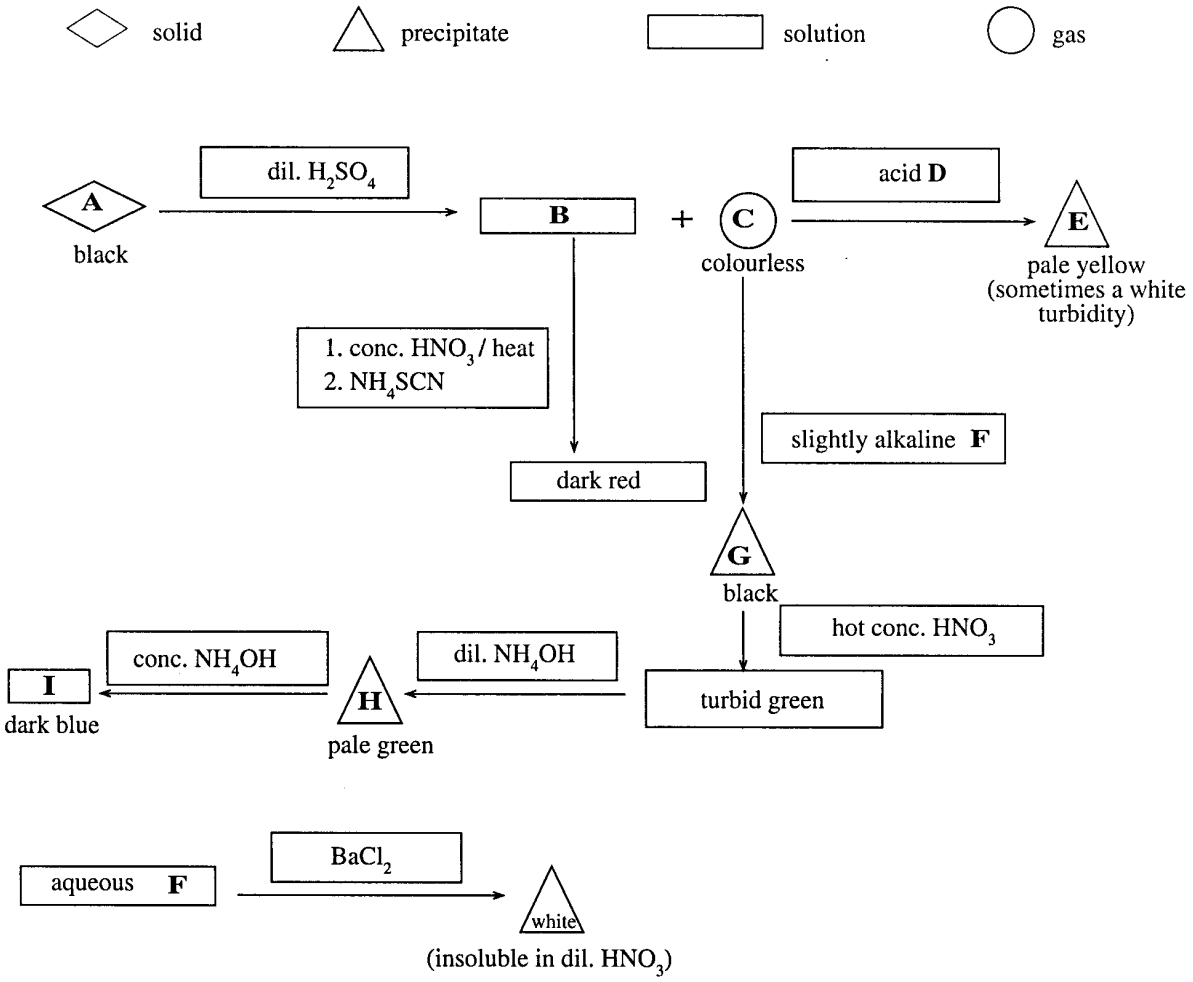
Tests carried out along with the observations to identify them are as follows:

Test	Observation
1. Water was added to the mixture.	The mixture dissolved giving a clear solution.
2. A few drops of phenolphthalein were added to a portion of the aqueous solution obtained from 1 above.	The clear colourless solution turned pink.
3. Dilute HCl was gradually added to another portion of the aqueous solution obtained from 1 above.	A white precipitate formed. It dissolved on further addition of the acid.

Giving reasons, identify the **two** compounds present in the mixture.

(ii) Write the **formulae** of the compounds **A – I** given in the diagram below. (**Balanced chemical equations and reasons are not required.**)

The following symbols are used to represent solids, precipitates, solutions and gases.



(7.0 *marks*)

(*b*) (i) A 3*d* block element **M** forms an ion $\mathbf{M}^{n+}$. This ion can be oxidized by MnO_4^- in a dil. H_2SO_4 medium to give the $\mathbf{MO}_2^+$ ion. In an experiment, 30.0 cm^3 of 0.100 mol dm^{-3} $KMnO_4$ was required to oxidize 5.00×10^{-3} mol of $\mathbf{M}^{n+}$ to $\mathbf{MO}_2^+$. Use this data to calculate the value of *n*.

(ii) The following procedures **I** and **II** were used to determine the percentage of Cu in the Cu–containing alloy **Z**.

Procedures:

I. A sample of 2.80 g of the alloy **Z** was dissolved in 500.0 cm^3 of dil. H_2SO_4. Addition of excess KI to 25.0 cm^3 of this solution produced the white precipitate CuI, and I_2 as the only products. The liberated I_2 was titrated with $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ solution required was 30.0 cm^3.

II. To 25.0 cm^3 of $K_2Cr_2O_7$ solution, prepared by dissolving 1.18 g in 500.0 cm^3 of distilled water, 20 cm^3 of dil. H_2SO_4 and excess KI were added. The liberated I_2 was titrated with the $Na_2S_2O_3$ solution used in procedure I with starch as the indicator. The volume of $Na_2S_2O_3$ required was 24.0 cm^3.

1. Give balanced chemical equations for the reactions taking place in procedures I and II.
2. Determine the percentage of Cu in alloy **Z**.
3. Indicate the colour changes you would observe at the end points of the titrations in procedures I and II.

(O = 16, K = 39, Cr = 52, Cu = 63.5)

(8.0 *marks*)

9. (*a*) (i) Answer the following questions which are based on the manufacture of sodium using Down's cell.

I. Name the starting material used in the manufacture of sodium.

II. A substance is added to lower the melting point of the starting material before electrolysis. Identify this substance.

III. State the approximate temperature at which the electrolytic cell operates.

IV. Identify the anode and cathode used in the Down's cell.

V. Give the balanced chemical equations for the half cell reactions that take place at the anode and cathode.

VI Why is it necessary to separate the anode from the cathode by a steel gauze?

VII Apart from separating the anode from the cathode, state an important precaution that must be taken during the manufacturing process.

VIII. State whether the following statement is true or false.
"A small current and a large voltage are used in the manufacture of sodium."

IX. Give the physical state in which sodium is obtained by this method.

X Give **two** uses of sodium and **one** use of the product obtained at the anode.

(ii) **Briefly** describe the four steps involved in the manufacture of soap.

(7.5 *marks*)

(*b*) (i) Consider the statements I to V given below:

I. Natural processes that support life on earth

II. Unfavourable processes that occur due to the interaction of solar radiation with atmospheric gases

III. Processes that may introduce harmful gases leading to environmental problems

IV. Environmental damage due to some agricultural practices

V. Environmental damage due to acid rain

Write the **three most suitable** choices from the list given below for each of the statements from I to V. (Write the statement numbers I to V on your answer script and the notation **A**, **B**, **C** . . . *etc.* of the three relevants choices in front of each statement number. You may use one choice more than once.)

A - photosynthesis	B - corrosion of metal or limestone structures
C - global warming	D - absorption of UV radiation by ozone layer
E - volcanic eruptions	F - dissolution of heavy metal salts in sediments
G - greenhouse effect	H - ozone layer depletion
I - coral reef distortion	J - fossil fuel combustion
K - photochemical smog	L - pollution of ground water
M - metal refining	N - rapid growth of algae in reservoirs (Eutrophication)

(ii) Contribution to acid rain from a coal power plant can be reduced by controlling the emissions of acidic gases. Suggest a suitable method to control the acidic emissions using locally available raw materials. Write balanced chemical equations to support your answer.

(iii) The acidic gases NO and SO_2 released to the atmosphere through numerous processes result in the formation of the acids HNO_3 and H_2SO_4 respectively, in the atmosphere. Write balanced chemical equations for the formation of these acids.

(iv) Consider the following compounds:

$CH_3(CH_2)_4CH_3$ $CFCl_3$ CF_2Cl_2 N_2 NO

Of these, identify the compounds that contribute to,

I. global warming

II. ozone layer depletion

(v) In the ozone layer, ozone is formed and destroyed naturally. Ozone is also lost catalytically on inclusion of radical forming compounds to the ozone layer region. Write balanced chemical equations for the following processes in the ozone layer:

I. Natural formation and destruction of ozone

II. Formation of radicals

III. Catalytic destruction of ozone

(7.5 *marks*)

10. (*a*) Give **four** important differences between fluorine chemistry and the chemistry of the rest of the halogens.

(2.5 *marks*)

(*b*) Sodium sulphite (Na_2SO_3) is sometimes added to sausage meat as a preservative. The following procedure was used to determine the amount of the preservative, Na_2SO_3 present in a sample of meat.

Step 1 : One kilogram (1.00 kg) of meat was boiled with an excess of dil. HCl.

Step 2 : The gas released was completely absorbed in an excess of 0.050 mol dm^{-3} I_2 solution. The volume of I_2 solution used was 40.0 cm^3.

Step 3 : The resulting solution from Step 2 was titrated with a 0.100 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The volume of the $Na_2S_2O_3$ solution required was 26.0 cm^3.

(O = 16, Na = 23, S = 32)

(i) Write balanced chemical equations for the **three** steps involved in the above procedure.

(ii) Calculate, in moles, the amount of Na_2SO_3 present in 1.00 kg of meat sample.

(iii) The amount of preservative present in meat samples is usually expressed as parts per million (ppm). (Hence, 1 ppm = 1 g of Na_2SO_3 in 10^6 g of meat).

Express in ppm, the amount of Na_2SO_3 determined in Part (ii) above.

(iv) Indicate the colour change at the end point of the titration.

(5.0 *marks*)

(*c*) A student conducted three experiments to investigate the kinetics of the following reaction at a constant temperature.

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

(i) In the first experiment, 500 cm^3 of 0.160 mol dm^{-3} solution of $I^-(aq)$ and 500 cm^3 of 0.040 mol dm^{-3} solution of $S_2O_8^{2-}(aq)$ were mixed to allow the above reaction to proceed. It was found that 2.8×10^{-5} moles of I_2 have been formed at the end of the initial 5 second period.

I. Calculate the rate of production of $I_2(aq)$.

II. Calculate the rate of consumption of $I^-(aq)$.

III. Calculate the rate of consumption of $S_2O_8^{2-}(aq)$.

(ii) In the second experiment, 500 cm^3 of 0.320 mol dm^{-3} solution of $I^-(aq)$ and 500 cm^3 of 0.040 mol dm^{-3} solution of $S_2O_8^{2-}(aq)$ were mixed. The rate of the reaction was then determined to be 1.12×10^{-5} mol dm^{-3} s^{-1}.

Calculate the order of the reaction with respect to $I^-(aq)$ using the information given in Parts (i) and (ii).

(iii) The order of the reaction with respect to $S_2O_8^{2-}(aq)$ was determined to be 1 in the last experiment conducted by changing the concentration of $S_2O_8^{2-}(aq)$.

I. Write the rate equation for this reaction.

II. Calculate the rate of the reaction when the volumes of both solutions in Part (ii) are doubled by adding distilled water and the solutions are then mixed.

(iv) I. What is meant by the half-life of a first order reaction?

II. The half-life of the above reaction when the concentration of $I^-(aq)$ is kept constant, is independent of the initial concentration of $S_2O_8^{2-}(aq)$. Explain this statement with the help of a graphical representation.

(7.5 *marks*)