Answer any **four** questions.

1 **(a)** Dinitrogen tetroxide N_2O_4 is one of the most important rocket propellants developed. N_2O_4 forms an equilibrium mixture with nitrogen dioxide NO_2.
NO_2 is favoured at higher temperatures, while at lower temperatures, N_2O_4 predominates.

(i) Draw dot-and-cross diagrams to show the bonding in the molecules of NO_2 and N_2O_4.

(ii) Suggest a value for the bond angle in each of the above two molecules.

[3]

(b) The chemistry of nitrogen oxides is very versatile.

(i) Given the following reactions and their standard enthalpy changes

Reaction 1 $NO(g) + NO_2(g) \rightarrow N_2O_3(g)$ $\Delta H^o{}_r = -39.8\ kJ\ mol^{-1}$
Reaction 2 $NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$ $\Delta H^o{}_r = -112.5\ kJ\ mol^{-1}$
Reaction 3 $2NO_2(g) \rightarrow N_2O_4(g)$ $\Delta H^o{}_r = -57.2\ kJ\ mol^{-1}$
Reaction 4 $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H^o{}_r = -114.2\ kJ\ mol^{-1}$
Reaction 5 $N_2O_5(s) \rightarrow N_2O_5(g)$ $\Delta H^o{}_r = +54.1\ kJ\ mol^{-1}$

Calculate the $\Delta H^o{}_r$ for
Reaction 6 $N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$

(ii) By considering the entropy and enthalpy change during reaction 5 and reaction 6, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude. Hence predict which reaction will be more spontaneous. Explain your reasoning.

[5]

(c) Compounds of elements in the second and third period of the Periodic Table show similar trends of periodicity. The Period II oxides are given as

Li_2O BeO B_2O_3 CO_2 N_2O_3/ N_2O_5

(i) The melting points of Li_2O and CO_2 are 1440°C and -79°C respectively. Explain for the differences in melting points.

(ii) BeO is an amphoteric oxide. Write equations for the reaction between BeO with an acid and with a base.

(iii) B_2O_3 is weakly acidic. The oxide acidity of the Group III elements decreases down the group. Suggest a possible reason for this trend.

[6]

(d) Halogens are also commonly found in many organic compounds, such as an aromatic compound **X** with the molecular formula of $C_8H_6Cl_2O$.

Given that one mole of **X** reacts with one mole of dimethylamine to form a neutral product **Y** and **Y** does not react with hot ethanolic ammonia, suggest the structures for compounds **X** and **Y**, explaining your reasoning.

Hence, discuss the reactivities of the two chlorine atoms in compound **X** towards substitution.

[6]

[Total: 20]

2 **(a)** Sodium chloride and silver chloride are two simple salts and their solubilities in water are being considered in this question.

Salt	ΔH_{soln}^{θ}/ kJ mol^{-1}	ΔS_{soln}^{θ}/ J mol^{-1}K^{-1}
NaC*l*	+3.6	+43.2
AgC*l*	+65.7	+34.3

(i) Use the values given in the table to calculate ΔG_{soln}^{θ} for each of the salts and hence deduce its solubility in water.

(ii) The solubility product, K_{sp}, of AgC*l* is related to ΔG_{soln}^{θ}(*AgCl*) by the following equation, $\Delta G_{soln}^{\theta} = -2.303RT \lg K_{sp}$ where R is 8.31 J mol^{-1}K^{-1} and T is the temperature in K.

Use the equation given above to calculate the value of K_{sp} of AgC*l* at 298K.

(iii) Explain how solubility of AgC*l* will change with increasing temperature?

[5]

(b) **(i)** Draw a fully labelled diagram of the electrochemical cell you would use to determine the standard electrode potential of the Ag^+(aq) I Ag(s) electrode system and show the direction of electron flow .

(ii) When aqueous sodium chloride is added to the Ag^+(aq)IAg(s) electrode system in the above electrochemical cell in **(b)(i)**, explain qualitatively how the E_{cell} will change as a result.

(iii) At 298K, the equation below relates the concentration of silver ions in solution with the electrode potential under non-standard conditions.

$$E = E^{\theta} + 0.060 \lg [Ag^+(aq)]$$ where

E= electrode potential of silver under non-standard conditions
E^{θ} = standard electrode potential of silver

The addition of excess aqueous sodium chloride, NaC*l*(aq), to the Ag^+(aq) I Ag(s) half-cell results in a chloride ion concentration of 2.1 mol dm^{-3}.

Using the value of the K_{sp} of AgC*l* calculated in **(a)(ii),** calculate the value of E, the electode potential of the Ag^+(aq)IAg(s) electrode system, after the addition of excess aqueous sodium chloride to the Ag^+(aq)IAg(s) half-cell.

[You may use this value of K_{sp} of AgC*l* = 2.00×10^{-10} for this calculation if you did not get an answer for **(a)(ii)**]

[7]

(c) Silver-oxide primary batteries account for over 20% of all primary battery sales in Japan. It is available in small sizes as button cells and are used in watches, cameras, heart pacemakers and hearing aids due to its very steady output.

A silver-oxide battery uses silver oxide as the positive electrode and zinc as the negative electrode and an alkaline electrolyte such as sodium hydroxide. The chemical reaction that takes place inside the battery is as follows:

$$Zn + Ag_2O \rightarrow ZnO + 2Ag \qquad E_{cell} = +1.6V$$

(i) Write the two half-equations that occur at the anode and cathode respectively.

(ii) Suggest a reason why this button battery is often used as stated in the question.

[3]

(d) Electrodes used in electrocardiography are disposable and many incorporate silver. The silver metal is deposited in a thin layer on a small plastic "button" and then some is converted to AgC*l*.

$$Ag(s) + Cl^-(aq) \rightleftharpoons AgCl\,(s) + e^-$$

The volume of silver used in plating one electrode is 1.5×10^{-2} cm^3. The density of silver metal is 10.5 g cm^{-3}.

(i) What is the mass of Ag used for plating one electrode?

(ii) If Ag is plated on the "button" from an Ag^+ solution with a current of 12.0 mA, how long does the plating take?

[3]

(e) Diammine silver (I) has the formula $[Ag(NH_3)_2]^+$ and is the active ion in Tollens' reagent. It produces a characteristic silver mirror on the side of the test-tube and this is used as the basis of the test for aldehydes.

Tollens' reagent also gives a positive result with methanoic acid which is fully oxidised to water and carbon dioxide.

Write two half-equations showing the reduction of Tollens' reagent and the oxidation of methanoic acid, followed by the balanced equation for the reaction between Tollens' reagent and methanoic acid.

[2]

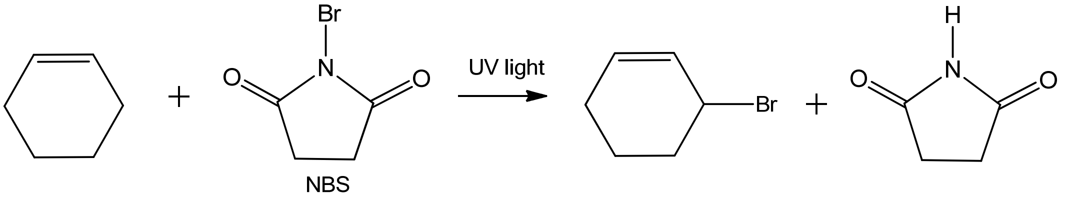
[Total: 20 marks]

3 This question is about halogens and halogenated organic compounds.

(a) One way to prepare brominated products is described as below:

Cyclohexene reacts with N-bromosuccinimide (NBS) in the presence of UV light to give 3-bromocyclohexene resulting from the substitution of hydrogen by bromine at the allylic position – the position next to the double bond.

The overall equation is shown below.



The allylic bromination with NBS works in a similar manner as free radical substitution. The steps in the mechanism are shown below.

Step 1:
Homolytic cleavage of the N-Br bond of NBS generates a Br radical.

Step 2:
The Br radical abstracts an allylic hydrogen from the cyclohexene to form an allylic radical.

Step 3:
The HBr formed reacts with NBS to produce a Br_2 molecule.

Step 4:
This Br_2 molecule reacts with the allylic radical formed in step 2, regenerating a new bromine radical that can begin the cycle again.

(i) Describe the mechanism, using curly arrows to represent the flow of electrons, of the reaction between cyclohexene and NBS. (You need not show arrows for step 3)

(ii) Suggest why NBS is used as the bromine source instead of adding Br_2 directly?

(iii) The enthalpy change of reaction in step 2 is -6 kJ mol^{-1}. Using the Data Booklet, calculate the bond energy of the allylic C-H bond.

(iv) By quoting relevant information from the Data Booklet, and using your answer from part (iii), explain why bromination using NBS occurs exclusively at an allylic position rather than any position in cyclohexene?

Your answer should also include the discussion of the stability of the allylic radical.

[7]

(b) Alkyl halides are used in the synthesis of Gilman reagents, which are very useful in organic synthesis because they make it possible to prepare larger molecules from smaller ones.

In the preparation of Gilman reagent, the following two steps take place:

$$RBr + 2\,Li \rightarrow RLi + LiBr$$

$$2\,RLi + CuI \rightarrow \underset{\text{Gilman reagent}}{R_2Cu^-Li^+} + LiI$$

This Gilman reagent can be used to synthesize bigger molecules from alkyl halides. For example, lithium dimethylcopper reacts with 1-iodododecane to give undecane as below:

$$(CH_3)_2CuLi + CH_3(CH_2)_8CH_2I \rightarrow CH_3(CH_2)_8CH_2CH_3 + LiI + (CH_3)Cu$$

The above reaction is called organometallic coupling reaction.

Similarly, ketones can be formed in organometallic coupling reactions between suitable Gilman reagents and acid chlorides.

Hence, suggest a suitable Gilman reagent and an acid chloride that can be used to synthesize 1-phenylpropan-1-one.

[2]

(c) It is known that halogens can form many compounds with different oxidation states under different conditions.

(i) With the aid of balanced equations, explain how different chlorine containing products are obtained when chlorine reacts with sodium hydroxide under different conditions. State the type of reaction that happens clearly.

(ii) It is given that 0.240 mol of chlorine was made to react with NaOH at a certain temperature that allowed two different reactions to occur. After all of the chlorine had reacted, it was found that the solution contained 0.320 mol of $NaCl$.

Calculate the amount of $NaClO_3$ produced.

[5]

(d) **(i)** The yellow gas chlorine dioxide, ClO_2 has been used for many years as a flour-improving agent in bread-making. It can be made in the laboratory by the following reaction.

$$2AgClO_3(s) + Cl_2(g) \rightleftharpoons 2AgCl(s) + 2ClO_2(g) + O_2(g) \qquad \Delta H = \text{zero}$$

Calculate and comment on the value of ΔH^o_f ClO_2 of given the following data:

$\Delta H^o{}_f$ $AgClO_3$ = -25 kJ mol^{-1}
$\Delta H^o{}_f$ $AgCl$ = -127 kJ mol^{-1}

(ii) Assuming that ∆H remains constant upon temperature change, suggest how the position of equilibrium will change when the temperature is increased. Explain your answer.

[4]

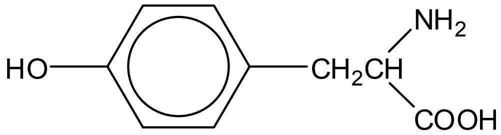
(e) The compound FO_2 does not exist but OF_2 does. By considering the possible types of bonding in the two compounds, suggest reasons for this difference.

(Assume that the fluorine and oxygen atom occupies the central position in FO_2 and OF_2 molecules respectively)

[2]

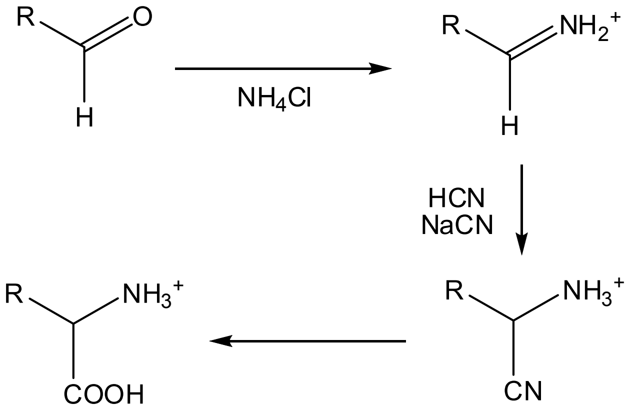
[Total: 20]

4 Tyrosine (Tyr) is synthesised from the essential amino acid phenylalanine (phe), which is derived from food products such as milk, peanuts, almonds, soy products, and bananas. The conversion of phe to tyr is catalyzed by the enzyme phenylalanine hydroxylase. This enzyme catalyzes the reaction causing the addition of a hydroxyl group to the end of the 6-carbon aromatic ring of phenylalanine, such that it becomes tyrosine.



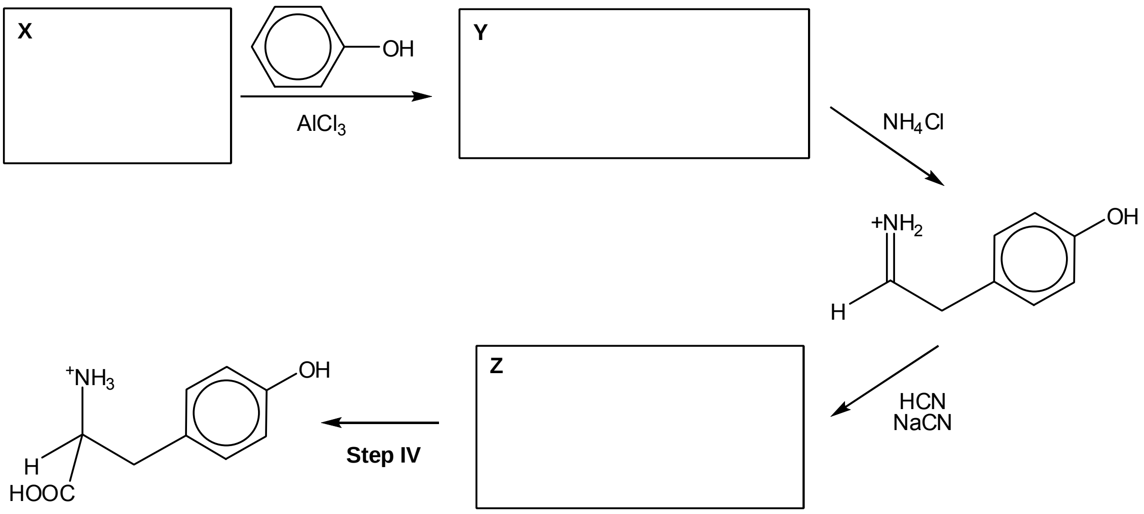
Tyrosine

(a) In the laboratory, amino acids can be formed from aldehydes using the Strecker amino acid synthesis. This is a sequence of chemical reactions that produces amino acids from aldehydes. The steps for the conversion are shown below.



Strecker amino acid synthesis

(i) A synthesis was proposed to form tyrosine from phenol.



(i) In light of the Strecker amino acid synthesis method, identify the structures of **X**, **Y** and **Z**.

(ii) Name the reagents and conditions for **Step IV**.

[4]

(b) **(i)** Tyrosine has three pK_a values.

pK_a of α-carboxyl = 2.20
pK_a of α-amino = 9.11
pK_a of R-group = 10.07

By referring to the pK_a values of tyrosine, sketch the graph of pH against volume of NaOH (cm^3) when excess 0.1 mol dm^{-3} NaOH (aq) is used to titrate 20.0 cm^3 of 0.1 mol dm^{-3} of aqueous tyrosine. In your answer, indicate where the equivalence points and maximum buffer capacities of the solution occur.

(ii) On your graph in **(b)(i)**, use '**X**' to label the point where the zwitterion is present in the highest concentration. Calculate the pH of this point.

(iii) 0.05g of solid NaOH is added to a 20 cm^3 solution containing 0.1 mol dm^{-3} of the tyrosine zwitterion. Calculate the pH of the resulting solution when the solid is completely dissolved.

You might find it useful to represent the zwitterion with HA.

(iv) With the help of equations, explain how the solution from (b)(iii) can act as a buffer.

[8]

(c) Compound **A** is an isomer of tyrosine. 1 mol of compound **A** reacts with Na to form 0.5 mol of hydrogen gas at room temperature and pressure. Compound **A** decolourises excess aqueous Br_2 to form **B**, $C_9H_9O_3NBr_2$. **A** does not decolourise cold alkaline $KMnO_4$. When **A** was heated with aqueous NaOH and distilled, compound **C** and a distillate **D** were formed. Compound **D** produced a yellow precipitate when warmed with alkaline aqueous iodine. Upon crystallisation, **C** is found to have a molar mass of 197 g mol^{-1}.

Suggest the structures of compounds **A** to **D**, giving reasons for your answer.

[8]

[Total: 20]

5 Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium was named after the Scandinavian goddess of beauty and fertility, Vanadis because of the wide range of colours found in vanadium compounds. The colours of the various vanadium ions are given in the table below.

Vanadium Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	Yellow	Blue	Green	Violet

(a) V^{2+} ions are used in a redox titration to determine the concentration of Fe^{3+} ions in an unknown solution. Fe^{3+} is be reduced to Fe^{2+} and the solution is acidic throughout the entire process. The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^-, form an intense blood red complex ion with Fe^{3+} in solution while it appears colourless when complexed with Fe^{2+}. It was found that V^{2+} reacts in a 1 : 1 ratio with Fe^{3+}.

(i) State the electronic configuration of the V^{2+} ion and hence explain why a solution containing V^{2+} ions is coloured.

(ii) Write the two half equations as well as the balanced equation for the titration reaction.

(iii) State the colour change observed at the end point of the titration.

[7]

(b) During his preparation of a 0.500 mol dm^{-3} solution of VSO_4, a student weighed out a certain mass of hydrated vanadyl sulfate ($VOSO_4.2H_2O$) and added a zinc to form V^{2+}. As it was getting late, the student decided to filter the solution and perform the titration the next day. He left the pale violet solution out on the bench uncovered and left. The next day, the student returned to find that his pale violet solution had taken on a slightly green tinge.

(i) Write out the equation for the reaction of V^{2+} with air and calculate the E_{cell}^{θ} to show that it is feasible.

(ii) The student also discovered the possibility of the following reaction between the V^{2+} ions and H^+ ions in solution:

$$2V^{2+}(aq) + 2H^+(aq) \rightarrow 2V^{3+}(aq) + H_2(g)$$

Fortunately for him, this reaction is very slow under normal conditions. Explain why this reaction is very slow. **[3]**

(c) 25.0 cm^3 samples of an iron (III) solution of unknown concentration were titrated against another freshly prepared 0.500 moldm^{-3} V^{2+} solution. The titration results obtained are in the table below.

	1	2	3
Final burette reading /cm^3	22.10	44.70	22.50
Initial burette reading /cm^3	0.00	22.10	0.30
Volume of V^{2+} solution used /cm^3	22.10	22.60	22.20

(i) Calculate the mass of $VOSO_4.2H_2O$ required to prepare 250cm^3 of the V^{2+} standard solution.

(ii) Calculate the mean titre from the titration results above and hence calculate the concentration of Fe^{3+} ions in the unknown solution.

[3]

(d) Another feature of transition metals is their ability to act as catalysts for reactions.

For example, Mn^{2+} (aq) acts as a *homogeneous catalyst* for the decomposition of hydrogen peroxide.

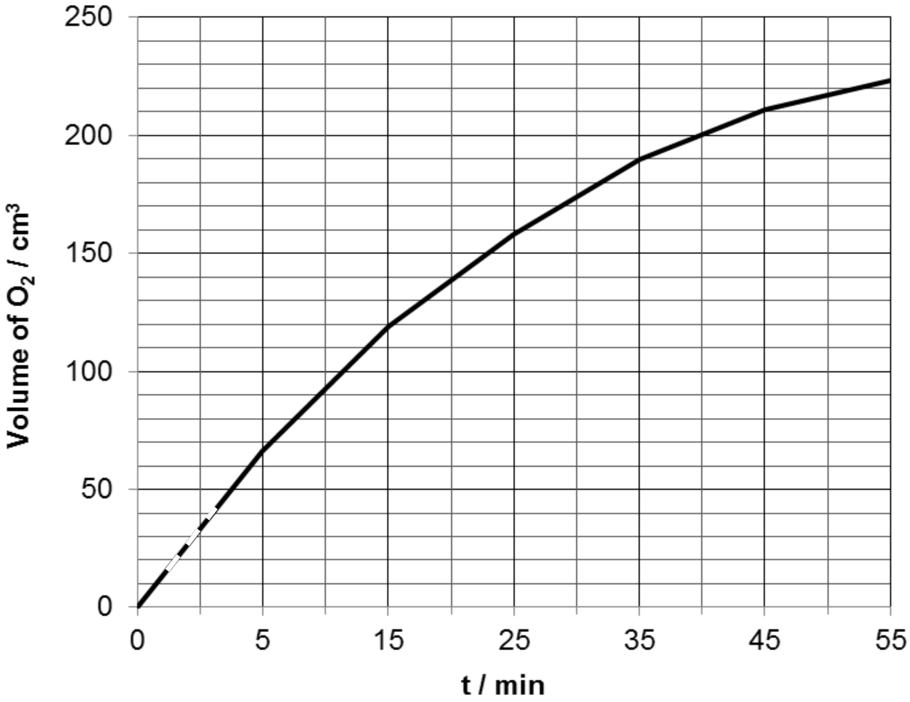
(i) What do you understand by the term *homogeneous* catalyst?

The decomposition of hydrogen peroxide takes place more slowly in the absence of Mn^{2+} (aq).

40.0 cm^3 of 0.50 mol dm^{-3} of acidified hydrogen peroxide solution was connected to a gas syringe in an air tight setup. The kinetics for the decomposition of hydrogen peroxide at room temperature was studied by measuring the volume of oxygen as it changes with time, t.

$$2H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$$

Time, t / min	0	5	15	25	35	45	55
Volume of O_2 / cm^3	0	66	119	158	190	211	223



(ii) Determine the volume of O_2 (g) formed at room temperature and pressure upon the completion of the reaction.

(iii) Using the graph provided above, determine the order of reaction with respect to H_2O_2 (aq).

Hence write the rate equation for the decomposition of H_2O_2.

(iv) With the aid of a Maxwell-Boltzmann Curve, explain how using Mn^{2+} helps to speed up the decomposition of H_2O_2.

[7]

[Total: 20 marks]

End of Paper