Answer **all** questions in the spaces provided.

1 Planning (P)

Paracetamol (acetaminophen) is commonly used for the relief of headaches and is a major ingredient in numerous cold and flu medicine.

It is a white solid (m.p. = $169 \, ^{\circ}C$) which can be prepared by a reaction between 4-aminophenol and ethanoic anhydride.

$HOC_6H_4NH_2$	(CH ₃ CO) ₂ O	CH₃CONHC ₆ H₄OH
4-aminophenol	ethanoic anhydride	paracetamol
$(M_{\rm r} = 109)$	$(M_{\rm r} = 102)$	$(M_{\rm r} = 151)$

A typical yield, based on 4-aminophenol, is 70%.

The crude product can be purified by recrystallisation from water.

The purity of the recrystallised product can be confirmed by determining its melting point.

Ethanoic anhydride can cause irritation of tissue, especially in nasal passages.

4-aminophenol is a skin irritant and is toxic.

- (a) Using the information above:
 - (i) Write a balanced equation for the formation of paracetamol;

 $HOC_6H_4NH_2 + (CH_3CO)_2O \rightarrow CH_3CONHC_6H_4OH + CH_3CO_2H$

(ii) Calculate the minimum masses of reactants needed to prepare 5 g of pure paracetamol.

Mass of 4-aminophenol required = $\frac{5}{151} \times \frac{100}{70} \times 109 = 5.16 \text{ g}$

Mass of ethanoic anhydride required = $\frac{5}{151} \times \frac{100}{70} \times 102 = 4.82 \text{ g}$

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(b)	Write a full description of the purification of the crude paracetamol. List the essential apparatus you would use in the process. You do not have to describe the preparation of paracetamol.			
-	<u>Apparatus</u> : Conical flask for dissolving crude solid (accept beaker) Hot plate for heating (accept oil bath but not water bath or heating mantle) Filter funnel/ conical flask for hot filtration Buchner apparatus for collecting pure crystals.			
-	<u>Method</u> : Dissolve crude solid in <u>minimum</u> amount of <u>hot water</u> Filter solution while hot Cool hot solution (in ice bath) Collects crystals using vacuum filtration/ reduced pressure (using Buchner apparatus) Wash with small amounts of cold water Dries crystals between filter paper/ under IR lamp.			
(c)	Write a brief description showing how you would use the melting point of the purified product to confirm its purity. You do not have to describe how you would obtain the melting point.			
1	Melts sharply/ over small temperature range Melting point agrees with data value (i.e. 169 °C)			
	[1]			
(d) Identify two potential safety hazards in this experiment and the relevant safety precautions you would take.				
Hazar	ď	Precaution		
4-ami Ethan	nophenol is a skin irritant and is toxic. oic acid is corrosive	Avoid skin contact; wear personal protective equipment (gloves, goggles); flood affected areas if there is spillage.		
Ethan tissue	Ethanoic anhydride can cause irritation of Perform experiment in fume cupboard.			
Ethan	oic anhydride is flammable	Do not use naked flames.		

- Precautions must be relevant to the hazard -
- -
- Do not allow "use fume cupboard as a precaution for toxicity. Do not allow "do not eat/ consume, do not breathe in" as precautions -

......[2]

[Total: 12]

2 Given the following thermochemical data:

Reaction	<u>∆H^e/ kJ mol^{−1}</u>
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	-75.0
$C(graphite) + O_2(g) \rightarrow CO_2(g)$	-393.5
$H_2(g) \hspace{.1in} + \hspace{.1in} {}^{1\!\!/_2}\!O_2(g) \hspace{.1in} \rightarrow \hspace{.1in} H_2O({\it I})$	-285.9

(a) With the aid of an energy cycle, calculate the enthalpy change for the reaction

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$$



By Hess' Law:

 $\Delta H = +75.0 + \{2(-285.9) + (-393.5)\}$ $= -890.3 \text{ kJ mol}^{-1}$

[3]

(b) The experimental enthalpy change is -801.7 kJ mol⁻¹ for the following reaction

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$$
(I)

(i) Calculate the enthalpy change of vaporisation of water at 298K.



[2]

(ii) Using bond energy data from the *Data Booklet*, calculate another value for ΔH for reaction (I) in (b). Account for any differences between your answer and the given experimental value in (b).

 $\Delta H = 4(410) + 2(496) - 4(460) - 2(740)$ = -688 kJ mol⁻¹

The value obtained from bond energy calculations is different because bond energies are only average values obtained from different molecules. They may not be the actual values for the molecules used.

> [3] [Total: 8]

- **3** Mixtures of citric acid, $C_5H_7O_4CO_2H$ ($K_a = 7.40 \times 10^{-4}$ mol dm⁻³), and its sodium salt are often used as acidity regulators for food. The mixture regulates the pH of food by acting as a buffer.
- (a) Prove that the pH of a mixture formed from 25.0 cm³ of 0.200 mol dm⁻³ citric acid and 2.48 g of sodium citrate ($M_r = 198$) is 3.53.

 $pH = pK_a + \log [C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H]$ $pH = -\log (7.40 \times 10^{-4}) + \log \frac{2.48/198}{0.025 \times 0.200}$ = 3.53

[2]

(b) When 0.059 g of an unknown solid was added to the mixture prepared in (a), the pH of the resultant solution is 3.73. Determine the molar mass of the solid and hence suggest its identity.

Since pH is raised on addition of the solid, the solid added must be a base. $C_5H_7O_4CO_2H + OH^- \rightarrow C_5H_7O_4CO_2^- + H_2O$

 $3.73 = -\log (7.40 \times 10^{-4}) + \log [C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H]$ [C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H] = 3.97

Let the molar mass of the solid be M $n_{citric \ acid} = 0.025 \times 0.200 - 0.059/M$ $n_{citrate} = 2.48/198 + 0.059/M$

 $\frac{2.48/198 + 0.059/M}{0.025 \times 0.200 - 0.059/M} = 3.97 \quad \Rightarrow M = 40.0$

Solid is sodium hydroxide.

[3]

(c) Determine the volume of 0.100 mol dm⁻³ of HCI(aq) that needs to be added to the solution in (a) to obtain a buffer at its maximum buffering capacity.

pH at max. buffering capacity = 3.13 $C_5H_7O_4CO_2^- + H_3O^+ \rightarrow C_5H_7O_4CO_2H + H_2O$ Let the volume of 0.100 mol dm⁻³ HCI required be V $n_{citric\ acid}$ = $0.025 \times 0.200 + 0.100V$ $n_{citrate}$ = 2.48/198 - 0.100V

At max. buffering capacity,

 $\begin{bmatrix} C_5H_7O_4CO_2H \end{bmatrix} = \begin{bmatrix} C_5H_7O_4CO_2^{-1} \end{bmatrix} \rightarrow n_{citric \ acid} = n_{citrate}$ 0.025 x 0.200 + 0.100V = 2.48/198 - 0.100V V = 0.0376 dm³ = 37.6 cm³

[2]

[Total: 7]

- 4 Cobalt and vanadium are transition metals.
- (a) Give one characteristic chemical property of cobalt and vanadium which shows that they are transition metals.

variable oxidation state or catalytic activity or complex ion formation or formation of coloured ions
[1]

(b) Aqueous cobalt(II) chloride, CoCl₂ is a pink solution. When a mixture of the pink solution and tartaric acid, HO₂CCH(OH)CH(OH)CO₂H, is added to aqueous hydrogen peroxide, the following changes take place.

The initially pink solution turns green and then oxygen is vigorously evolved. Finally, the solution turns pink again.

Suggest a role for the $CoCl_2(aq)$ and for the tartaric acid. Write an equation for the overall reaction.

CoCl ₂ (aq):	catalyst	
Tartaric acid:	Ligand	
Equation:	$2H_2O_2 \rightarrow 2H_2O + O_2$	

[3]

(c) Aqueous CoCl₂ also undergoes the following reaction.

 $\begin{array}{ccc} \text{CoCl}_2(aq) & \xrightarrow{\text{NH}_4\text{Cl}, \text{NH}_3} & \xrightarrow{\text{Crystals of}} \\ & \text{and } \text{O}_2 & \xrightarrow{\text{salt } \textbf{K}} \end{array}$

I

(i) Crystals of salt, K has the following composition by mass:

Co, 22.0%; N, 31.4%; H, 6.7%; Cl, 39.8%

On adding an excess of $AgNO_3(aq)$ to an aqueous solution containing 0.01 mol of **K**, 4.29 g of AgCI(s) is precipitated.

Calculate the empirical formula of K, and draw the structure of the cation present in K to show the geometry around the central ion.



(ii) State the types of reactions occurring in step I.

Ligand exchange and redox

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(iii) E^{Θ} data for some cobalt complex ions are given below. $[Co(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}(aq) \qquad E^{\Theta} = +0.57 \text{ V}$ $[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}(aq) \qquad E^{\Theta} = +0.11 \text{ V}$

Use the E° data given above to predict the reaction, if any, of adding C₂O₄²⁻ to **K**. Explain your prediction.

 Co^{3+} is more stable when NH₃ is the ligand as seen from the **smaller** E° value for the reduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ to $[\text{Co}(\text{NH}_3)_6]^{2+}$.

The ligand $C_2O_4^{2-}$ is unable to displace the ammonia ligands in K.

No ligand exchange reaction takes place when $C_2O_4^{2-}$ is added to **K**.

[7]

(d) Some of the ions of vanadium and their corresponding colours are shown in the table below.

formula of vanadium ion	VO ₃ ⁻	VO ²⁺	V ³⁺	V ²⁺
colour of aqueous solution	yellow	blue	green	violet

The colour of the reaction mixture changes from yellow to green when a transition metal is added to an aqueous solution containing the salt of a vanadium ion.

By reference to the *Data Booklet*, suggest a possible identity of the transition metal and explain the colour change observed.

Explanation: $VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$ $E_e^{\theta} = + 1.00 V$ $VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$ $E_0^{\circ} = + 0.32 V$ $V^{3+} + e^{-} \rightleftharpoons V^{2+}$ $E^{\circ} = -0.26 V$ $E^{\circ} = -0.28 V$ $Co^{2+} + 2e^{-} \rightleftharpoons Co$ $Fe^{3+} + 3e^{-} \rightleftharpoons Fe$ $E^{\circ} = -0.04 V$ $Ni^{2+} + 2e^{-} \rightleftharpoons Ni$ $E^{\circ} = -0.25 V$ Co reducing V(+5) to V(+3) $E_{cell}^{\circ} = +1.00 - (-0.28) = 1.28 \text{ V} > 0$ $E_{cell}^{\circ} = +0.32 - (-0.28) = 0.60 \text{ V} > 0$ $E_{cell}^{\circ} = -0.26 - (-0.28) = 0.02 \text{ V} > 0 \text{ but too small}$ Fe reducing V(+5) to V(+3)

 $E^{\circ}_{cell} = +1.00 - (-0.04) = 1.04 \text{ V} > 0$ $E^{\circ}_{cell} = +0.32 - (-0.04) = 0.36 \text{ V} > 0$ $E^{\circ}_{cell} = -0.26 - (-0.04) = -0.22 \text{ V} < 0$

Ni reducing V(+5) to V(+3) $E_{cell}^{\circ} = +1.00 - (-0.25) = 1.25 \text{ V} > 0$ $E_{cell}^{\circ} = +0.32 - (-0.25) = 0.57 \text{ V} > 0$ $E_{cell}^{\circ} = -0.26 - (-0.25) = 0.01 \text{ V} > 0$ but too small The E_{cell}° potential for Co ²⁺ /Co (Fe ³⁺ /Fe or Ni ²⁺ /Ni) is bigger(less negative/more positive) than that for V ³⁺ /V ²⁺ .	
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	•
	•
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[3	;] ,

[Total: 14]

For Examiner's

5 The standard enthalpy change of fusion (ΔH^{e}_{fus}) is the energy required to convert one mole of a substance in the solid state to the liquid state under standard pressure. The table below shows numerical values of standard enthalpy change of fusion for the respective elements:

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Element	ΔH^{e}_{fus} / kJ mol ⁻¹
Na	2.60
AI	10.7
Si	50.2
CI	6.41

(a) Explain, in terms of structure and bonding, the difference in the ΔH^{Θ}_{fus} between: (i) Si and Cl

Silicon has a <u>giant covalent structure</u> while chlorine has a <u>simple molecular</u> <u>structure</u>.

Melting of silicon requires breaking the <u>numerous strong covalent bonds</u> <u>between the atoms</u> while melting of chlorine requires overcoming the <u>weak</u> <u>dispersion forces between the molecules</u>.

Hence, more energy is required for silicon.

......[2]

(ii) Na and Al

Both aluminium and sodium have <u>giant metallic structures with strong</u> metallic bonds between the cations and delocalised sea of electrons.

<u>Aluminium contributes more electrons for metallic bonding</u> than sodium and the cation has smaller ionic radius. Hence the metallic bonds in aluminium are stronger and more energy is required for the fusion process.

......[2]

(b) Experimental results show that the first ionisation energies for the elements phosphorus and iodine are similar. Suggest an explanation for the observations.

lodine has more protons \rightarrow has a higher nuclear charge.

However, valence electrons are further away from the nucleus \rightarrow experiences greater screening effect.

As a result, the valence electron in I experiences similar effective nuclear effect as that in $P \rightarrow$ requires similar energies to remove the electron.

......[2]

[Total: 6]

 X_2 and Y_2 are halogens and they are known to be more soluble in organic solvents.

In an experiment, excess X_2 was mixed with Na₂S₂O₃(aq). When hexane was added, two immiscible layers were observed and was later separated using a separatory funnel. A reddish brown organic layer was obtained and the aqueous layer was divided into 2 portions.

To one portion of the aqueous layer, $Y_2(aq)$ was added and shaken. When CCl_4 was added, a violet organic layer was obtained.

To another portion of the aqueous layer, $AgNO_3(aq)$ was added. The precipitate formed does not dissolve in aqueous $NH_{3.}$

(a) Suggest a suitable identity of X_2 and Y_2 .

X₂: Bromine

Y₂: lodine

[1]

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(b) Write a balanced ionic equation for the reaction between $Na_2S_2O_3$ and X_2 .

 $4Br_2(l) + S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Br^{-}(aq) + 10H^{+}(aq)$

.....[1]

- (c) Explain in energy terms, why halogens are more soluble in organic solvent than in water.
 - In order for halogens to be soluble in organic solvents,
 - Interactions between the halogen molecules and the solvent molecules must be formed,
 - Since the intermolecular forces are similar in both halogen molecules and the solvent molecules are similar (e.g. van der Waals' forces),
 - The energy evolved in bond formation is likely able to compensate the energy that is needed to break the interactions. Hence, it is energetically favourable.

......[2]

[Total: 4]

7 Keratin refers to a family of fibrous proteins which is the key component of hair and nails. The keratins in hair consist of α-helically coiled single protein strands, further twisted into superhelical ropes that may be further coiled. The presence of keratins determines the strength and structure of hair i.e. straight or wavy. Nails, which are less flexible and elastic, contains keratins which have β-pleated sheets twisted together, stabilised and hardened by R-group interactions.

The table below shows the amino acid composition of 2 samples of keratins. One sample was extracted from nails, the other sample from hair.

	_	Amino acid composition		
Acid	R group	Sample A	Sample B	
asp	-CH2CO2H	3.0	3.0	
asn	CH ₂ CONH ₂	3.0	2.0	
thr	-CH(OH)CH ₃	6.9	4.5	
ser	-CH ₂ OH	11.7	8.5	
glu	$-CH_2CH_2CO_2H$	6.1	6.1	
tyr	—CH2 — ОН	1.9	4.2	
pro	CH ₂ CH ₂ (cyclic)	3.6	3.2	
gly	_H	6.5	5.6	
ala	-CH ₃	4.8	3.2	
cys	-CH ₂ SH	17.5	28.2	
val	-CH(CH ₃) ₂	5.9	5.9	
met	$-CH_2CH_2SCH_3$	0.5	3.5	
ile	-CH(CH ₃)CH ₂ CH ₃	2.7	2.7	
leu	-CH ₂ CH(CH ₃) ₂	6.1	6.0	
gln	$-CH_2CH_2CONH_2$	6.0	5.8	
phe		1.4	4.5	
trp	-CH ₂ -C	3.7	3.0	
lys	$-CH_2CH_2CH_2CH_2NH_2$	2.3	3.8	
his	$-CH_2 - C$	0.8	2.1	
arg	$-CH_2CH_2CH_2NHC(NH_2)=NH_2^+$	5.6	6.2	

(a) Draw a diagram representing the secondary structure of keratins found in nails. In your diagram, show clearly the bonding that is involved in stabilising the secondary structure. You may represent the R groups using the symbol "**R**".



[3]

- (b) By referring to the amino acid composition data, answer the questions below:
 - (i) State the R group interaction that is mainly responsible for the stabilisation of the tertiary structure of keratins. Write an equation to support your answer.

Disulfide bonds

$$-CH_2-S-H + H-S-CH_2- + [O] \rightarrow -CH_2-S-S-CH_2- + H_2O$$

(ii) In order to straighten wavy hair permanently, using a heating iron is insufficient. Instead, one will need to go to the hairdresser to undergo a treatment of chemicals. Explain why.

Disulfide bonds are covalent and strong, hence not easily broken by heating. Treatment with chemicals is required.

(iii) Which sample belongs to keratins extracted from a nail sample? Explain.

Nails are less flexible implying that there are more disulfide bonds (i.e. cross linkages) formed between the R groups.

Hence the sample with greater amount of cys residues is probably keratins from nail.

[5]

[Total: 8]

8(a) There are four stereoisomers of compound P.



What is the type of stereoisomerism exhibited by **P**? Draw the stereoisomers of **P**. Type of stereoisomerism: *cis-trans* / geometric.....





- 9 When methylbenzene is nitrated by a mixture of concentrated nitric acid and concentrated sulfuric acid, the product consists largely of two isomers, V and W, of formula C₇H₇NO₂. V has a plane of symmetry perpendicular to the plane of the benzene ring in its molecule, while W does not. The formation of V proceeds via an organic intermediate X.
- (a) Draw the displayed formulae of V and X, showing clearly the geometry of the bonds around the carbon atom bonded to the nitrogen atom.



(b) What is the name of the mechanism of the reaction for the formation of V? Briefly outline the mechanism of this reaction using equations.

Name of mechanism: Electrophilic substitution

Mechanism:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$



[2]

[Total: 4]