Question 1

This question is about an analysis of brass.

Brass is an alloy which contains copper. When brass is reacted with concentrated nitric(V) acid a solution containing Cu^{2+} ions is produced. If this solution is reacted with aqueous potassium iodide, copper(I) iodide is precipitated and iodine is produced.

i) Write the equation for the reaction between Cu^{2+} ions and potassium iodide solution.

The iodine produced may be estimated by titration with sodium thiosulfate solution ($Na_2S_2O_3$ (aq)).

ii) Write a balanced equation for this reaction.

2.80 g of brass were reacted with a minimum quantity of concentrated nitric(V) acid and the resulting solution made up to 250 cm^3 with water.
25.0 cm^3 samples of the mixture are treated with sodium carbonate to neutralize the excess acid, the resulting precipitate dissolved in a minimum volume of ethanoic acid and then excess potassium iodide solution added. The resulting samples were titrated with 0.100 mol dm^{-3} sodium thiosulfate solution to estimate the iodine present. The average titre was 29.8 cm^3.

iii) Write an equation for the neutralization of the excess nitric acid.

iv) How many moles of copper are in the original solution?

v) What is the percentage of copper in the brass?

Question 2

This question is about the chemistry of air bags.

One method used to inflate air bags in cars is to use nitrogen produced chemically from the decomposition of sodium azide:

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g) \qquad (1)$$

The sodium formed reacts with potassium nitrate to give more nitrogen:

$$10Na + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g) \qquad (2)$$

i) In what ratio (by mass) must the sodium azide and potassium nitrate be mixed in order that no metallic sodium remains after the reaction?

ii) Calculate the total mass of the solid mixture needed to inflate a 60 dm^3 air bag at room temperature and atmospheric pressure.

The sodium azide is prepared commercially by the reaction between dinitrogen monoxide and sodium amide:

$$N_2O(g) + 2NaNH_2(s) \rightarrow NaN_3(s) + NaOH(s) + NH_3(g)$$

$\Delta H_r = +55.8$ kJ mol^{-1}

iii) Draw 'dot and cross' diagrams for dinitrogen monoxide and the azide anion.

iv) Using the information below, calculate ΔH_r for reaction (1) above, the decomposition of sodium azide.

Compound	ΔH_f / kJ mol^{-1}
$N_2O(g)$	+82.0
$NaNH_2(s)$	–123.7
$NaOH(s)$	–425.2
$NH_3(g)$	-46.1

Room temperature = 298 K; atmospheric pressure = 101325 Pa;
R = 8.314 J K^{-1} mol^{-1}.
The molar volume of an ideal gas is 24.0 dm^3 at 298K.

Question 3

This question is about dragons.

Dragons are able to breathe fire because the parasitic bacteria that live in their intestines and lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx. There are several different species of dragons, each of which plays host to a different species of parasitic bacteria. The gas exhaled by the Black Dragon contains 25 mole % of hydrogen, the gas exhaled by the Red Dragon contains 30 mole % of methane (CH_4), and the gas exhaled by the Gold Dragon contains 20 mole % of hydrogen sulfide (H_2S). The gas exhaled by all species of dragon contains 15 mol % of oxygen. The average volume of a dragon's lungs is 5.1 m^3 and, due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is 15 $dm^3\ mol^{-1}$.

Enthalpies of combustion:

$\Delta H(H_2) = -240\ kJ\ mol^{-1}$

$\Delta H(CH_4) = -800\ kJ\ mol^{-1}$

$\Delta H(H_2S) = -520\ kJ\ mol^{-1}$

i) Calculate the total amount of gas in moles contained in a dragon's lungs.

ii) Calculate the amount of oxygen in moles contained in a dragon's lungs.

iii) Write equations for reactions that describe the burning of gas exhaled by the Black, Red, and Gold Dragons respectively.

iv) How many additional moles of oxygen are required for the complete combustion of one exhalation of the Black, Red, and Gold Dragons respectively?

v) Calculate the energy released during the combustion of one exhalation of the Black, Red, and Gold Dragons respectively.

Mole % is the percentage of each gas in a mixture expressed in moles.

Question 4

This question is about a double titration.

The use of two different indicators makes the quantitative analysis of certain mixtures possible by using an acid-base titration. The reaction between sodium hydroxide and hydrochloric acid occurs in a single stage, whereas that between sodium carbonate and hydrochloric acid occurs in two stages, with the hydrogencarbonate ion as the intermediate product.

Ionically:

$OH^- + H^+ \rightarrow H_2O$ (I)

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (2)

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$ (3)

With phenolphthalein as indicator, the end-point is seen at the completion of reactions (I) and (2). With methyl orange as indicator, the end-point is seen at the completion of all three reactions.

Mixture **A** contained solid sodium carbonate and sodium hydrogencarbonate, but mixture **B** contained sodium carbonate and sodium hydroxide.

One of these mixtures was dissolved in deionized water and the solution made up to 100.0 cm^3.

20.00 cm^3 samples were titrated using 0.200 mol dm^{-3} hydrochloric acid.

In the presence of phenolphthalein, 36.15 cm^3 of acid was used, but a second 20.00 cm^3 sample required 43.80 cm^3 of acid in the presence of methyl orange.

i) Which mixture, **A** or **B**, was analysed?

ii) Calculate the masses of both components in the original mixture used.

Question 5

This question is about organic mechanisms.

Acyl chlorides can be reduced to aldehydes or primary alcohols. Reduction of ethanoyl chloride takes place in four suggested steps. The attacking species is the AlH_4^- ion which, in effect, is a carrier of hydride ions, H^-.

Using the information above, write an equation for each of the steps below.

Use curly arrows to show any electron movement.

Step 1 Attack of the nucelophile H^- at the carbonyl carbon of ethanoyl chloride gives a tetrahedral intermediate.

Step 2 The tetrahedral intermediate formed in Step 1 decomposes to an aldehyde with the loss of chloride ion.

Step 3 Nucleophilic attack of the H^- ion at the carbonyl carbon of the aldehyde yields the ethoxide anion.

Step 4 The ethoxide anion reacts with aqueous acid to give ethanol.

Question 6

This question is about inorganic analysis.

C is a hydrated salt, **D**$C_2O_4.xH_2O$, where **D** is the cation. The lemon yellow-coloured solid dissolves in water to give a yellow solution. On addition of sodium hydroxide solution a green gelatinous precipitate, **E**, is formed. On warming, the yellow solution decolourises acidified potassium manganate(VII) solution, and if a drop of ammonium thiocyanate (NH_4SCN) solution is added to the resulting solution, a blood red colouration, **F**, is seen.

i) Identify **E** and **F** and hence suggest the identity of ion **D**.

C may be estimated by titration with potassium manganate(VII) after acidification with dilute sulfuric acid and warming to 70 °C. 1.75 g of **C** was dissolved in dilute sulfuric acid and made up to 250 cm^3. 25.00 cm^3 of this solution was titrated against 0.0200 mol dm^{-3} potassium manganate(VII) solution. 29.15 cm^3 of this solution was required for complete oxidation.

ii) Write three half equations for the redox reactions involved in the titration.

iii) Hence write a balanced equation for the reaction between **C** and acidified potassium manganate(VII).

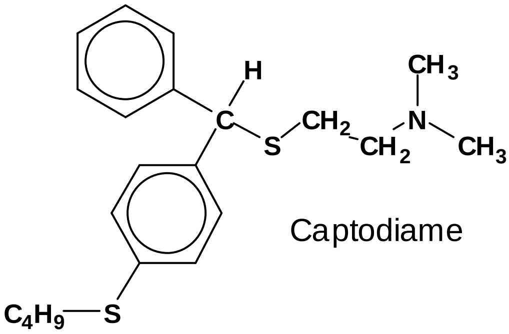
iv) Find the number of moles of water of crystallisation present in 1 mole of **C**.

v) Give the formula of **C**.

Question 7

This question is about organic synthesis

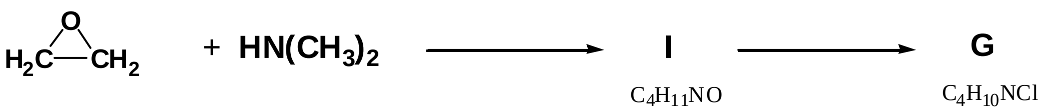
Captodiame (shown below) is a sedative and tranquilliser and is made by a multi-step synthesis, the final step of which is the combination of two compounds, **G** and **H**.



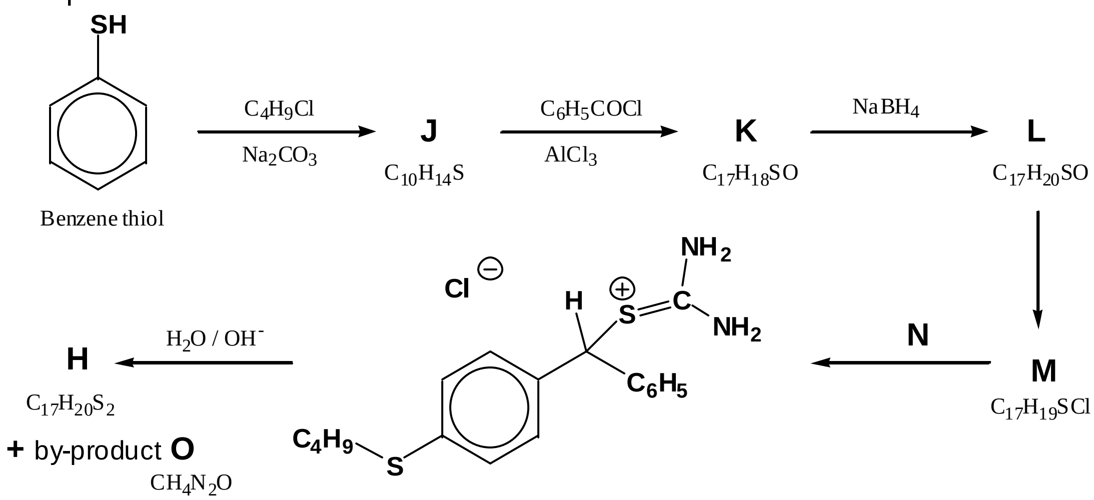
$$\mathbf{G} + \mathbf{H} \xrightarrow{\text{Base}} \text{Captodiame}$$

The syntheses for compounds **G** and **H** are outlined below:

Compound **G**:



Compound **H**:



Identify and draw the structures for the intermediate compounds **G** to **M**, the reagent **N**, and the by-product **O**.

Question 8

This question is about the kinetics of the oxidation of arsenic(III) acid.

Arsenic(III) acid may be oxidized to arsenic(V) acid using iodine (present as I_3^- ions).

i) Write a balanced equation for this reaction.

The rate law for this reaction may be written:

$$\text{rate} = k\,[I_3^-]^w [H_3AsO_3]^x [H^+]^y [I^-]^z$$

where *w*, *x*, *y* and *z* are the orders of reaction with respect to the concentrations of I_3^-, H_3AsO_3, H^+ and I^- respectively.

In a series of experiments to determine the orders of reaction, the concentrations of H_3AsO_3, H^+ and I^- were varied, but for each experiment the concentration of I_3^- ions was kept much less than the concentrations of the other species. This meant that as the I_3^- ions were used up, the concentrations of the other species effectively remained constant, allowing the rate law to be simplified to:

$$\text{rate} = c\,[I_3^-]^w$$

where the constant $c = k\,[H_3AsO_3]^x [H^+]^y [I^-]^z$

For each run, the time taken for $[I_3^-]$ to halve was noted.

$[I_3^-]$	Run 1	Run 2	Run 3	Run 4
	time / s			
0.246	0	0	0	0
0.123	16	7	31	248
0.0615	31	15	62	496
0.0308	47	23	93	744
0.0154	62	30	125	990

The concentrations of the different species (in mol dm^{-3}) for each run is given by the following table:

	Run 1	Run 2	Run 3	Run 4
$[I_3^-]$	0.246	0.246	0.246	0.246
$[H_3AsO_3]$	2.47	4.94	2.47	2.47
$[H^+]$	2.74	2.74	5.48	2.74
$[I^-]$	1.56	1.56	1.56	6.24

i) What is the order of the reaction with respect to $[I_3^-]$?

Explain your reasoning.

iii) What are the orders of reaction with respect to each of $[H_3AsO_3]$, $[H^+]$, and $[I^-]$?

iv) Calculate the value of the rate constant, *k*, including units.