Answer any **four** questions.

1 (a) Bradykinin is a nonapeptide (polypeptide with nine residues) which is a pain-causing agent. Complete hydrolysis of this polypeptide yields the following amino acids.

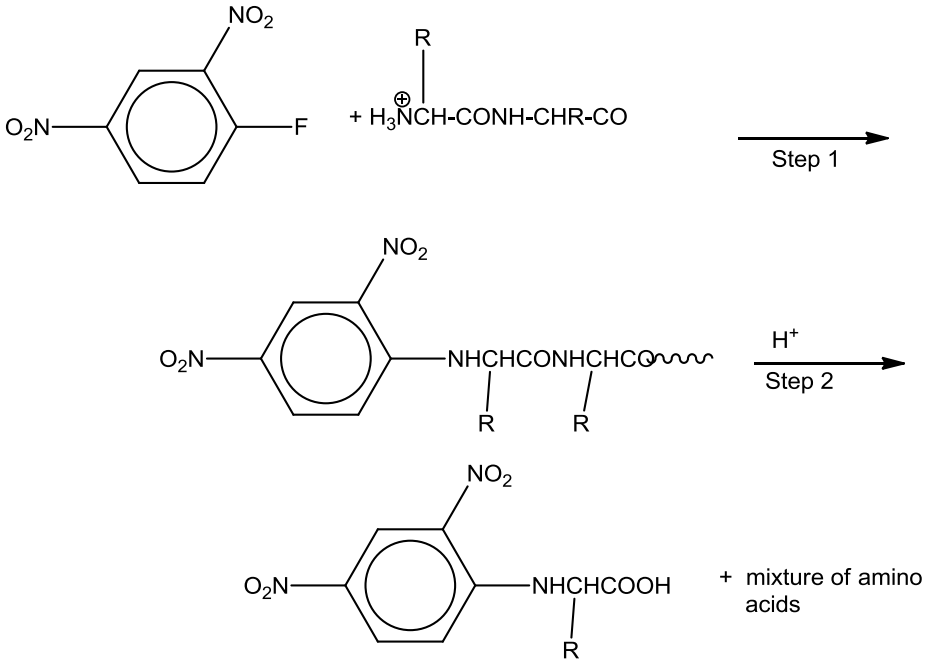
Amino acid	Pro	Ser	Arg	Gly	Phe
No. of residues	3	1	2	1	2

Partial acid hydrolysis of bradykinin gave the following di- and tripeptides.

Phe-Ser; Pro-Gly-Phe; Pro-Pro; Ser-Pro-Phe; Phe-Arg; Arg-Pro

Given that both the terminal residues in the nonapeptide are arginine (Arg), deduce the primary structure of bradykinin. **[2]**

(b) Frederick Sanger used 2,4-dinitrofluorobenzene (2,4-DNFB) in a basic solution to bind to the free amino group of the N-terminal of a polypeptide thereby labelling the N-terminal residue leading to its identification after hydrolysis. The reaction is shown below:

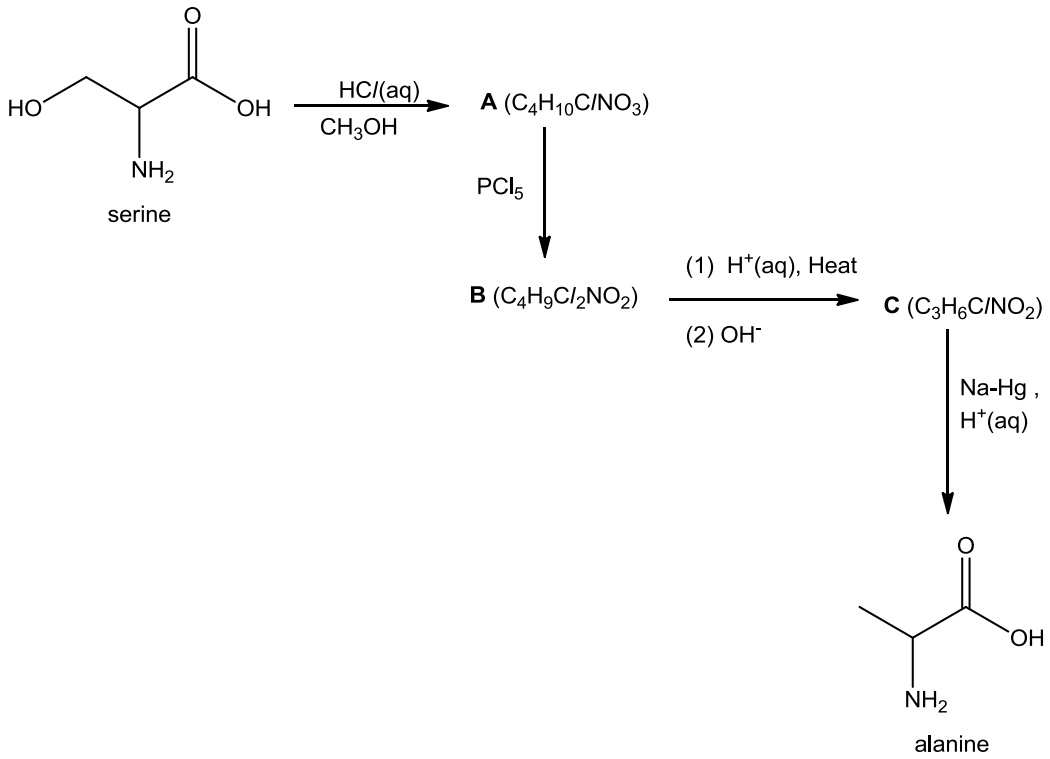


A nucleophilic aromatic substitution occurs between 2,4-DNFB and the N-terminal residue in the first step of the process.

(i) Suggest why a basic solution is used in reaction step 1, involving 2,4-DNFB and the peptide.

(ii) Generally, halobenzenes do not undergo nucleophilic aromatic substitution. However, in the above reaction, 2,4-DNFB seemingly undergoes nucleophilic aromatic substitution. Explain why this is possible, in this instance. **[3]**

1 (c) Emil Fischer used the following reaction scheme to convert serine into alanine.



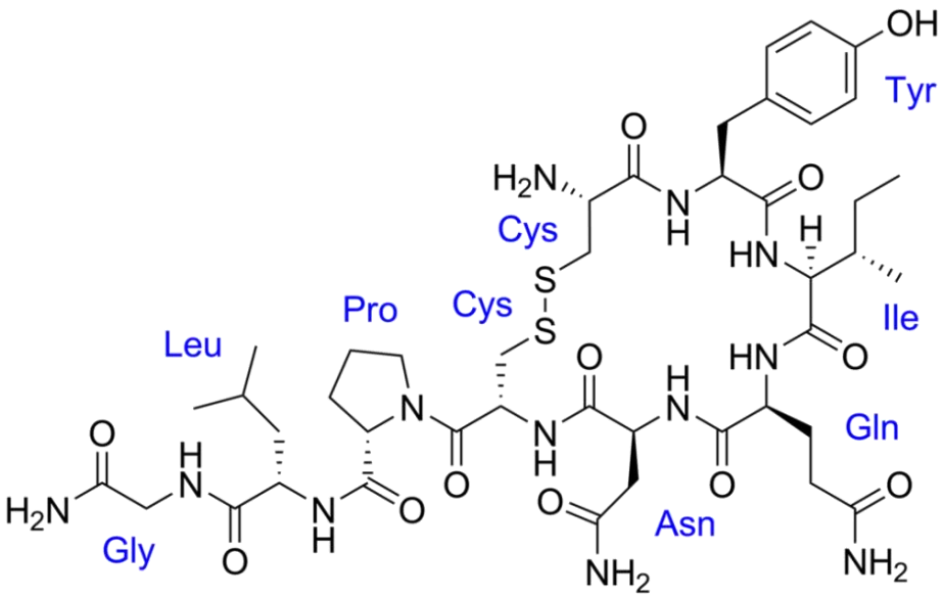
(i) Draw the structural formula for **A** and state the type(s) of reactions that have taken place.

(ii) Draw the structure of **B** and use it to explain why the first step is necessary for the overall conversion of serine into alanine.

(iii) Identify **C** and hence state what type of reaction has taken place in the conversion of **C** to alanine.

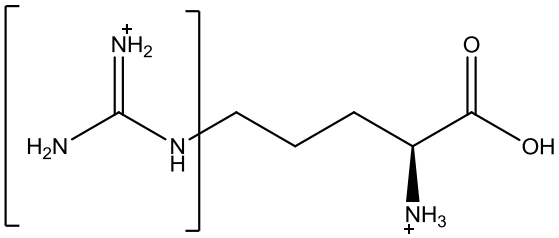
(iv) Would you expect the absolute configuration about the chiral centre to have changed in the conversion of serine to alanine in the above scheme? Explain. **[8]**

1 (d) A small polypeptide, oxytocin, when treated with certain reducing agents (eg. Na/NH_3) brings about a single chemical change that can be reversed by air oxidation. Based on the structure of oxytocin shown below, describe and explain what chemical changes were involved.



[2]

(e) The guanidine group (in brackets) of arginine, shown below, is one of the most strongly basic of all organic groups, with a pK_a of 12.5. Explain why this is so, using appropriate illustrations.



arginine

[2]

(f) There are three pK_a values associated with arginine: 2.2, 9.0 and 12.5. Derive the pI value of this amino acid, explaining your reasoning.

[3]

[Total: 20]

2 Transition elements have different properties that distinguish them from the main group elements. This question hence discusses about cobalt and its properties, such as, able to exist in variable oxidation states and form coloured complexes etc.

(a) When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **W** can be isolated. **W** has the following composition by mass:

Co, 23.4 %; N, 28.0 %; H, 6.0 %; C*l*, 42.6 %

On adding an excess of aqueous silver nitrate to an aqueous solution containing 0.01 mol of **W**, 2.87 g of silver chloride is precipitated.

(i) Determine the structural formula of the cation in **W**. Hence, calculate the oxidation number of the cobalt atom in **W**.

(ii) If a solution of hydrogen peroxide is added to a separate solution containing only $CoCl_2$ and NH_4Cl, what observation(s) would you expect? Explain your answer with reference to the Data Booklet.

[5]

(b) The traditional method for synthesis of organic compounds is via chemical routes, which usually involves multiple steps. However, over the last century, there is an increase in the use of electrochemical methods for organic synthesis, otherwise known as electrosynthesis.

Electrosynthesis of organic compounds is carried out with the application of a constant current. The yield of electrosynthesis is expressed both in terms of the chemical yield and current efficiency, which is the ratio of Coulombs consumed in forming the products to the total number of Coulombs passing through the cell. Occurrence of side reactions decreases the current efficiency.

The most successful organic electrosynthesis process is the cathodic reduction of acrylonitrile to form adiponitrile (ADN), which is a key intermediate for the production of nylon-6,6 polymers:

$$4\ CH_2{=}CHC{\equiv}N\ (l) + 2\ H_2O\ (l) \rightarrow 2\ N{\equiv}C(CH_2)_4C{\equiv}N\ (l) + O_2\ (g)$$

An example of the operation conditions of this process is as follows:

Cathode:	Pb
Anode:	Fe (Ni 9%)
Supporting electrolyte:	Aqueous solution of $(EtBu_3N)_2HPO_4$ + K_2HPO_4 + $K_2B_4O_7$
Current efficiency:	90.7%
Production per year:	300,000 tonnes

(i) Write a half-equation, including state symbols, for the cathodic reduction of acrylonitrile to form adiponitrile.

(ii) Based on the overall equation, deduce the half-equation, including state symbols, for the anodic reaction.

[2]

2 (b) (iii) Given that the E^{o}_{red} (acrylonitrile/adiponitrile) is x V, what is the minimum voltage required for the electrosynthesis of adiponitrile?

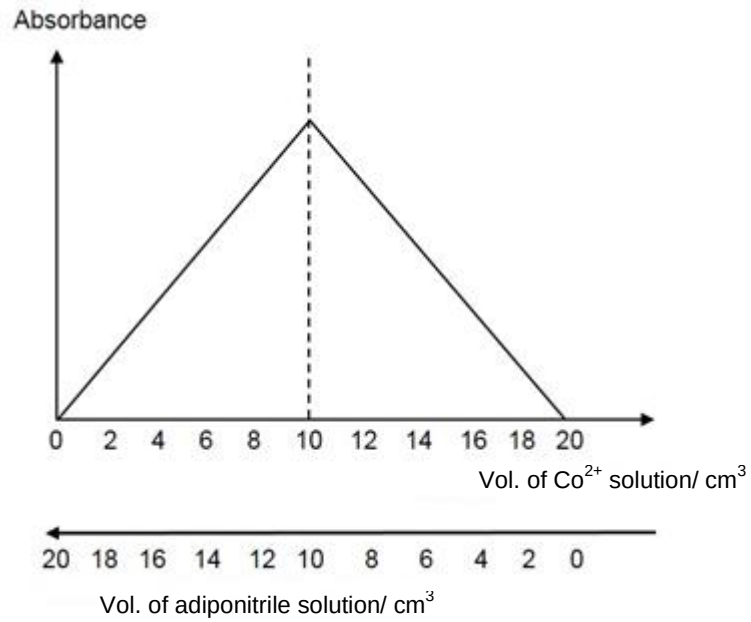
(iv) Based on the operation conditions in the electrosynthesis of adiponitrile, calculate the current required for the production plant to operate 24 hours all year round.

[5]

(c) A coordination polymer contains metal cation centers lined by organic ligands. In recent years, due to their unique structural architectures, these polymers have increased applications in fields, such as biochemistry, material science etc. One such example is a cobalt(II) coordination polymer, containing the adiponitrile (ADN) ligand.

(i) Co^{2+} ion forms a pale yellow complex with adiponitrile.

Various samples containing different volumes of 1×10^{-5} mol dm^{-3} Co^{2+} and 3×10^{-5} mol dm^{-3} adiponitrile were prepared. The following graph was obtained when the colour intensity of the samples was measured using a colorimeter:



Based on the above information, deduce the coordination number of Co^{2+} ion.

[2]

2 (c) (ii) The following table provides information about the wavelengths absorbed when Co^{2+} ion is coordinated with different ligands:

Cobalt(II)-complex ion	**aqueous solution of Co^{2+}**	**Co(II)-adiponitrile solution**
Wavelength absorbed	Green	Violet

By considering the above information and the wavelengths of the visible light spectrum, what deduction can be made about the size of the d-orbital splitting in the two complexes? Explain your answer.

(iii) The stability constant, K_{stab}, is an equilibrium constant for the formation of a complex ion relative to its aqua-complex in a solution:

The following table shows the lg K_{stab} values of cobalt(II)-complex ion with the various ligands:

Ligands	**H_2O**	**NH_3**	**$EDTA^{4-}$**
lg K_{stab} (of cobalt(II)-complex ion)	-	4.9	16.3

(1) Write a balanced equation, with state symbols, representing the ligand exchange reaction between NH_3 and $EDTA^{4-}$ in the cobalt(II)-complex ion.

(2) Hence account for the lg K_{stab} values, in terms of strength of the ligands.

(iv) Hence suggest, with reason, a value for lg K_{stab} of the cobalt(II)-complex ion formed with adiponitrile ligands.

[6]

[Total: 20]

3 This question is about sodium boron hydride and lithium aluminium hydride, two common reducing agents in organic chemistry.

(a) Sodium boron hydride can also be used in fuel cells.

In conventional fuel cells, hydrogen can be regenerated for a fuel cell by hydrolysing the borohydride: The by-product is $NaBO_2$.

(i) Write the balanced equation for the hydrolysis of sodium boron hydride.

In the direct borohydride fuel cell (DBFC), the boron hydride is directly oxidised by O_2 to $NaBO_2$ without involving hydrogen.

(ii) Write the half-equation for the oxidation of $NaBH_4$ to $NaBO_2$.

(iii) Given that the standard cell potential of the DBFC is + 1.64 V, find the standard reduction potential of the above half-reaction.

(iv) The DBFC produces more energy than conventional fuel cells.
Suggest another advantage of the DBFC.

[5]

(b) Lithium aluminium hydride is thermally unstable.

It is converted to Li_3AlH_6 at about 150 ^{0}C.

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$$

Li_3AlH_6 in turn decomposes to LiH at 200 ^{0}C.

$$2Li_3AlH_6 \rightarrow 6LiH + 2Al + 3H_2$$

An lithium-aluminium alloy is formed from LiH and aluminium at temperatures above 400 ^{0}C.

$$LiH + Al \rightarrow LiAl + \tfrac{1}{2} H_2$$

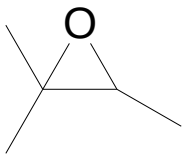
(i) Give the overall equation of the thermal decomposition of lithium aluminium hydride at temperatures above 400 ^{0}C.

(ii) The decomposition temperatures of Li_3AlH_6 and Na_3AlH_6 are 200 ^{0}C and 269 ^{0}C respectively.

Explain this trend.

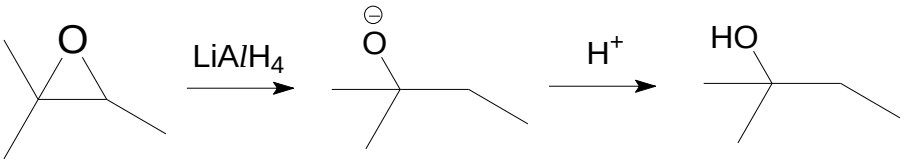
[3]

3 (c) Ozone can be used on alkenes to form epoxides, which are three-membered cyclic ethers. An example of an epoxide is shown below.



(i) The above epoxide exists as a pair of optical isomers. Draw their three-dimensional structures.

(ii) $LiAlH_4$ can be used to convert epoxides to alcohols.



Treating $LiAlH_4$ as H^-, draw the mechanism for the scheme above. **[2]**

(d) **A**, a cyclic compound, $C_{11}H_{16}$, undergoes ozonolysis to give **B** and **C**.

Ozonolysis is the cleavage of an alkene with ozone to form ketones and/or aldehydes. It complements the manganate(VII) oxidative cleavage of alkenes, which form carboxylic acids instead of aldehydes.

B, $C_8H_{12}O_2$, can be reduced by both $NaBH_4$ and $LiAlH_4$ to give the same product. A silver mirror was formed when **B** was reacted with an ammonical solution of silver nitrate. **B** reacts with hydrazine, N_2H_4, to form a product **F**, $C_8H_{12}N_2$.

C, $C_3H_4O_2$, can also be produced as the distillate from **D**, $C_3H_8O_2$, after treatment with hot acidified $K_2Cr_2O_7$ (aq). 12 dm^3 of a colourless and odourless gas is formed when excess sodium was added to 38 g of **D** under room conditions.

D can be obtained from **E**, $C_3H_4O_3$, using $LiAlH_4$ in dry ether. However, when **E** was reacted with $NaBH_4$ instead, a product of molecular formula $C_3H_6O_3$ was formed. This same product can be formed by reacting ethanal with HCN and a small amount of NaOH, followed by heating in acid.

Deduce the structures of **A** to **F**, writing your deductions as clearly as possible. **[10]**

[Total: 20]

4 (a) Thermodynamic stability refers to the potential energy of a compound, and is related to the bond energies of its constituent atoms. Chemical stability refers to a compound's resistance to chemical reaction with a variety of reagents, and is related to the activation energy barrier it presents to possible chemical change.

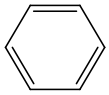
A comparison of cyclohexene and benzene provides a good example of this distinction. Both compounds react with hydrogen in exothermic reactions to give cyclohexane as a common product.

(i) Write the relevant equation for the reaction between cyclohexene with hydrogen to form cyclohexane.

(ii) The enthalpy changes of combustion of cyclohexene (*l*), cyclohexane (*l*) and hydrogen (g) are -3751 kJ mol^{-1}, -3920 kJ mol^{-1} and -287 kJ mol^{-1} respectively. Calculate the enthalpy change of hydrogenation of cyclohexene.

(iii) Kekulé first suggested the structure of benzene to be the structure given below. Carbons are arranged in a hexagon, with alternating double and single bonds between them. Each carbon atom has a hydrogen atom attached to it. Even though the Kekulé structure is frequently used for benzene compounds, there is much evidence that this representation is inadequate and incorrect.

Using the value you calculated in **a(ii)**, predict the enthalpy change of hydrogenation of the Kekulé structure of benzene, which proposed that benzene contains three double bonds.



Kekulé proposed structure of benzene

(iv) The enthalpy change of hydrogenation of benzene was found to be -208 kJ mol^{-1}. Based on the value you calculated in **a(iii)**, explain the relative thermodynamic stability of benzene and the Kekulé structure of benzene.

[5]

(b) (i) Cyclohexene reacts rapidly with bromine, whereas benzene only reacts with bromine in the presence of a catalyst.

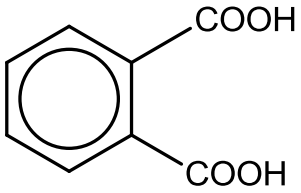
Describe the mechanism for the reaction between benzene and bromine in the presence of anhydrous aluminium bromide.

(ii) Explain why aluminium bromide is required for the reaction in **b(i)** and why aluminium bromide has to be anhydrous.

(iii) Aluminium bromide is a white solid which is soluble in non-polar solvent, such as benzene. Suggest a reason for its ability to dissolve in benzene.

[6]

4 (c) Compounds **F** and **G**, both $C_{10}H_{12}$, and compound **H**, $C_{10}H_{14}O$, are all oxidised by hot concentrated acidified potassium manganate(VII) to give benzene-1,2 dicarboxylic acid.



Compound **G** decolourised bromine in CCl_4 to form compound **J**, but compound **F** does not.

Compound **H** undergoes dehydration to form only a single organic product, **G.**

Compound **H** reacts with alkaline aqueous iodine to give yellow crystals, compound **H** also reacts with acidified potassium dichromate(VI) to form compound **K**.

Compound **K** forms an orange precipitate with 2,4-dinitrophenylhydrazine and also reacts with alkaline aqueous iodine to give yellow crystals.

Deduce the structures for compounds **F** to **K**. **[9]**

[Total: 20]

5 (a) Dinitrogen pentoxide, N_2O_5 can be used to prepare explosives. It decomposes according to the following equation:

$$N_2O_5 \rightarrow 2NO_2 + ½\ O_2$$

In one experiment at 30°C, the volumes of O_2 produced over time are determined as follows.

Time / s	0	2400	4800	9600	14400	32000	∞
Vol / cm^3	0	16	28	46	58	77	85

(i) Plot a graph of volume of O_2 against time, based on the following scales.

y-axis : 10 cm^3 per 10 smallest squares
x-axis: 4000 s per 10 smallest squares

(ii) Use your graph to determine the order of reaction with respect to N_2O_5. Show clear working.

(iii) Calculate the rate constant. Include units in your answer.

(iv) With the aid of a sketch of Boltzmann distribution, explain how an increase in temperature affects the rate of the reaction. **[9]**

(b) During a chemistry practical lesson, one teacher told a group of students that the rate equation for the reaction between magnesium ribbon and dilute hydrochloric acid is:

$$\text{Rate} = k[HCl]^2$$

The students are then tasked to perform experiments to confirm whether this rate equation is true, using the gas collection method. They carry out experiments individually with fresh samples of magnesium ribbons. All of their results do not agree with the given rate equation.

(i) Student **A** used concentrated hydrochloric acid in his experiments. He finds that the reaction is zero order with respect to HC*l*.
Explain why the reaction is zero order with respect to HC*l* in this case.

(ii) Student **B** uses same mass of magnesium in powder form in his experiments. He finds that the rate is faster than that suggested by teacher.
Explain why the rate is faster in this case.

(iii) Student **C** was absent that day. He performed the experiment the next day with magnesium ribbons being exposed to air for one day already. His results show that the reaction was slow initially, then became faster, and slowed down in the end. Explain this observed kinetics. **[4]**

(c) State and explain the solubility trend of hydroxides in water down Group II. **[4]**

(d) Beryllium oxide, BeO, is an amphoteric oxide. Write balanced equations to show this property. Explain why BeO shows this property. **[3]**

[Total: 20]

END OF PAPER