1 Planning (P)

For Examiner's use

When a solute is added to two solvents, A and B, which do not mix, some of the solute dissolves in each of the solvents and an equilibrium is set up between the two solvents. It has been shown that for dilute solutions, at equilibrium the ratio of the two concentrations is a constant known as the **Partition Coefficient**, ***K***, and it will remain a constant if the solute remains in the same molecular state in the two solvents.

$$\frac{\text{Concentration of solute in solvent A}}{\text{Concentration of solute in solvent B}} = K$$

An experiment was conducted to verify the above observation. Ethanoic acid (solute) was shaken with two immiscible solvents (water and cyclohexane, (C_6H_{12})), so that the solute distributed itself between the two solvents. The concentrations of the two solutions were then determined so that the ratio $[CH_3COOH]_{aq}$ / $[CH_3COOH]_S$ known as the ***Partition Coefficient, K*** can be calculated at a given temperature.

Using apparatus which are found as standard items in a school laboratory, an experiment was carried out to determine the ***Partition Coefficient***, ***K*** for ethanoic acid, CH_3COOH, between water and cyclohexane, (C_6H_{12}).

The following steps were carried out:

1. 5.0 g of the sample was first dissolved in 50 cm^3 of water in a beaker and the aqueous solution was then transferred into a separating funnel.

2. 50 cm^3 of cyclohexane was then poured into the separating funnel containing the aqueous solution, stoppered and shaken intermittently.

3. The concentration of ethanoic acid in the two layers was then determined by titration with 0.05 mol dm^{-3} NaOH.

(a) (i) Outline how a fixed volume of the sample of the aqueous layer can be removed from the mixture in the separating funnel for titrimetric analysis. (Note: The organic layer is less dense compared with the aqueous layer.)

[2]

For Examiner's use

(ii) Outline stepwise how the removed sample could be analysed by titration to determine the concentration of the solute that had dissolved in that layer.

[2]

(b) When analysing the organic layer, a fixed volume of water (about twice the volume) is added to the pipetted volume of cyclohexane solution in the conical flask and shaken vigorously, prior to the titration. Explain the purpose of this action.

[2]

(c) Based on your procedure, state and explain one significant error or limitation that could be encountered in determining an accurate value for the distribution ratio.

[1]

(d) Suggest one possible modification that would minimise the error or limitation that you have stated in **(c)**. Explain how this modification leads to an improvement in the accuracy and reliability of the results.

[1]

For Examiner's use

(e) A student did the above experiment but carried out only one titration using a fixed aliquot of the aqueous layer and then proceeded to use the titre value to calculate a value for K. Assuming the student obtained a titre value of ***y*** cm^3 of ***M*** mol dm^{-3} NaOH (aq) when 10.0 cm^3 of the aqueous layer was titrated, outline how the student could have used the result to determine a value for K.

[3]

(f) When a solute is distributed between the two immiscible solvents, it is important to ensure that the resulting solutions are dilute for the distribution to occur and the partition coefficient to remain constant. Suggest why this is critical in this experiment.

[1]

[Total: 12]

2 (a) A hydrocarbon **W** contains 92.3 % carbon. On complete combustion, 0.005 mol of **W** produces 1.76 g of CO_2.

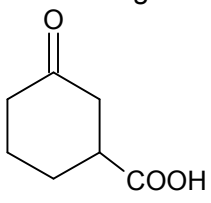
(i) Determine the molecular formula of **W**.

For Examiner's use

(ii) Given that 1 mol of **W** reacts with 1 mol of bromine in tetrachloromethane, draw the displayed formula of **W**.

[3]

(b) Apart from using aqueous bromine or bromine in an inert solvent, describe one other simple chemical test you could carry out to distinguish

W from 

State clearly how **each** compound behaves in the test and write an equation for the reaction involved.

Reagent(s) & conditions:

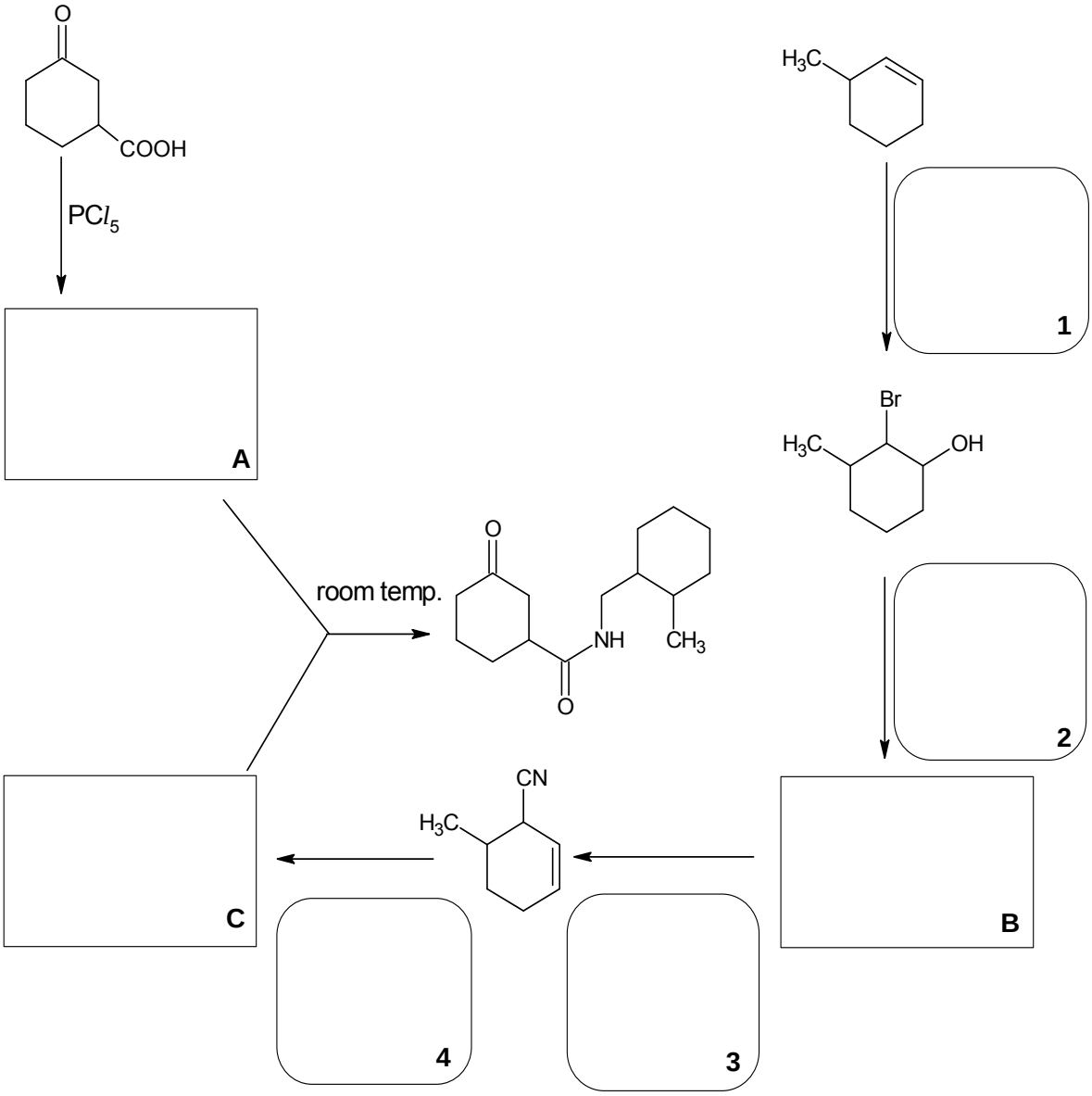
Observations:

Equation:

[3]

(c) Complete the reaction scheme below by writing the structural formula of the organic products (**A-C**) and the reagents and conditions (**1-4**) in the spaces below.

For Examiner's use



[7]

[Total: 13]

For Examiner's use

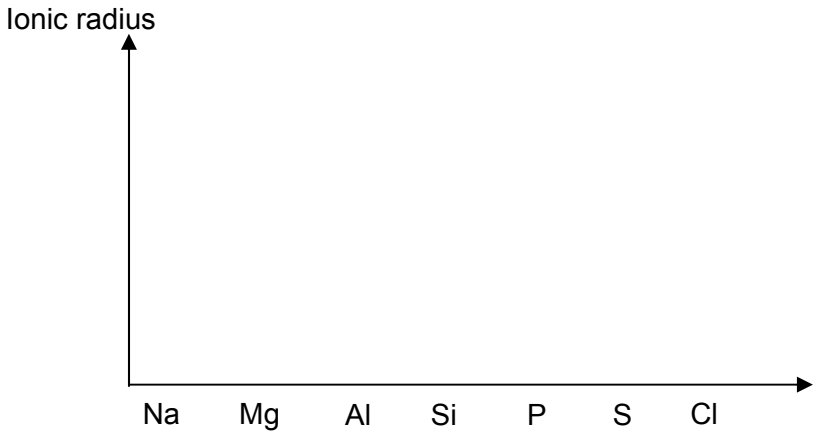
3 (a) Nitrogen and phosphorus belong to Period 2 & 3 respectively. At 373 K, both phosphorus trichloride (boiling point = 350 K) and nitrogen trichloride (boiling point = 344 K) exist as a gas.

(i) State one assumption in the kinetic theory of gases that causes the deviation of a real gas from ideal behaviour.

(ii) Predict with reasons, which of the two gases will deviate more from ideality.

[3]

(b) (i) Sketch the ionic radius of the elements in Period 3 on the axes provided.



For Examiner's use

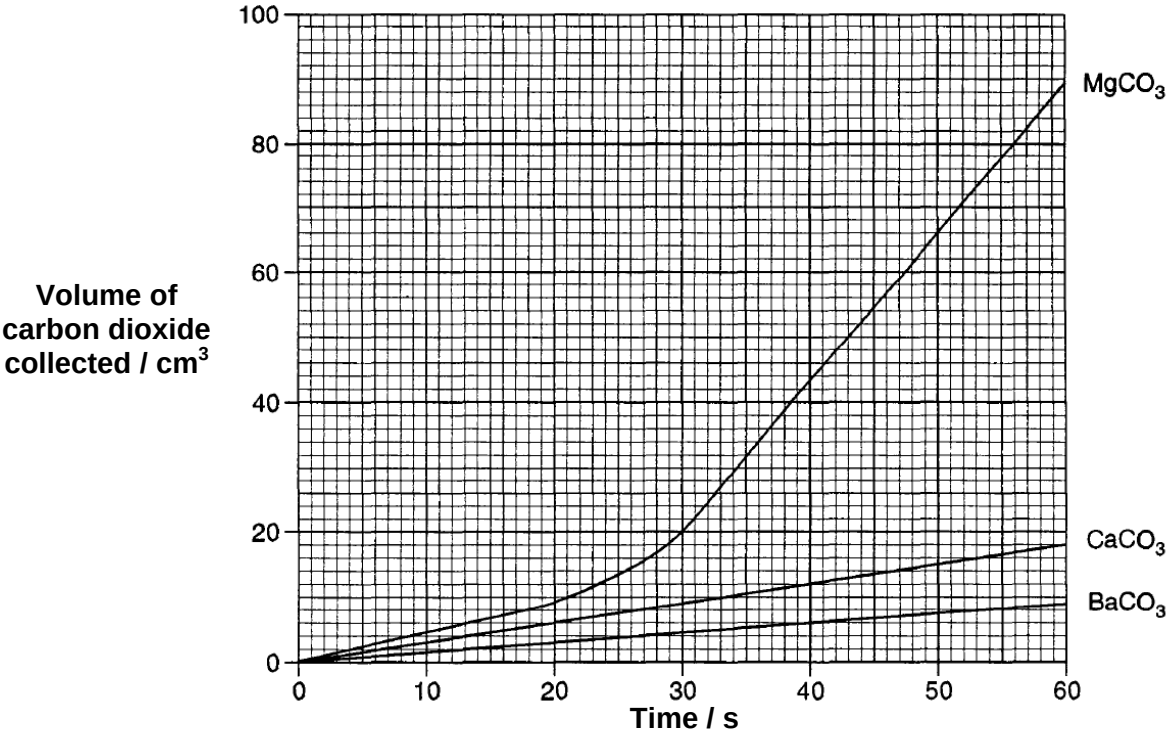
(ii) Explain the shape of your sketch.

[4]

(c) A student investigated the thermal decomposition of the carbonates of some of the Group II elements.

He separately heated the carbonates of magnesium, calcium and barium and recorded the total volume of carbon dioxide collected every 10 seconds. In each experiment, he used the **same amount, in moles**, of each carbonate and used the hottest part of the Bunsen flame.

The graph of his experimental results is given below.



(i) From the graph, identify which carbonate is the least stable.

[1]

For Examiner's use

(ii) What evidence from the graph supports your answer to **c(i)**?

[1]

(iii) Write an equation to represent the thermal decomposition of calcium carbonate.

[1]

(iv) How and why does the lattice energy of calcium carbonate differ from its residue after it has been formed from decomposition?

[2]

(v) Given that the decomposition of $MgCO_3$ is an endothermic process, predict and explain the sign of ΔG for the reaction at high temperatures.

[2]

(vi) A 4.19 g sample of a carbonate of a Group II metal, **X**, lost 1.25 g in mass when heated strongly. Identify metal **X**.

[3]

[Total: 17]

For Examiner's use

4 (a) (i) In the following reaction, discuss whether its behaviour is what you would expect from the position of the element in the Periodic Table.

$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

[1]

(ii) Write the balanced equation for the reaction of BeO with dilute HCl(aq).

[1]

(iii) Dissolving small amounts of $BeCl_2$ in water gives an acidic solution. Write balanced equation(s) for the reaction, if any.

[1]

(iv) Describe what happens if dilute NaOH(aq) is slowly added to the solution in **a(iii)** until in excess.

[2]

(b) Iodine is a Group VII element. On 11 March 2011, a major earthquake struck Japan. Subsequently it caused a nuclear meltdown and the Japanese were given potassium iodide to protect their thyroid glands from radioactive iodine released from nuclear accidents.

(i) State the physical state of iodine under room conditions.

[1]

(ii) Iodine is not soluble in water. An aqueous solution of iodine can only be prepared by dissolving iodine in excess KI(aq) to form a dark reddish brown solution. Identify the iodine-containing species that is formed in this reaction.

[1]

For Examiner's use

(iii) Describe what happens when aqueous silver nitrate is added to aqueous sodium iodide. Write balanced equation(s) for the reaction, if any.

[1]

(iv) What changes (if any) occur when aqueous ammonia is added slowly to mixture in **b(iii)** until in excess?

[1]

(v) What happens when concentrated sulfuric acid is added to solid sodium iodide? Write balanced equation(s) for the reaction, if any.

[1]

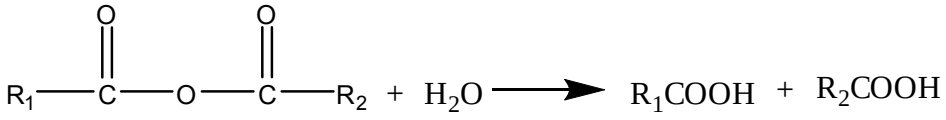
(vi) Iodine undergoes a disproportionation reaction with dilute NaOH(aq). Describe what happens and write a balanced equation for the reaction.

[1]

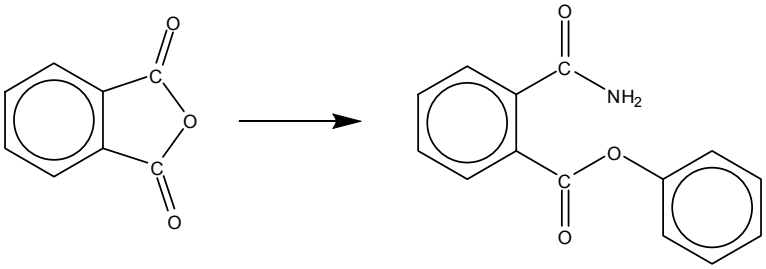
For Examiner's use

(c) Acid anhydrides undergo the same reactions as acid chlorides, but a little more slowly. Whilst acid chlorides yield a molecule of HCl, anhydrides yield a molecule of carboxylic acid.

For example, acid anhydrides undergo hydrolysis as follows:



Hence, suggest a synthesis pathway for the following reaction:



Synthesis Pathway:

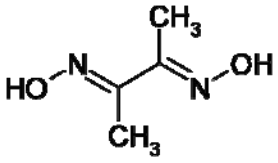
[4]

[Total: 15]

For Examiner's use

5 Ligand substitution reactions are commonly used for the synthesis of nickel (II)-complexes, where one or more ligands are replaced by another.

(a) Dimethylglyoxime (dmg) is used as a reagent in the gravimetric analysis of nickel and its structural formula is given as follows:



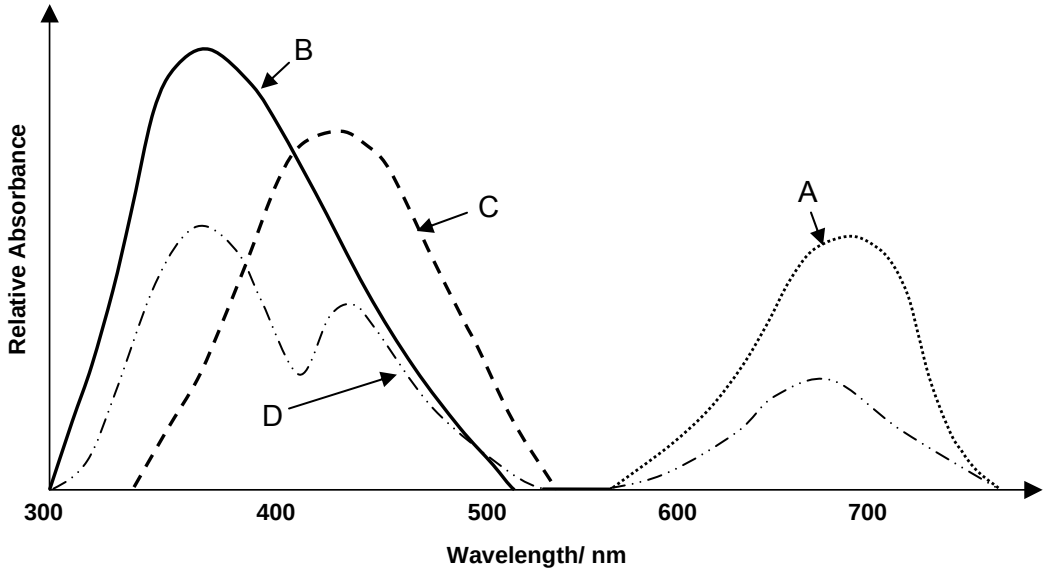
Based on its structural formula, deduce the number of co-ordinate bonds which each dmg molecule can form with a Ni^{2+} ion.

[1]

(b) The following solutions **A**, **B**, **C** and **D** are made up by mixing 0.1 mol dm^{-3} solution of Ni^{2+}, NH_3, $EDTA^{4-}$ and dmg. The table below gives the volumes of each used:

Solution	Volumes of 0.1 mol dm^{-3} solution / cm^3			
	$Ni^{2+}(aq)$	NH_3	$EDTA^{4-}$	dmg
A	1	99	0	0
B	1	0	99	0
C	1	0	0	99
D	1	33	33	33

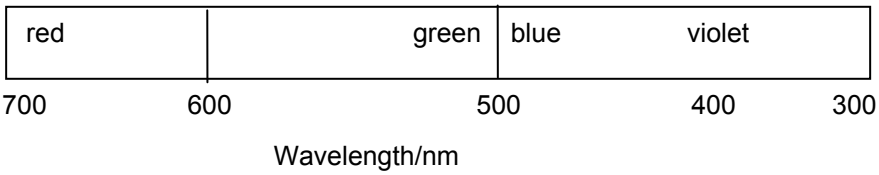
The UV-visible absorption spectra of the four aqueous solutions are shown below:



For Examiner's use

(i) Given that $[Ni(EDTA)]^{2-}$ is colourless and with the aid of the information below deduce the colour of the solutions **A** and **C**.

White Light Spectrum



(ii) The spectra shows that the peak in the curve for the solution **A** is at a longer wavelength than the peak in the curves for solutions **B** and **C**.

What deduction can be made from this fact about the size of the d-subshell splitting in the three complexes? Explain your answer.

(iii) The absorbance of a solution at a particular wavelength is proportional to the concentration of the ion responsible for the absorption.

Use this information and the given absorption spectra to suggest and explain which ligand, NH_3, $EDTA^{4-}$ or dmg, forms the stronger bond with Ni^{2+}.

[7]

For Examiner's use

(c) In the presence of cyanide ions, $[Ni(NH_3)_6]^{2+}$ is able to undergo ligand exchange reaction as shown below:

$$[Ni(NH_3)_6]^{2+}\ (aq) + 4CN^-\ (aq) \rightleftharpoons [Ni(CN)_4]^{2-}\ (aq) + 6NH_3\ (aq)$$
Blue — Colourless

(i) When 1.00 dm^3 of aqueous $[Ni(NH_3)_6]^{2+}$ solution was added to an equal volume of sodium cyanide solution, colour changes are observed.

Given that 0.6 moles of $[Ni(NH_3)_6]^{2+}$, 1.0 moles of CN^- and 0.6 moles of $[Ni(CN)_4]^{2-}$ were mixed together, and when equilibrium was attained, only 0.4 moles of $[Ni(NH_3)_6]^{2+}$ remained.

Determine the K_c for this reaction.

(ii) State the observation when excess aqueous ammonia is added to the above mixture. Explain your answer.

For Examiner's use

(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 $[Ni(NH_3)_6]^{2+}$ and $[Ni(CN)_4]^{2-}$:

Nickel (II)-complex ion	$[Ni(NH_3)_6]^{2+}$	$[Ni(CN)_4]^{2-}$
lg K_{stab}	7.7	31.3

Based on the lg K_{stab} values, account for the K_c value calculated in **(c)(i)**, in terms of exchange of ligands.

[7]

[Total: 15]