NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME									
CLASS	1	1			INDEX NO.				TUTOR

CHEMISTRY 9647/02

Paper 2 Structured **10 September 2012**

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
1	P	/12
2	/ 8	
3	/ 7	
4	/ 14	
5	/ 6	
6	/ 4	
7	/ 8	
8	/ 9	
9	/ 4	/60

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 ^{o}C) which can be prepared by a reaction between 4-aminophenol and ethanoic anhydride.

$HOC_6H_4NH_2$	$(CH_3CO)_2O$	$CH_3CONHC_6H_4OH$
4-aminophenol	ethanoic anhydride	paracetamol
(M_r = 109)	(M_r = 102)	(M_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;

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

[3]

(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.

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(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.**

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(d) Identify two potential safety hazards in this experiment and the relevant safety precautions you would take.

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..... [2]

[Total: 12]

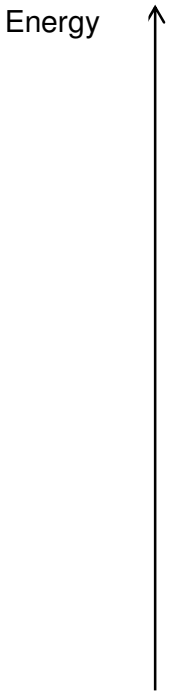
For Examiner's Use

2 Given the following thermochemical data:

Reaction	**$\Delta H^{\ominus}$ / kJ mol^{-1}**
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	–75.0
$C(graphite) + O_2(g) \rightarrow CO_2(g)$	–393.5
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	–285.9

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

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



[3]

[Turn over

For Examiner's Use

(b) The experimental enthalpy change is –801.7 kJ mol^{-1} for the following reaction

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g) \text{ ……..(I)}$$

(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)**.

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[3]

[Total: 8]

3 Mixtures of citric acid, $C_5H_7O_4CO_2H$ (K_a = 7.40 x 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 cm^3 of 0.200 mol dm^{-3} citric acid and 2.48 g of sodium citrate (M_r = 198) is 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.

[3]

(c) Determine the volume of 0.100 mol dm^{-3} of HCl(aq) that needs to be added to the solution in **(a)** to obtain a buffer at its maximum buffering capacity.

[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.

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..... [1]

(b) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution. When a mixture of the pink solution and tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$, 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.

$CoCl_2(aq)$:.....

Tartaric acid: .....

Equation: .....

[3]

For Examiner's Use

(c) Aqueous $CoCl_2$ also undergoes the following reaction.

$$CoCl_2(aq) \xrightarrow[\text{and } O_2]{\text{I } NH_4Cl,\ NH_3} \text{Crystals of salt } \mathbf{K}$$

(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 AgCl(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**.

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(iii) $E^{\ominus}$ data for some cobalt complex ions are given below.

$[Co(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}(aq)$ $\quad E^{\ominus} = +0.57$ V

$[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}(aq)$ $\quad E^{\ominus} = +0.11$ V

Use the $E^{\ominus}$ data given above to predict the reaction, if any, of adding $C_2O_4^{2-}$ to **K**. Explain your prediction.

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[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.

Identity of the transition metal: .....

Explanation:

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..... [3]

[Total: 14]

For Examiner's Use

5 The standard enthalpy change of fusion ($\Delta H^{\ominus}_{fus}$) 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:

Element	$\Delta H^{\ominus}_{fus}$ / kJ mol^{-1}
Na	2.60
Al	10.7
Si	50.2
Cl	6.41

(a) Explain, in terms of structure and bonding, the difference in the $\Delta H^{\ominus}_{fus}$ between:

(i) Si and Cl

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(ii) Na and Al

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

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[Total: 6]

6 $\mathbf{X_2}$ and $\mathbf{Y_2}$ are halogens and they are known to be more soluble in organic solvents.

In an experiment, excess $\mathbf{X_2}$ was mixed with $Na_2S_2O_3$(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, $\mathbf{Y_2}$(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 $\mathbf{X_2}$ and $\mathbf{Y_2}$.

$\mathbf{X_2}$: …… $\mathbf{Y_2}$: ……[1]

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

..... [1]

(c) Explain in energy terms, why halogens are more soluble in organic solvent than in water.

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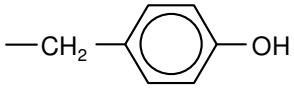
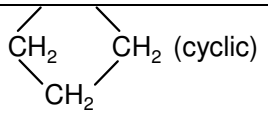
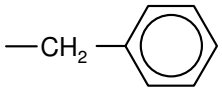
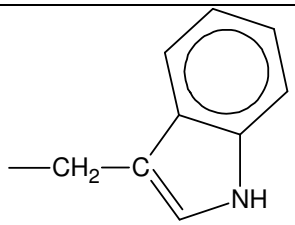
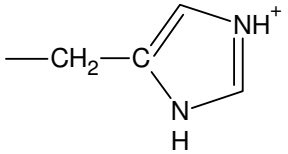
[Total: 4]

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.

Acid	R group	Amino acid composition	
		Sample A	Sample B
asp	$-CH_2CO_2H$	3.0	3.0
asn	CH_2CONH_2	3.0	2.0
thr	$-CH(OH)CH_3$	6.9	4.5
ser	$-CH_2OH$	11.7	8.5
glu	$-CH_2CH_2CO_2H$	6.1	6.1
tyr		1.9	4.2
pro		3.6	3.2
gly	$-H$	6.5	5.6
ala	$-CH_3$	4.8	3.2
cys	$-CH_2SH$	17.5	28.2
val	$-CH(CH_3)_2$	5.9	5.9
met	$-CH_2CH_2SCH_3$	0.5	3.5
ile	$-CH(CH_3)CH_2CH_3$	2.7	2.7
leu	$-CH_2CH(CH_3)_2$	6.1	6.0
gln	$-CH_2CH_2CONH_2$	6.0	5.8
phe		1.4	4.5
trp		3.7	3.0
lys	$-CH_2CH_2CH_2CH_2NH_2$	2.3	3.8
his		0.8	2.1
arg	$-CH_2CH_2CH_2NHC(NH_2)=NH_2^+$	5.6	6.2

[Turn over

For Examiner's Use

(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.

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(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.

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

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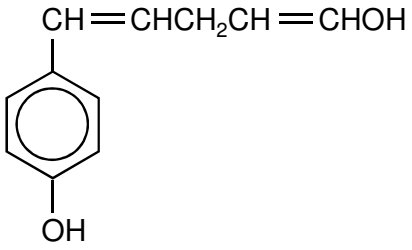
[5]

[Total: 8]

For Examiner's Use

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



P

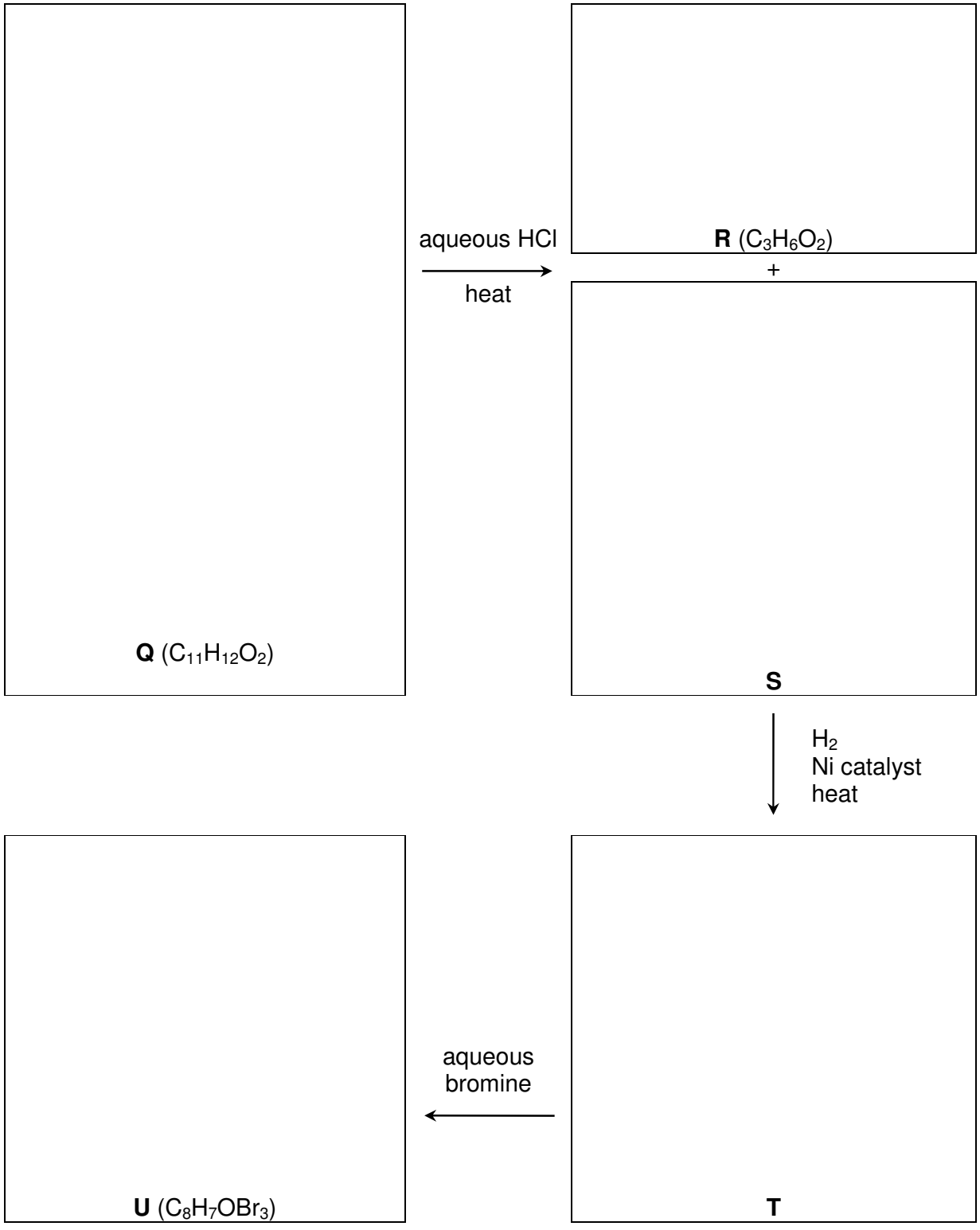
What is the type of stereoisomerism exhibited by **P**? Draw the stereoisomers of **P**.

Type of stereoisomerism: .....

[4]

For Examiner's Use

(b) **Q** is a structural isomer of **P** in **(a)**.
Suggest the structures of **Q**, **R**, **S**, **T** and **U** in the reaction scheme below.



[5]

[Total: 9]

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 $C_7H_7NO_2$. **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.

isomer **V**	*organic intermediate* **X**

[2]

(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: .....

Mechanism:

[2]

[Total: 4]

[End of Paper]