

# CHEMISTRY

9729/02

Paper 2 Structured Questions

2 hours

## READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question, or part question.

Question	1	2	3	4	5	6	Total
Marks scored							
Maximum Marks	12	11	11	12	8	21	75

- 1 (a) In 1967, scientists around the world met up to determine the standard of the second. Prior to that, the second was not properly standardised across the world.

$^{133}\text{Cs}$  atomic clocks were used to determine the standard of the second. When an atom is placed under an electromagnetic field, its valence electrons oscillate at a fixed rate. The rate of oscillation was used to determine the standard of the second. It's estimated that the margin of error is at 1 second per 1.4 million Earth years.

- (i) Cs is vaporised to ensure more accurate measurements. The interactions in Cs at room temperature may interfere with the measurements taken.

Describe these 'interactions' in Cs at room temperature. Refer to the structure and bonding in Cs.

.....  
.....  
.....  
.....[2]

- (ii) As there were many atomic clocks at that time, much of the discussion centred around what element was to be used. 2 of the criteria are listed below:

- low number of active electrons
- easy to vapourise

A student proposed 2 other elements that can be used: Pb and Li.

Suggest why these elements are poorer candidates compared to Cs.

.....  
.....  
.....  
.....[2]

- (b) (i) State how the reducing power of the Group 1 metals varies down the group with reference to relevant standard electrode potential values.

.....  
.....[1]

(ii) Explain the variation of the first ionisation energy of the Group 1 metals down the group.

.....  
.....[1]

(c) (i) A student attempted to measure the standard electrode potential of the reduction of the aqueous  $\text{Cs}^+$  ion to Cs metal directly against a standard hydrogen electrode.

Explain why his method would **not** work.

.....  
.....  
.....  
.....[2]

(ii) Molten CsF was electrolysed. A constant current of 2.00 A was passed through the setup for 48 hours. Calculate the mass of molten Cs that is extracted.

[2]

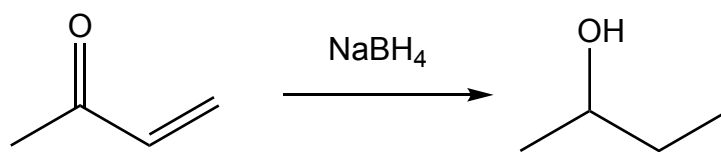
(d) Group 1 metals form peroxides (general formula:  $\text{M}_2\text{O}_2$ ) after long exposure to oxygen. Under heating, these peroxides decompose to their respective oxides, and oxygen gas is produced as a byproduct.

Suggest an explanation for the variation of the decomposition temperatures of the peroxides  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{O}_2$ ,  $\text{Rb}_2\text{O}_2$  and  $\text{Cs}_2\text{O}_2$ .

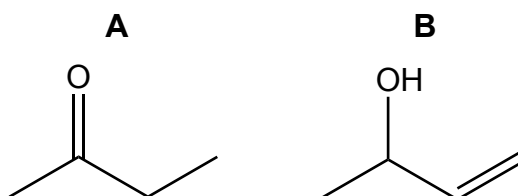
.....  
.....  
.....  
.....[2]

[Total: 12]

2 But-3-en-2-one may be reduced by  $\text{NaBH}_4$  to form a racemic mixture of butan-2-ol.



(a) (i) This reaction occurs through an intermediate. The intermediate is either **A** or **B**.



By considering which intermediate can react with  $\text{NaBH}_4$ , suggest which intermediate is produced in this reaction. Explain your answer.

.....  
.....  
.....  
.....[2]

(ii) State **2** tests which may distinguish **A** from **B**. State the accompanying observations.

.....  
.....  
.....  
.....[2]

(iii) Explain why a racemic mixture of butan-2-ol is produced.

.....  
.....[1]

(iv) State another set of reagent(s) and conditions which converts but-3-en-2-one to butan-2-ol.

.....[1]

(b) Equal amounts of aqueous Br<sub>2</sub> were added to 2 separate test tubes **X** and **Y** containing equal amounts but-3-en-2-one and **B** respectively.

In test tube **Y**, 2 products were formed. One product contains a 3-membered ring.

(i) Describe the mechanism in test tube **Y** where the product containing the 3-membered ring is formed.

[3]

(ii) Explain whether the solution in test tube **X** or **Y** will decolourise faster after aqueous bromine is added to it.

.....  
.....  
.....  
.....[2]

[Total: 11]

3 (a) State the electronic configuration of the Ni<sup>2+</sup> ion.

..... [1]

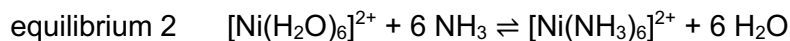
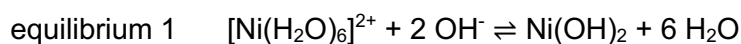
(b) An aqueous solution of NiCl<sub>2</sub> is green. This is due to the colour of the ion [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Explain why the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion is green in colour.

.....  
.....  
.....  
..... [3]

(c) State Le Chatelier's principle.

.....  
..... [1]

(d) Equilibrium 1 and 2 are 2 reactions that the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion may undergo.



A student recorded the following observation:

When aqueous ammonia was added dropwise, a green precipitate formed. The green precipitate subsequently dissolved to form a blue solution after addition of more aqueous ammonia.

Use Le Chatelier's principle to explain the observation.

.....  
.....  
.....  
..... [2]

- (e) When 4 ligands are bonded to a metal centre, the geometry of the metal centre may be either square planar or tetrahedral.

The complex ion  $[\text{Ni}(\text{Br})_2(\text{CN})_2]^{2-}$  exhibits stereoisomerism.

Draw the 3-dimensional structures of the 2 stereoisomers of  $[\text{Ni}(\text{Br})_2(\text{CN})_2]^{2-}$  and assign a stereochemical descriptor for the isomers.

[2]

- (f) The Mond process is used to purify nickel from nickel ores that contain trace amounts of iron and cobalt. The process may be described as:

1. Impure nickel reacts with gaseous carbon monoxide (CO) to form  $\text{Ni}(\text{CO})_4$ .
2. The liquid  $\text{Ni}(\text{CO})_4$  collected is then heated to reform pure nickel metal.

- (i) Draw the dot-and-cross diagram of CO.

[1]

- (ii) Briefly explain why this process has fallen out of use.

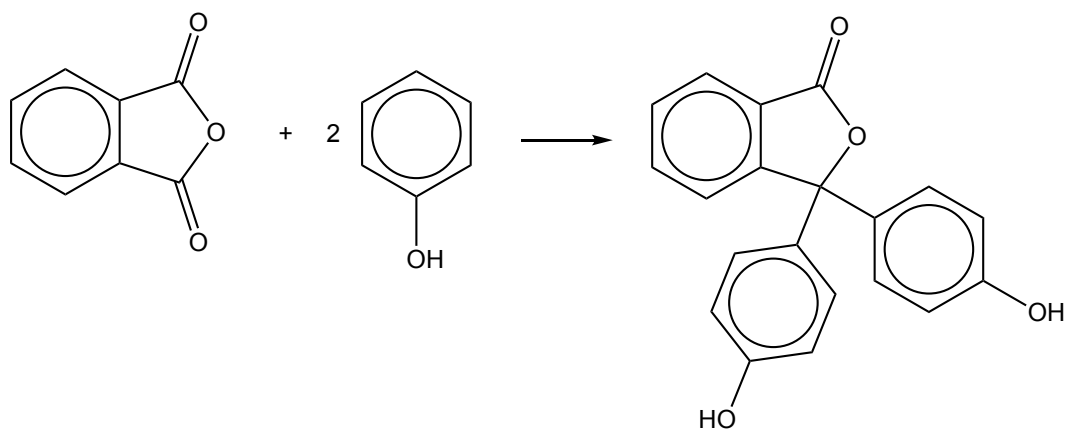
.....

.....[1]

[Total: 11]

4 (a) Phenolphthalein ( $M_r = 318.3$ ) is a common indicator used in acid-base titrations.

(i) Phenolphthalein can be synthesised from phenol.



State the type of reaction occurring above.

.....[1]

(ii) Complete the skeletal structure of the resultant organic product(s) formed when phenolphthalein is subjected to the following reagents and conditions:

excess hot NaOH(aq)	
excess Br <sub>2</sub> (aq)	

[2]



- (b) Phenolphthalein may be represented as HIn. The violet colour of the  $\text{In}^-$  species makes phenolphthalein a good pH change detector. At  $25^\circ\text{C}$ ,  $\text{p}K_a(\text{HIn}) = 9.30$ .

“Disappearing ink” contains a small amount of phenolphthalein. When mixed with a suitable concentration of sodium hydroxide, the ink turns pink. However, after leaving the ink exposed to the atmosphere for an extended period of time, the ink turns colourless. This can be explained by the presence of carbon dioxide in the atmosphere.

- (i) Write a balanced chemical equation for the reaction between carbon dioxide and hydroxide ions to form carbonate ions.

.....[1]

- (ii) Suggest whether a very dilute solution of ammonia can be used in “disappearing ink”.

.....  
.....[1]

- (iii) In a brand of “disappearing ink”, the pH of the ink was recorded to be 11.0 at  $25^\circ\text{C}$ . The “disappearing ink” also contains 0.01% w/v phenolphthalein. Assume that phenolphthalein does not interfere with the basicity of the solution.

Find the final pH of  $5.00\text{ cm}^3$  of disappearing ink up to the extent where the reaction in (i) is complete.

$[\text{p}K_a(\text{HCO}_3^-) = 10.3 \text{ at } 25^\circ\text{C}]$

[2]

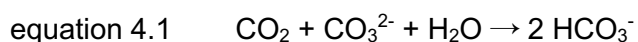
(iv) "1% w/v" means 1 gram of solute per 100 cm<sup>3</sup> of solvent.

Assume that for there to be a pink colour still visible by the naked eye, [In<sup>-</sup>] must be at least  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>.

Determine if the sample of "disappearing ink" is effective if the manufacturer is expecting the phenolphthalein indicator to decolourise at pH 8.5 at 25°C.

[2]

(v) Carbonate ions will further react with CO<sub>2</sub> to form HCO<sub>3</sub><sup>-</sup> ions via equation 4.1.



Starting with 5.00 cm<sup>3</sup> of a fresh solution of "disappearing ink", complete the graph of pH against amount of CO<sub>2</sub> reacted with "disappearing ink" to the extent where the reaction in equation 4.1 is complete at 25°C. You do not need to indicate the final pH of the solution.



(vi) The colour of "disappearing ink" can be modified by changing the indicator used. Suggest another indicator that will achieve this effect, and state the ink colour.

.....[1]

[Total: 12]

- 5 (a) When a reactant displays second-order kinetics, its subsequent half-life is 2 times that of its previous.

A hydrocarbon, **H**, with only 1 alkene functional group is reacted with bromine. Both chemicals are dissolved in tetrachloromethane.

In the space below, sketch a graph of **[H]** against time when the initial concentrations are

(i)  $[\text{H}]_{\text{initial}} = 0.100 \text{ mol dm}^{-3}$  and  $[\text{Br}_2]_{\text{initial}} = 2.00 \text{ mol dm}^{-3}$

(ii)  $[\text{H}]_{\text{initial}} = [\text{Br}_2]_{\text{initial}} = 0.100 \text{ mol dm}^{-3}$

[3]

- (b) The hydrocarbon **H** is aromatic too.

Explain why aromatic compounds will **not** undergo addition reactions with  $\text{Br}_2$ .

.....  
..... [1]

(c) The  $M_r$  of **H** is 132 to the nearest integer.

When **H** is heated with concentrated  $\text{KMnO}_4$  under acidic conditions, only benzoic acid was formed as an organic product.

Deduce the/all possible isomer(s) of **H** by drawing its/their skeletal structure(s).

[4]

[Total: 8]

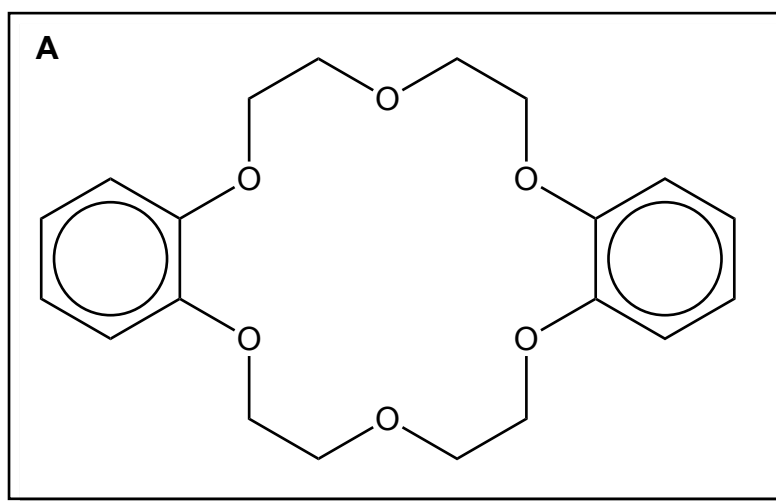
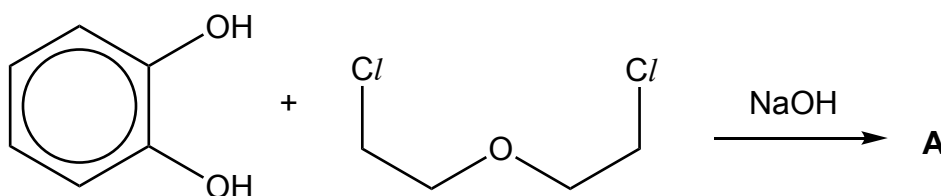
6 Molecular capsules are large molecules that can capture a small molecule or ion through chemical interactions.

(a) (i) A common issue organic chemists face is that salts like  $\text{KMnO}_4$  do not dissolve readily into organic solvents such as benzene.

Suggest an explanation for this.

.....  
.....[1]

The molecular capsule **A** can assist the solution of  $\text{KMnO}_4$  in benzene. Its synthetic route is shown below.



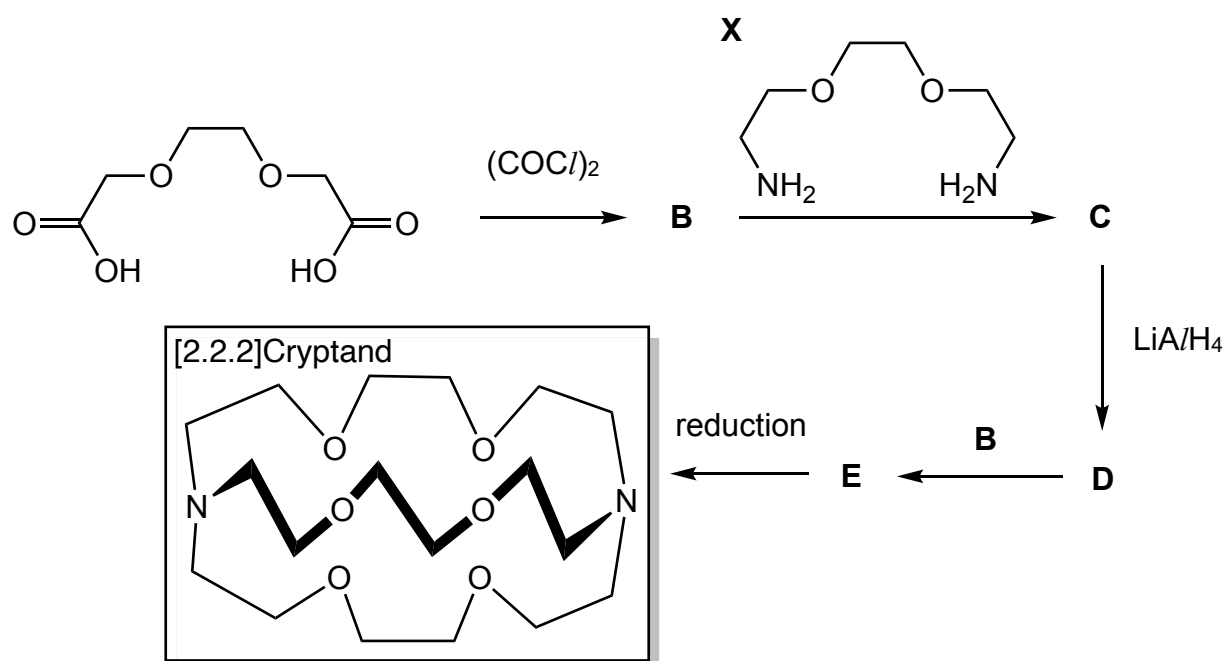
(ii) Suggest a mechanism for this reaction. You may use the space in the next page.

[4]

(iii) Explain why without the use of NaOH, this reaction would proceed much slower.

.....  
.....[1]

The following synthetic pathway is used to synthesise [2.2.2]cryptand, another molecular capsule.



(iv) **B** has an elemental composition of 33.52% carbon, 3.75% hydrogen and 29.76% oxygen by mass. Determine the molecular formula of **B**, and hence, draw the structure of **B**.

[3]

(v) Suggest 2 reagents that can be used in the place of  $(\text{COCl})_2$  to synthesise **B**.

.....[1]

(vi) Draw the structures of **C** and **D**. **D** has a molecular formula of  $\text{C}_{12}\text{H}_{26}\text{O}_4\text{N}_2$ .

[2]

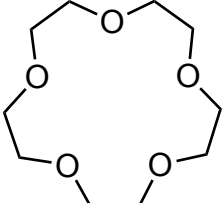
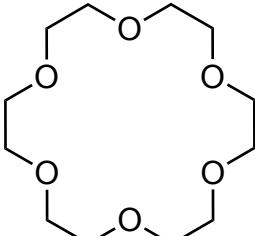
(vii) When **B** is reacted with amine **X**, other byproducts can be formed.

Suggest why conducting the reaction in a large volume of an appropriate solvent will favour a high yield of **C**.

.....  
.....  
.....[2]

(b) Crown ethers are a family of molecular capsules which can solvate Group 1 ions in organic solvents.

The table shows 2 crown ethers with the diameters of their cavities (space within the molecule).

Crown ether	Diameter of cavity / pm	Group 1 ion
	170 to 220	
	260 to 320	

In order for the crown ether to most effectively capture a Group 1 ion, the Group 1 ion should fit in the cavity most compactly.

Fill in the ion that would most effectively be captured by the crown ether. [1000 pm = 1 nm] [1]

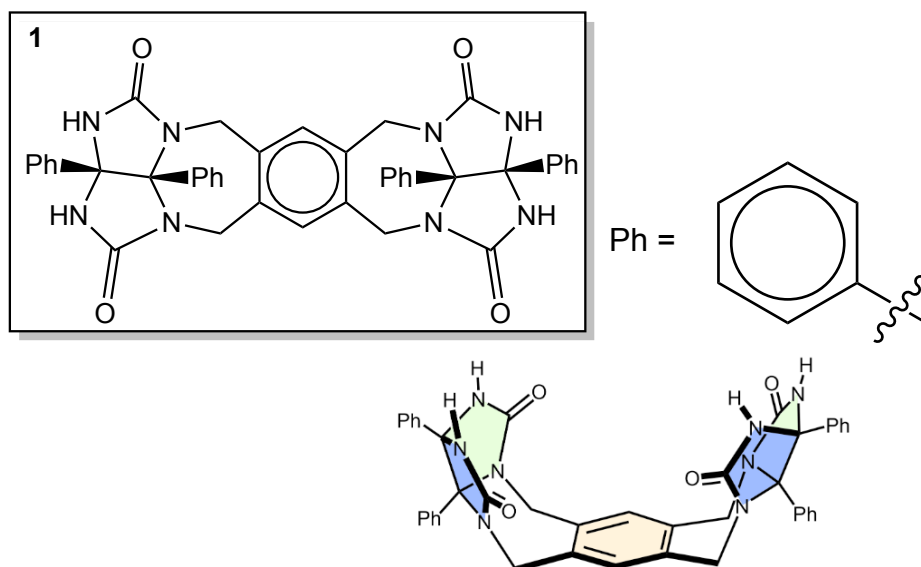
(c) A tennis ball can be unseamed, revealing 2 U-shaped pieces.



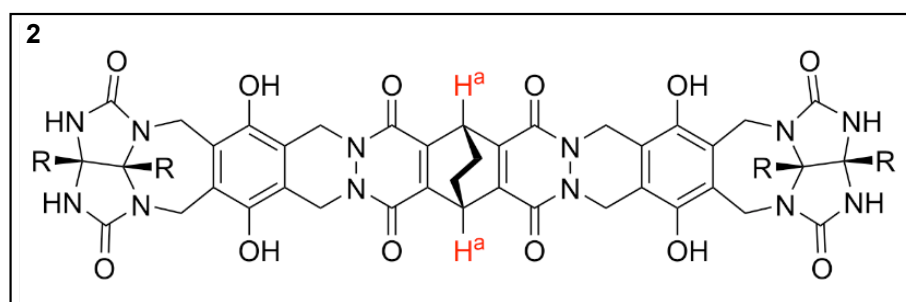


Based on this idea, molecules **1** and **2** were synthesised to study their encapsulation behaviour for different molecules.

The structure of **1** and **2** is shown below.



**Fig 6.1.** 3D model of **1**



- (i) Analysis shows that **1** forms a dimer with itself through hydrogen bonds.

The hydrogen atoms covalently bonded to N in **1** are involved in hydrogen bonding.

On the structure of **1**, circle the other atom(s) that is/are involved in hydrogen bonding, and state the number of hydrogen bond(s) formed in a dimer of **1**.

.....[2]

- (ii) The dimer of **2** can encapsulate 2 molecules of benzene, PhH, or 2 molecules of fluorobenzene, PhF.

Nuclear Magnetic Resonance (NMR) spectroscopy can be used to determine the different types of hydrogen atoms in a molecule.

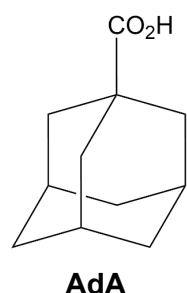
When a hydrogen atom records a different chemical shift in the NMR spectrum, it means that the hydrogen atom is in a different chemical environment.

Solvent	Chemical shift of H <sup>a</sup> on <b>2</b>
PhH	4.60
PhF	4.71
mixture of PhH and PhF	4.60, 4.71, 4.82

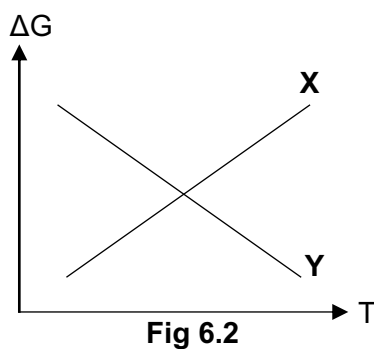
Explain how this set of results in the table on this page show that the dimer of **2** can encapsulate 1 molecule of PhH and 1 molecule of PhF.

.....  
 .....[1]

(iii) The dimer of **2** can encapsulate 1 molecule of **AdA**.



**Fig 6.2** illustrates how the Gibbs Free Energy may vary with respect to temperature, T, of the encapsulation of the molecule **AdA** by the dimer of **2** when dissolved in benzene.



Which line represents the encapsulation of **AdA** by the dimer of **2**? Explain your answer.

It would help to consider that 2 molecules of benzene are encapsulated by the dimer of **2** initially when **2** is dissolved in benzene.

.....  
 .....  
 .....[3]

[Total: 21]