(a) An unknown solid sample, with a mass of 1.50 g, contains three sodium salts, NaC*l*, NaC*l*O₃ and NaNO₃. The sample was completely dissolved in water and diluted in a 250 cm³ volumetric flask to obtain solution L.

In one experiment, a 50 cm³ portion of solution **L** was reacted with excess silver nitrate solution. The AgC*l* precipitate formed was removed by filtration, dried and weighed. The AgC*l* precipitate was found to have a mass of 0.240 g.

In another experiment, a gas was bubbled into a new 50.0 cm³ portion of solution **L** to convert ClO_3^- to Cl^- . Excess silver nitrate was then added to the resulting mixture. The AgC*l* precipitated formed was treated similarly as before and found to have a mass of 0.285 g.

(i) Determine the amount of C/O_3^- ions present in 50 cm³ of solution L.

[2]

[2]

(ii) Hence, determine the percentage by mass of $NaCIO_3$ present in the original solid sample.

(b) Suggest whether NaCl or NaClO₃ has a lower melting point. Explain your answer.

(c) (i) Draw a dot-and-cross diagram of the ClO_3^- anion.

(ii) Chlorine forms a number of oxides, one of which is Cl_2O_7 . Cl_2O_7 is a symmetrical molecule, with a central oxygen atom bonded to two chlorine atoms.

Draw the structure of Cl_2O_7 .

(iii) The bonds in Cl_2O_7 exhibit two different bond lengths, namely, 0.141 nm and 0.171 nm. However, all the bonds in the ClO_3^- ion have the same bond length of 0.149 nm.

Suggest why the bond length in ClO_3^- is intermediate between those present in Cl_2O_7 .

(iv) The bond angle formed between the central oxygen atom and its two surrounding chlorine atoms is larger than expected with a value of 118.6°.

Suggest a possible reason why.

[1] [Total: 11]

2 (a) Use of the *Data Booklet* is necessary for this part of the question.

The sub-atomic makeup of certain ions formed from isotopes of cobalt and lead is given below:

	number of neutrons	number of electrons
Co ion	33	25
Pb ion	122	

In a particular experimental set–up, a beam containing the above ions of cobalt was passed through an electric field and was deflected by an angle of +10.2°.

Under identical conditions, another beam containing the above ions of lead was deflected by an angle of $+6.0^{\circ}$.

What is the overall charge of the lead ions?

(b) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

 CoF_6^{3-} and $[Co(NH_3)_6]^{3+}$ are both complexes with cobalt in the +3 oxidation state. However, only CoF_6^{3-} displays paramagnetism while $[Co(NH_3)_6]^{3+}$ does not. This is determined by whether the electronic configuration of the Co^{3+} ion in the complex displays a "high spin" or a "low spin" state.

The following diagram shows how the d-orbitals are split in an octahedral environment.



In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

(i) Draw the shapes of the d_{xy} and d_{z^2} orbitals. Label your drawings clearly.

(ii) Using \uparrow or \downarrow to represent electrons, show, on the two diagrams below, the electronic distribution of a Co³⁺ ion in a high spin state, and in a low spin state.

Hence, identify the cobalt complex that corresponds to each particular spin state.

-

		d orbitals after splitting	d orbitals after splitting
		High spin	Low spin
	Complex:		[2]
(iii)	Suggest why pairs.	electrons usually prefer to c	occupy orbitals singly rather than in
			[1]
(iv)	Using the exp state and exp gap, E, betwe	lanation in (b)(iii) , together w lain which of the two cobalt co en its d orbitals.	ith the information given above, omplexes contains the larger energy
			[1] [Total: 8]

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3 Frederick Thomas Trouton was an Irish physicist who observed a relationship between boiling points and enthalpy changes of vaporisation after studying many liquids. He published his findings and formulated Trouton's rule which states that the molar *entropy* of vaporisation, ΔS_{vap} , for most liquids is about 85 J K⁻¹ mol⁻¹.

The boilir	ig points	and	enthalpy	changes	of	vaporisation	of	several	organic	liquids	are	as
follows:												

substance	boiling point / °C	$\Delta H_{\rm vap}$ / kJ mol ⁻¹	ΔS_{vap} / J K ⁻¹ mol ⁻¹
propanone, (CH ₃) ₂ CO	56.1	29.1	
dimethyl ether, (CH ₃) ₂ O	-24.8	21.5	86.6
ethanol, CH ₃ CH ₂ OH	78.4	38.6	
octane, CH ₃ (CH ₂) ₆ CH ₃	125.6	34.4	86.3
pyridine,	115.3	35.1	90.4

(a) Explain the term *entropy* and why ΔS_{vap} at constant pressure is positive.

[2]

(b) Complete the above table by calculating the ΔS_{vap} for propanone and ethanol. Show your working for the calculation of ΔS_{vap} for propanone.

(c) By considering the structure and bonding of the various substances in this question, state and explain the relationship between strength of intermolecular forces of attraction and the entropy of a substance in the liquid state.

[2]

(d) (i) With the aid of a diagram, show and label the bonding between two methanoic acid molecules in the **gaseous** phase.

[1]

(ii) Hence, predict if ΔS_{vap} for methanoic acid is more or less positive than predicted by Trouton's rule. Explain your reasoning.

[No marks will be awarded if a prediction has no reasoning.]

[2] [Total: 9] 4 Ozone, O₃, is fairly stable but rapidly decomposes, with the release of heat, to form oxygen in the presence of silver catalyst. A silver catalyst was added to 800 cm³ of a mixture of oxygen and ozone. The volume increased as follows and the reaction is complete at 1800 s.

total volume of gas mixture, V_{total} / cm ³	800	805	810	815	818	819
volume of O ₃ (g) /cm ³						0
time, t / s	0	210	420	860	1350	1800

(a) (i) Write a chemical equation to represent the overall process of the decomposition of ozone to form oxygen.

.....

(ii) By considering the stoichiometry of the reaction, calculate the initial volume of ozone and initial volume of oxygen in the mixture.

[1]

[1]

(iii) Given that volume of O_3 reacted = 2 ($V_{total} - 800$), complete the above table by calculating the volume of ozone in the mixture at the various times stated. Fill in the volume of O_3 at t = 0 s using your answer in **a(ii)**.

[1]

(iv) The decomposition of ozone is a *first order* reaction.

Write down the rate equation and explain the term first order.

(v) Show, by means of a suitable graph, that these data are consistent with a first order reaction.

[If you are unable to solve **(iii)**, sketch the graph without data points and indicate clearly how it can be used to verify the order of reaction.]



- (b) (i) Silver is a heterogeneous catalyst in this reaction. Outline how a heterogeneous catalyst works.
 - (ii) Draw a labelled energy profile diagram for the decomposition of ozone, with and without the use of a catalyst.

[2] [Total: 11] 5 (a) Nitrogen is one of the key elements present in α -amino acids, the building block of proteins. α -amino acids have the following general formula.

$$H_2 N - CO_2 H$$

The table below shows the R groups of the α -amino acids present in a polypeptide, J.

α –amino acid	Mr	R group
asp	133.0	$-CH_2CO_2H$
lys	146.0	$-CH_2CH_2CH_2CH_2NH_2$
gln	146.0	$-CH_2CH_2CONH_2$

You have to refer to the table above when answering **a(i)** and **a(ii)**.

(i) When polypeptide J undergoes hydrolysis, three aspartic acid, two lysine and one glutamine molecules were formed as shown in the following reaction:

 $J \longrightarrow 3 \operatorname{asp} + 2 \operatorname{lys} + 1 \operatorname{gln}$

Calculate the M_r of polypeptide **J**.

(ii) A dipeptide, *gln–lys*, is obtained upon hydrolysis of polypeptide **J** by an enzyme. Draw the structural formula of this dipeptide at pH 1.

(iii) A sample of lysine, extracted from the hydrolysis of polypeptide **J** rotated plane polarised light anticlockwise. However, a second sample of lysine obtained from laboratory synthesis had no effect on plane polarised light.

Suggest an explanation for these observations.

[2]

(iv) Part of the chain of another polypeptide K is shown below.

CONHCHCON--CHCONH-CH₂CONH₂

Draw the structure of the organic products formed when polypeptide **K** is treated with excess aqueous KOH under prolonged heating.

(b) The following titration curve is obtained when a solution of fully protonated aspartic acid, H₃N⁺CH(CH₂CO₂H)CO₂H is titrated with NaOH(aq). X, Y and Z denote the first, second and third equivalence point respectively.



(i) Identify the species present at X and Z.

[1]

(ii) Hence, explain why there is a sharp increase in pH when a small amount of NaOH(aq) is added to solution at **Z**.

[1]

(iii) At pH 10.0, the mixture can act as a buffer. Identify the two species present in this buffer. With the aid of an equation, show how the buffer works when a small amount of acid is added to it.

(iv) Calculate the ratio of the concentrations of the two species in the buffer required to maintain the pH in (b)(iii).

[2]

(c) Pyridine is a cyclic structure containing nitrogen and is analogous to that of benzene. It can be reduced to piperidine with Raney nickel (RaNi) as shown in the following reaction:



(i) State the type of hybrid orbital occupied by the lone pair of electrons on the N atom in pyridine and piperidine.

Pyridine:

Piperidine:

[1]

(ii) Hence, suggest how the basicity of pyridine might compare to that of piperidine. Give reasons for your answers.

(iii) In an attempt to form a quaternary amine salt, a student treated piperidine with excess iodomethane under acidic condition. Explain why this synthesis will **not** be successful.

 [2] [Total: 17]

6 (a) In most of its compounds, iron has the oxidation state +2 or +3. However, other oxidation states of iron are possible. For example, potassium ferrate(VI), K₂FeO₄, contains iron in the +6 oxidation state. Reflecting its high oxidation state, FeO₄²⁻ is a powerful oxidising agent.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



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(iv) Write an equation to illustrate the acidic nature of K.

[1]

(v) Using relevant data from the Data Booklet, predict whether a reaction will occur when iodide ions are mixed with K and L separately. Write an equation for any reaction that occurs.

[2]

(b) In an aromatic substitution reaction, the position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.



(i) Name the type of reaction mechanism between phenol and the incoming group, E.

.....[1]

(ii) Both phenylamine, C₆H₅NH₂, and phenol, activate the benzene ring in a similar manner so that the ring becomes highly susceptible to the incoming group, E. Comparing the difference in electronegativity between oxygen in phenol and nitrogen in phenylamine, explain the relative rate of phenol and phenylamine with the incoming group, E.

19

 [2]
[4]

(iii) From your answers in (b)(ii), outline the reaction mechanism for the monosubstitution of 4-aminophenol with the incoming group, E⁺.

)∕—NH₂ HO-4-aminophenol

- (c) The choice of solvent used in the bromination of phenol can greatly affect the type of product formed.
 - (i) Draw the structure of the product formed when phenol undergoes reaction with Br₂ in water and with Br₂ in a non-polar organic solvent like CS₂ separately.

[1]

[1]

- (ii) By considering the nature of the incoming group, **E**, suggest an explanation for the difference in the reaction between phenol and bromine dissolved in the two different types of solvent mentioned in (c)(i).
- (d) Suggest the reagents and conditions required to carry out the following transformation and explain the rationale for the choice.

