

1 Planning (P)

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, (C₆H₁₂)), so that the solute distributed itself between the two solvents. The concentrations of the two solutions were then determined so that the ratio $[\text{CH}_3\text{COOH}]_{\text{aq}}/[\text{CH}_3\text{COOH}]_{\text{s}}$ 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, CH₃COOH, between water and cyclohexane, (C₆H₁₂).

The following steps were carried out:

1. 5.0 g of the sample was first dissolved in 50 cm³ of water in a beaker and the aqueous solution was then transferred into a separating funnel.
 2. 50 cm³ 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.)

Either

- Place a finger on the open end of a 10.0 cm³ pipette and insert it into the bottom aqueous layer.
- Gently blow lightly into the pipette to dispel any organic layer that may have entered the pipette before withdrawing the required amount of sample

Or

- Drain the aqueous layer into one dry beaker and the organic layer into another
- Pipette 10.0 cm³ of the aqueous layer into a conical flask

[2]

- (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.

- Place the pipetted sample into a 250 cm³ conical flask
- Add a drop of phenolphthalein
- Fill a burette with 0.05 mol dm⁻³ aqueous NaOH
- Titrate the sample until a faint pink colour is obtained
- Repeat titration for consistent results

[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.

- NaOH(aq) will not be able to neutralise the ethanoic acid in the organic layer
- The ethanoic acid must be first extracted into the water for complete reaction with the alkali during neutralisation

[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.

- Short equilibration time for partitioning
- Some organic layer could have been sucked up the pipette when collecting aqueous layer for analysis (if student withdrew sample directly from separating funnel)
- Titre reading for organic layer may be lesser than expected due to limited or partial partitioning of acid into water

[Any one of the above - 1]

[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.

- Allow a longer time for partitioning/distribution of acid between the two solvents
- Add/use more water to extract acid quantitatively into aqueous layer before titration or use a fixed volume of standard alkali for extraction and determine solute by back titration with standard acid.

[Any one of the above - 1]

[1]

- (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 $y \text{ cm}^3$ of $M \text{ mol dm}^{-3}$ 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.

No of moles of CH_3COOH in 50 cm^3 of aqueous layer = $(5My / 1000) \text{ mol}$

Thus $[\text{CH}_3\text{COOH}]_{\text{aq}} = (My / 10) \text{ mol dm}^{-3}$

Total No of moles of CH_3COOH used = $5 / 60$

No of moles of CH_3COOH in 50 cm^3 of organic layer = $(5/60 - 5My/1000)$

Thus, $[\text{CH}_3\text{COOH}]_{\text{s}} = (5/60 - 5My/1000) \times (1000/50) \text{ mol dm}^{-3}$
 $= [5/3 - My / 10] \text{ mol dm}^{-3}$

$$K = (My / 10) / [5/3 - My / 10]$$

$$\text{or } (0.1My) / (1.67 - 0.1My)$$

[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.

- Ethanoic acid may dimerise by way of hydrogen bonding in the organic layer when it is concentrated and thus affect the distribution ratio.

[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**.

mole ratio C : H = 1 : 1

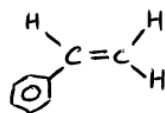
$\therefore$ empirical formula of **W** is **CH**.

Amount of CO_2 = 0.0400 mol

$\therefore$ mole ratio **W** : CO_2 = 0.005 : 0.0400
 $= 1 : 8$

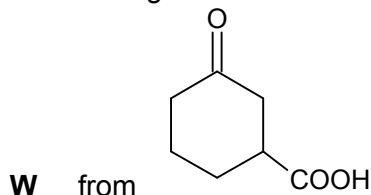
$\therefore$ Molecular formula of **W** is **C₈H₈**.

- (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



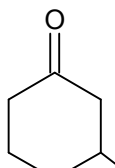
State clearly how **each** compound behaves in the test and write an equation for the reaction involved.

Reagent(s) & conditions:

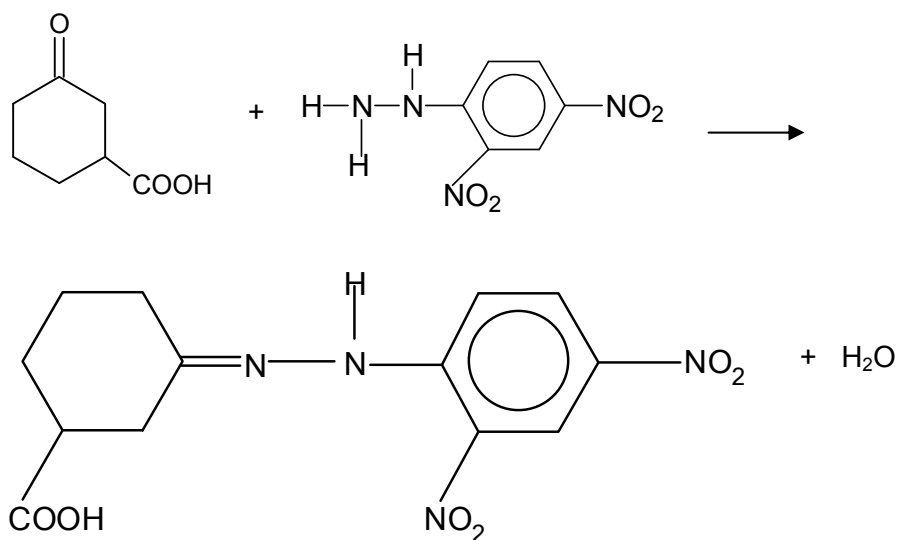
2,4-DNPH, rt

Alternative answers: (1) - Na(s) or Na₂CO₃(aq) or PCl₅
 (2) - H⁺/KMnO₄, heat

Observations:


 Yellow/Orange ppt obtained for  but no yellow/orange ppt for W.

Equation:



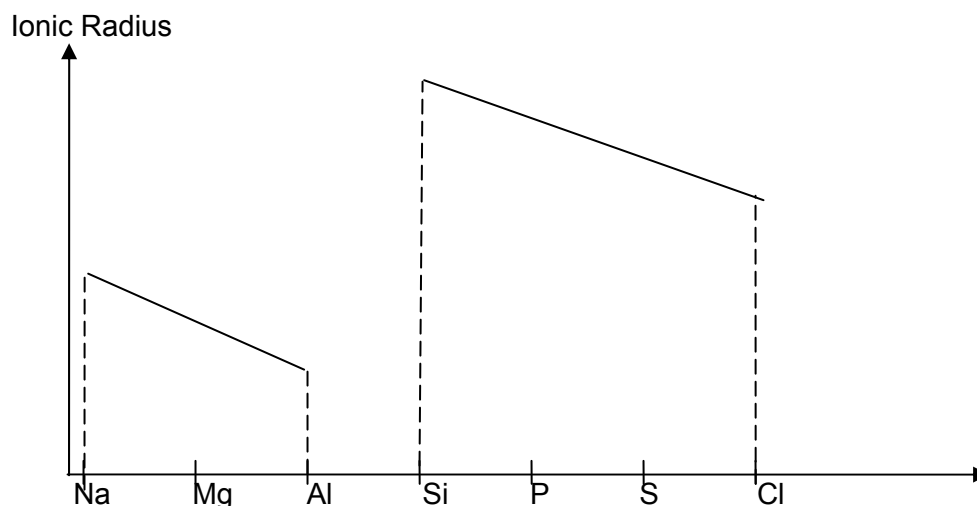
[3]

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

- Both phosphorous trichloride and nitrogen trichloride are simple molecular structures with net dipole moment.
- However, phosphorous trichloride has a **larger electron cloud/larger number of electrons** as compared to nitrogen trichloride.
- This results in **stronger intermolecular van der Waals' forces of attraction** and hence, phosphorous trichloride will show a **greater relative deviation** from ideality than nitrogen trichloride.

[3]

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



(ii) Explain the shape of your sketch.

There are two **isoelectronic** series in period 3.

Within each series, an **increasing number of protons or nuclear charge** and **constant screening effect** (same no of electrons) results in **increasingly stronger nuclear attraction experienced by the valence electrons or increasing effective nuclear charge**.

Or accept increasing p:e ratio

Valence electrons are pulled closer to nucleus, leading to a decreasing trend in ionic radius.

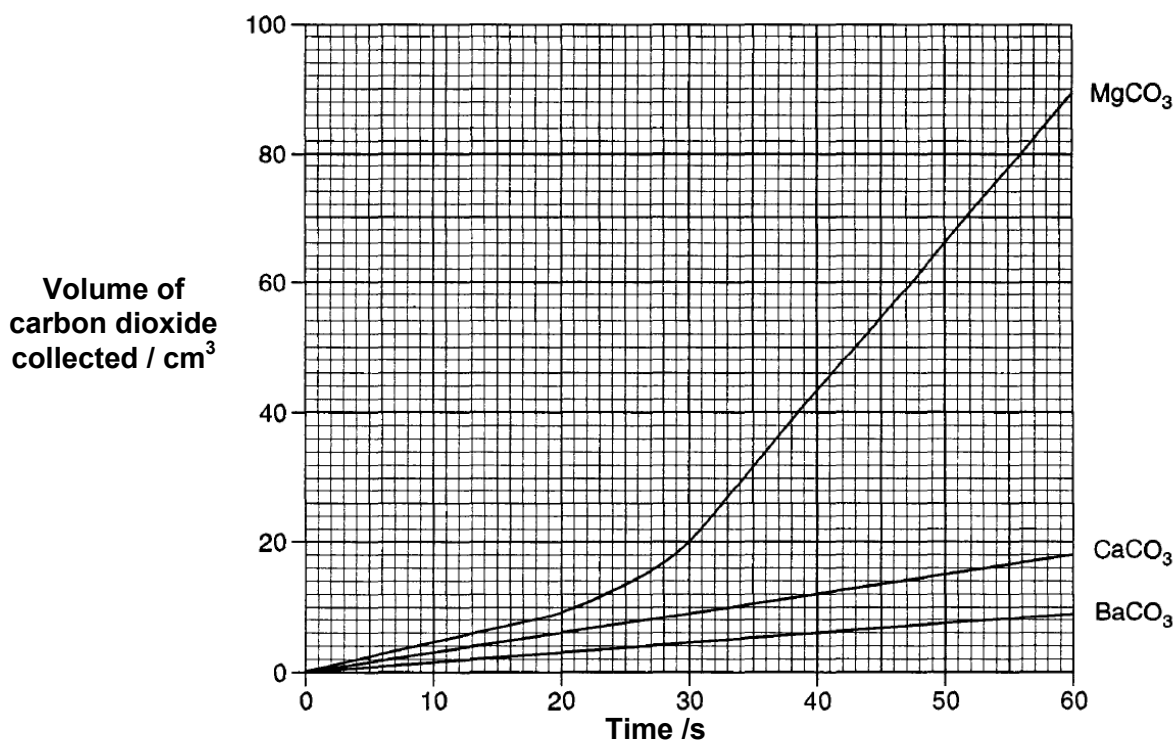
Anionic series has a larger size than cationic series as the **valence electrons are in a higher principal quantum shell or have 1 more filled shell**. Hence, experience weaker nuclear attraction and are less tightly held.

[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.

MgCO₃ is the least thermally stable.

[1]

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

The **gradient/slope of the graph** for MgCO₃ is the **steepest**.

[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?

$$\text{L.E} \propto \frac{q_+ q_-}{r_+ + r_-}$$

Both CO₃²⁻ and O²⁻ anions are **doubly charged**.

But **CO₃²⁻ has a larger ionic radius/size than O²⁻ anion**.

Thus, **magnitude of the lattice energy of CaCO₃ is smaller** than that of CaO.

[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.

ΔS is positive (> 0) due to

Increase in no. of moles of gas in the products

$$\Delta G = \Delta H - T\Delta S$$

$$|T\Delta S| > |\Delta H|$$

ΔG becomes negative (< 0) 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**.



$$\text{Amount of CO}_2 = 1.25/44.0 = 0.0284 \text{ mol}$$

$$\text{Amount of XCO}_3 = 0.0284 = 4.19/M_r \text{ of XCO}_3$$

$$M_r \text{ of XCO}_3 = 147.5$$

$$147.5 = A_r \text{ of X} + 12.0 + 3(16.0)$$

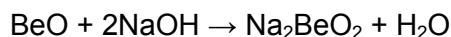
$$A_r \text{ of X} = 87.5$$

X is strontium.

[3]

[Total: 17]

- 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.

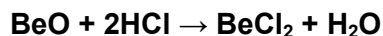


This behaviour of BeO is not expected.

Be (Group II element) is metallic in character and is expected to form basic oxide. However, due to the high charge density of Be^{2+} ion, BeO shows high degree of covalency and is amphoteric (like Al_2O_3).

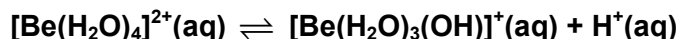
[1]

- (ii) Write the balanced equation for the reaction of BeO with dilute $\text{HCl}(\text{aq})$.



[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.

A white precipitate formed.

The precipitate dissolves to form a colourless solution.

[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.

Solid

[1]

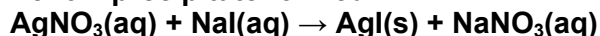
- (ii) Iodine is not soluble in water. An aqueous solution of iodine can only be prepared by dissolving iodine in excess KI(aq) to form a dark reddish brown solution. Identify the iodine-containing species that is formed in this reaction.

I_3^-

[1]

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

Yellow precipitate formed.



[1]

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

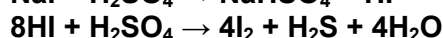
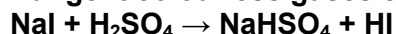
Precipitate remains insoluble in $NH_3(aq)$.

[1]

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

Black solid formed.

Pungent colourless gases evolved



[1]

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

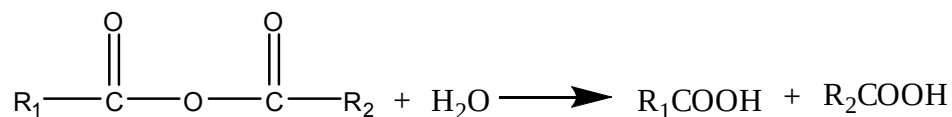
Solid dissolved to form a colourless solution.



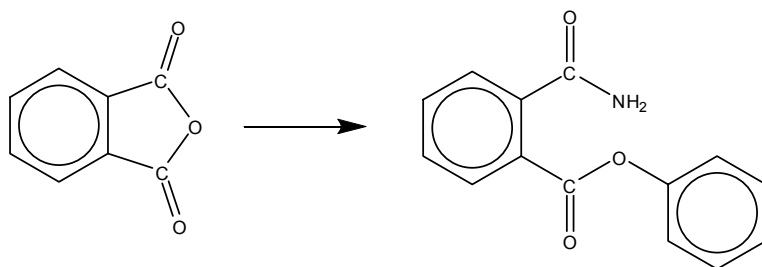
[1]

- (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.

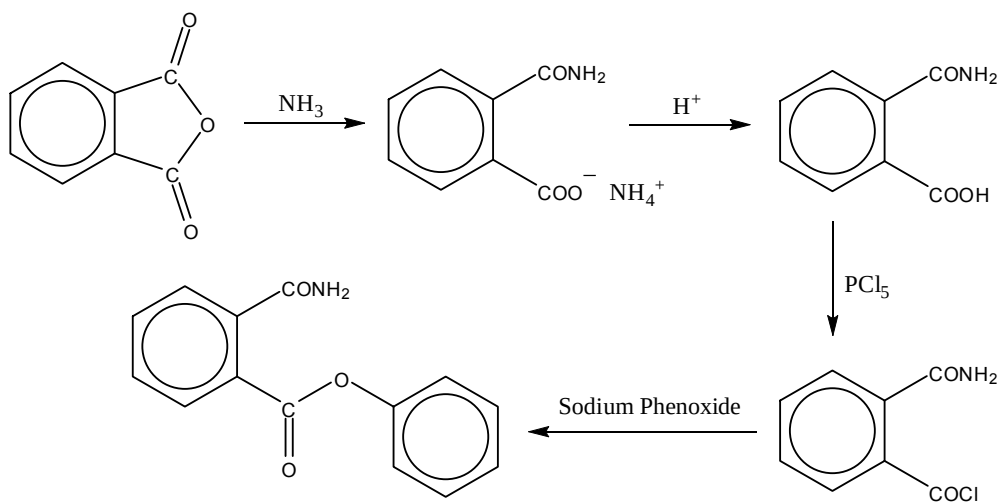
For example, acid anhydrides undergo hydrolysis as follows:



Hence, suggest a synthesis pathway for the following reaction:



Synthesis Pathway:

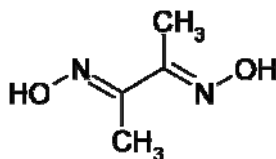


[4]

[Total: 15]

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.

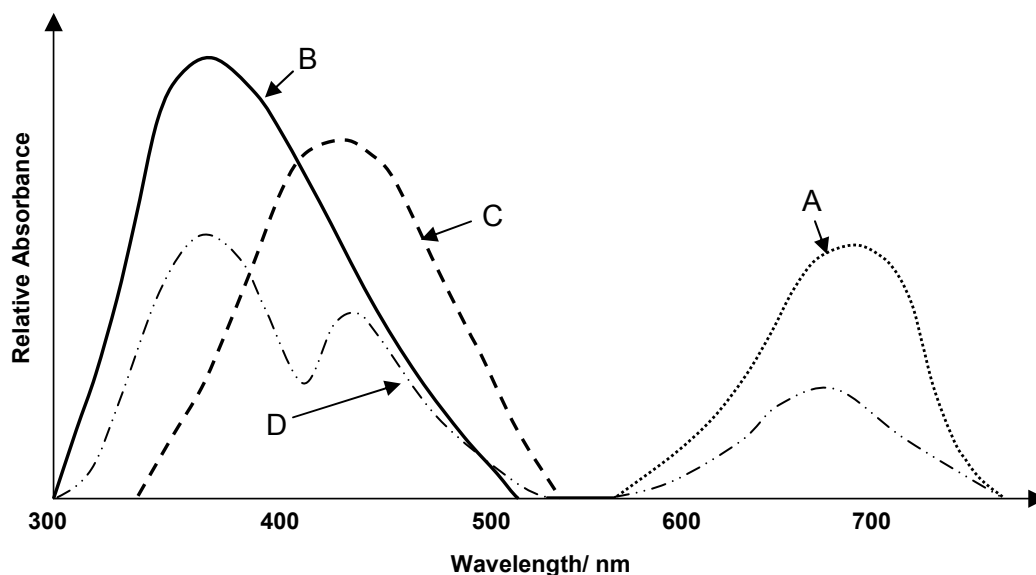
No. of co-ordinate bonds: 2

[1]

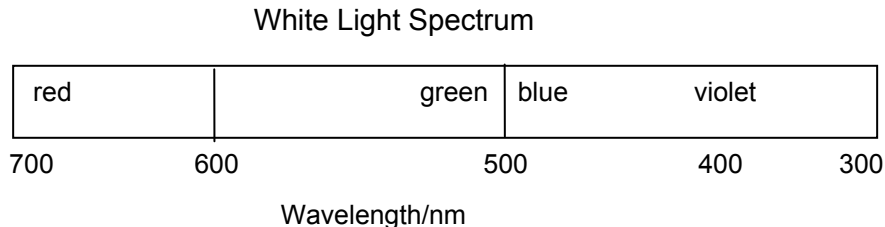
- (b) The following solutions **A**, **B**, **C** and **D** are made up by mixing 0.1 mol dm^{-3} solution of Ni^{2+} , NH_3 , EDTA^{4-} and dmg. The table below gives the volumes of each used:

Solution	Volumes of 0.1 mol dm^{-3} solution / cm^3			
	$\text{Ni}^{2+}(\text{aq})$	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:



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



Solution A: Blue/ Violet
Solution C: Red/ Orange

- (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.

d-subshell splitting: $A < C < B$

A complex ion absorbs energy from the electromagnetic spectrum to bring about the splitting of d-subshell. The longer the wavelength, the smaller the energy absorbed by the complex ion, hence the smaller the splitting of d-subshell.

- (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+} .

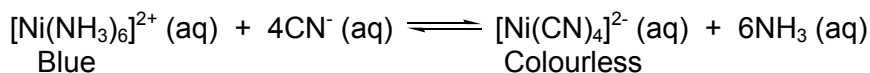
$\text{NH}_3 < \text{dmg} < \text{EDTA}^{4-}$

Based on curve D, although the concentrations of the ligand are the same, the peak of absorbance follows the order of $[\text{Ni}(\text{EDTA})]^{2-} > [\text{Ni}(\text{dmg})_2] > [\text{Ni}(\text{NH}_3)_6]^{2+}$.

The higher the concentration of a particular complex ion present in an aqueous solution, the more stable the complex formed, hence the ligand will form a stronger bond with Ni^{2+} .

[7]

- (c) In the presence of cyanide ions, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is able to undergo ligand exchange reaction as shown below:



- (i) When 1.00 dm^3 of aqueous $[\text{Ni}(\text{NH}_3)_6]^{2+}$ solution was added to an equal volume of sodium cyanide solution, colour changes are observed.

Given that 0.6 moles of $[\text{Ni}(\text{NH}_3)_6]^{2+}$, 1.0 moles of CN^- and 0.6 moles of $[\text{Ni}(\text{CN})_4]^{2-}$ were mixed together, and when equilibrium was attained, only 0.4 moles of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ remained.

Determine the K_c for this reaction.

Reaction	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	+	4CN^-	$\rightleftharpoons$	$[\text{Ni}(\text{CN})_4]^{2-}$	+	6NH_3
Initial conc./ mol dm^{-3}	0.3		0.5		0.3		0
Change in conc./ mol dm^{-3}	- 0.1		- 0.4		+ 0.1		+ 0.6
Equilibrium conc./ mol dm^{-3}	0.2		0.1		0.4		0.6

$$K_c = \frac{[\text{Ni}(\text{CN})_4]^{2-}[\text{NH}_3]^6}{[\text{Ni}(\text{NH}_3)_6]^{2+}[\text{CN}^-]^4} = \frac{(0.4)(0.6)^6}{(0.2)(0.1)^4} = 933 \text{ mol}^2 \text{ dm}^{-6} \text{ (3 s.f.)}$$

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

The intensity of blue colour of the solution will increase, due to the formation of blue $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ions.

By Le Chatelier's Principle, addition of excess aqueous ammonia will cause the position of equilibrium of the above reaction to shift to the left.

- (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 $\lg K_{\text{stab}}$ values of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$:

Nickel (II)-complex ion	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	$[\text{Ni}(\text{CN})_4]^{2-}$
$\lg K_{\text{stab}}$	7.7	31.3

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

Based on the $\lg K_{\text{stab}}$ values, CN^- ligands are able to form a more stable complex ion as compared to NH_3 ligands, since CN^- ligands have stronger binding power than NH_3 ligands.

The position of equilibrium of the above reaction will thus shift more to the right

and favour the formation of $[\text{Ni}(\text{CN})_4]^{2-}$, hence K_c for the above reaction is much larger.

[7]

[Total: 15]