

1. Nov/2020/Paper_41/No.5

A solution is made by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in an excess of aqueous ammonia. This solution contains the copper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

$$K_{\text{stab}} =$$

[1]

(ii) State the colour of the solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

..... [1]

The solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $\text{Cu}(\text{OH})_2$ forms and is collected.

A sample of $\text{Cu}(\text{OH})_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $\text{Cu}(\text{OH})_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[\text{Cu}(\text{NH}_3)_4]^{2+}$, **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to form $\text{Cu}(\text{OH})_2$ as the aqueous solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated.

..... [1]

(c) Suggest an equation for the reaction of $\text{Cu}(\text{OH})_2$ with concentrated hydrochloric acid, forming **Y**.

..... [2]

(a) When $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ is added to a solution containing $\text{Ag}^+(\text{aq})$ ions, a linear complex, **P**, is formed. $\text{S}_2\text{O}_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

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

(ii) Give the formula of **P**, including its charge.

..... [1]

(b) When $1.0 \text{ mol dm}^{-3} \text{ NaCN}(\text{aq})$ is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when $\text{NaCN}(\text{aq})$ is added to a solution of **P**.

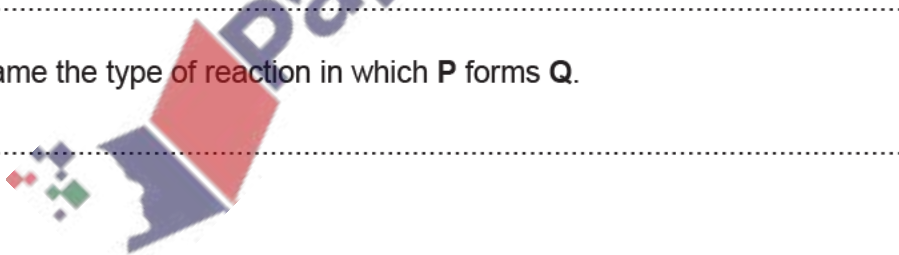
..... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

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

(iii) Name the type of reaction in which **P** forms **Q**.

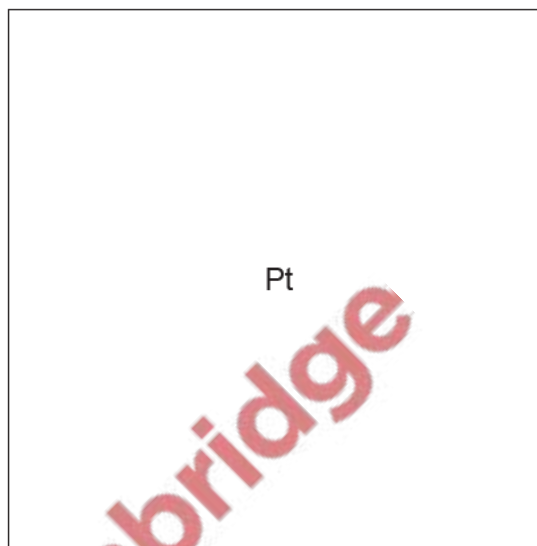
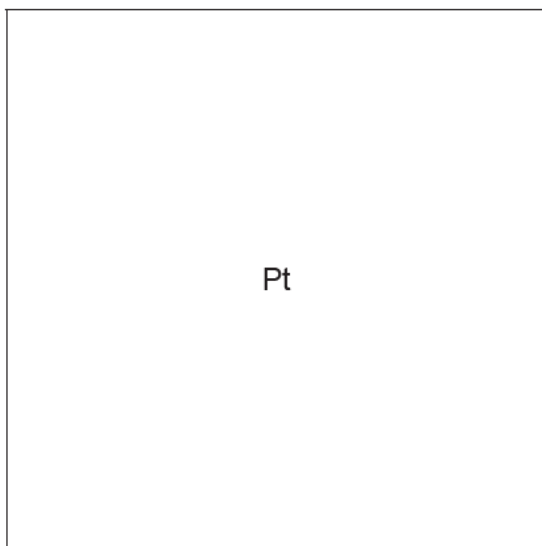
..... [1]



(c) Platinum forms a complex ion with the formula $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$. In this complex ion the carbon atom of each CN^- ligand bonds to the platinum ion. This complex shows stereoisomerism.

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



[1]

(ii) Describe the geometry of $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

(iii) Name the type of stereoisomerism shown by $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

[Total: 9]



(a) Define the term *transition element*.

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

(b) (i) Complete the electronic configuration of an isolated gaseous Fe^{3+} ion.

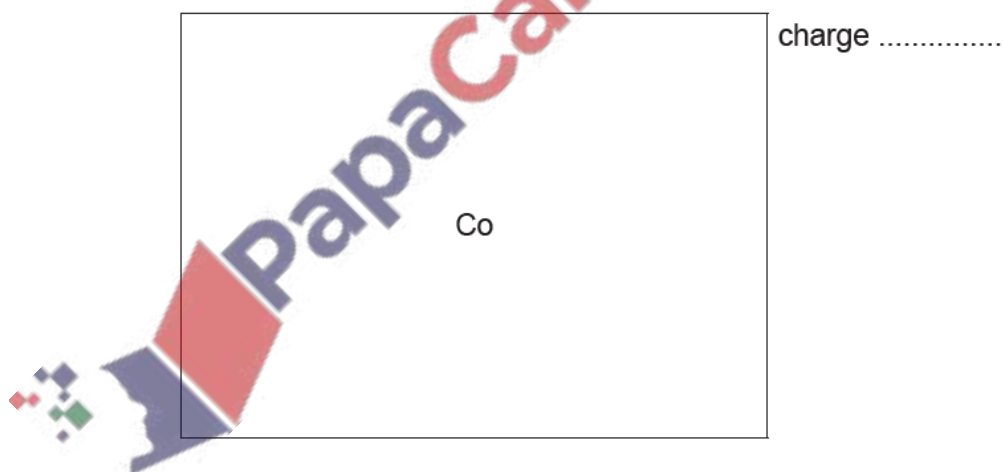
$1s^2$

(ii) Name **two** transition elements whose isolated gaseous **atoms** have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion.

..... [1]

(c) Cobalt(II) sulfate is added to water to form a pink solution containing complex ion **P**. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion **Q**.

(i) Complete the diagram to show the three-dimensional structure of **Q**.
State the charge on this complex ion.



[2]

(ii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(iii) Explain why solutions that contain transition element ions are often coloured.

.....
.....
.....
.....
.....
..... [4]

(iv) Explain why the colours of **P** and **Q** are different.

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

(d) A solution of the bidentate ligand 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$.

This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

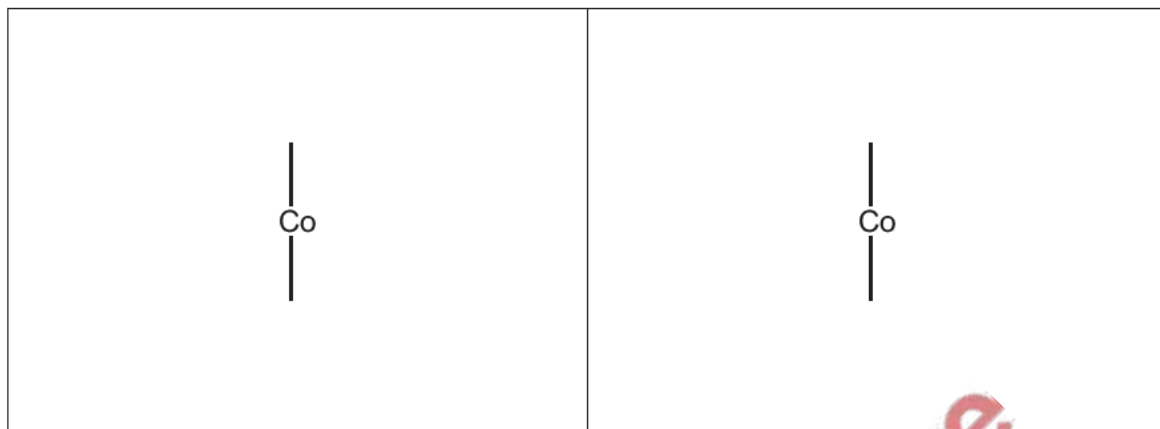
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in (c)(ii).

Name the **other** type of reaction that cobalt undergoes.

..... [1]

(ii) Draw the three-dimensional structures of the two isomeric complexes in the boxes.

You may use  to represent a molecule of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



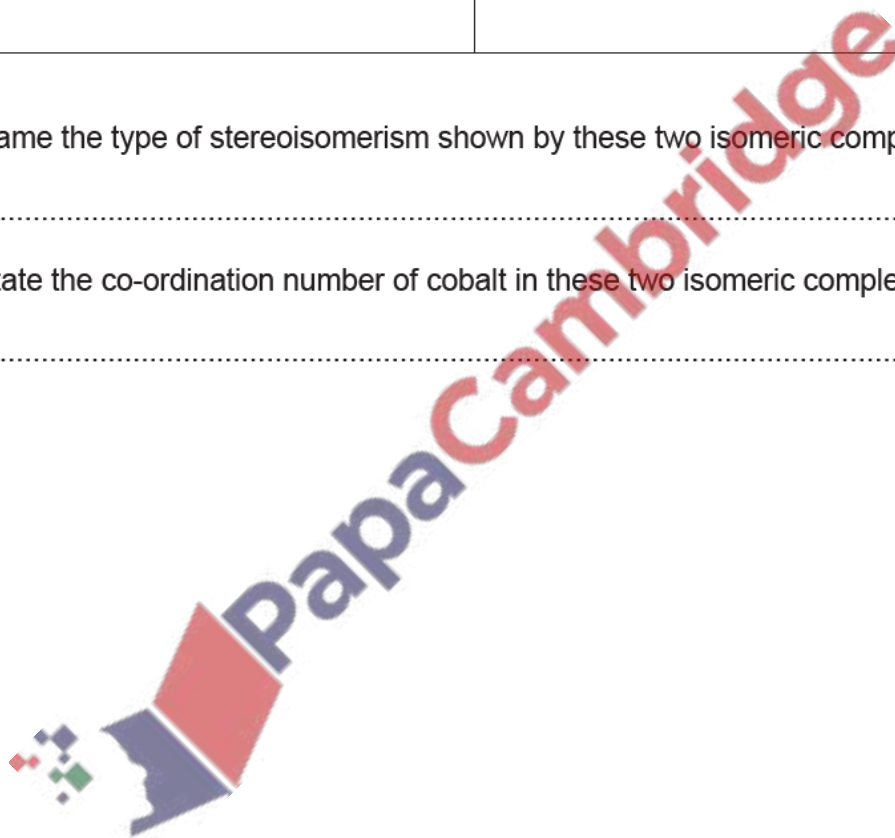
[2]

(iii) Name the type of stereoisomerism shown by these two isomeric complexes.

..... [1]

(iv) State the co-ordination number of cobalt in these two isomeric complexes.

..... [1]



(e) The stability constants, K_{stab} , of three complexes of mercury(II) are given in the table.

complex	K_{stab}
$[\text{Hg}(\text{CN})_4]^{2-}$	2.5×10^{41}
$[\text{HgCl}_4]^{2-}$	1.7×10^{16}
$[\text{HgI}_4]^{2-}$	2.0×10^{30}

(i) Write an expression for the K_{stab} of $[\text{Hg}(\text{CN})_4]^{2-}$.

$$K_{\text{stab}} =$$

[1]

(ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of $\text{CN}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{I}^-(\text{aq})$. The mixture is left to reach equilibrium.

Predict which of the complexes $[\text{Hg}(\text{CN})_4]^{2-}$, $[\text{HgCl}_4]^{2-}$ and $[\text{HgI}_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

[Total: 20]



Iron is a transition element in the fourth period. Iron forms compounds containing the ions Fe^{2+} and Fe^{3+} .

(a) (i) Define the term *transition element*.

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

(ii) Compare the melting point and density of iron with those of calcium, an s-block element in the fourth period.

melting point

density [1]

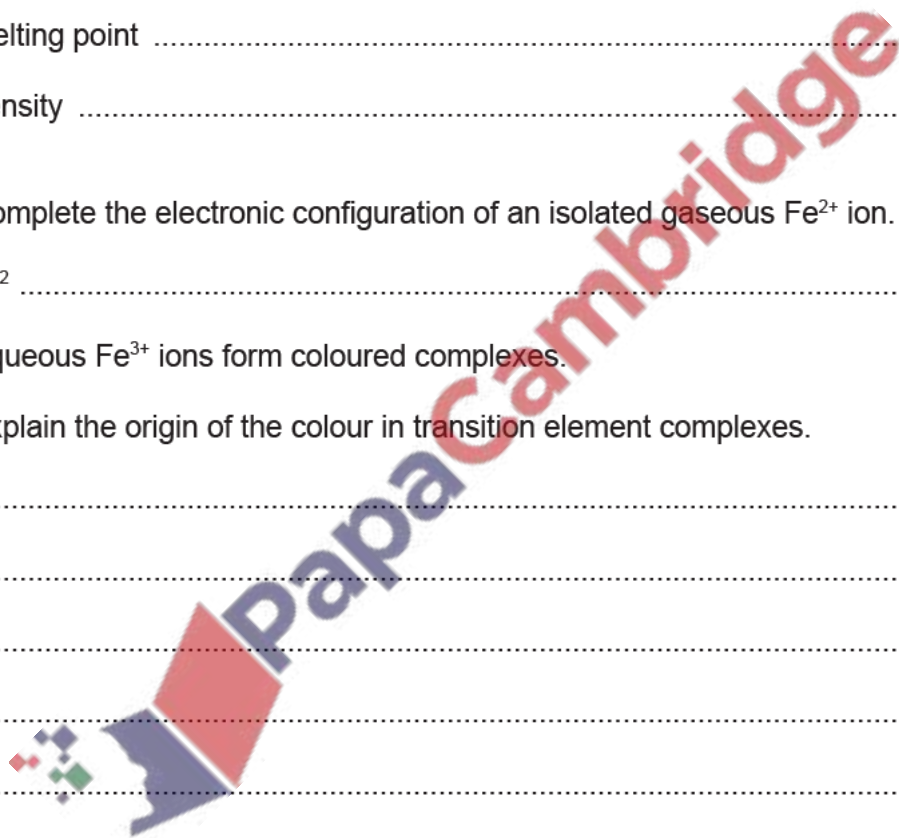
(iii) Complete the electronic configuration of an isolated gaseous Fe^{2+} ion.

$1s^2$ [1]

(iv) Aqueous Fe^{3+} ions form coloured complexes.

Explain the origin of the colour in transition element complexes.

.....
.....
.....
.....
.....
.....
..... [4]



(b) When an excess of $\text{CN}^-(\text{aq})$ ions is added to green $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ions, yellow $[\text{Fe}(\text{CN})_6]^{4-}$ complex ions are formed.

Heating $[\text{Fe}(\text{CN})_6]^{4-}$ with dilute nitric acid and then neutralising the product with $\text{Na}_2\text{CO}_3(\text{aq})$ produces red crystals, containing the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.

NO is a neutral, monodentate ligand.

(i) State the shape of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ complex ion.

..... [1]

(ii) Write the equation for the reaction between $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ions and an excess of $\text{CN}^-(\text{aq})$ ions.

..... [1]

(iii) Deduce the oxidation states of iron in:

$[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ [1]

(iv) Define the term *monodentate ligand*.

..... [2]

(v) Complete the diagram to show the three-dimensional structure of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.



[1]

(vi) The two complex ions $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ are different colours.

Explain why the colours of the two complex ions are different.

..... [2]

(c) **E** is a complex ion, $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.

(i) Define the term *coordination number*.

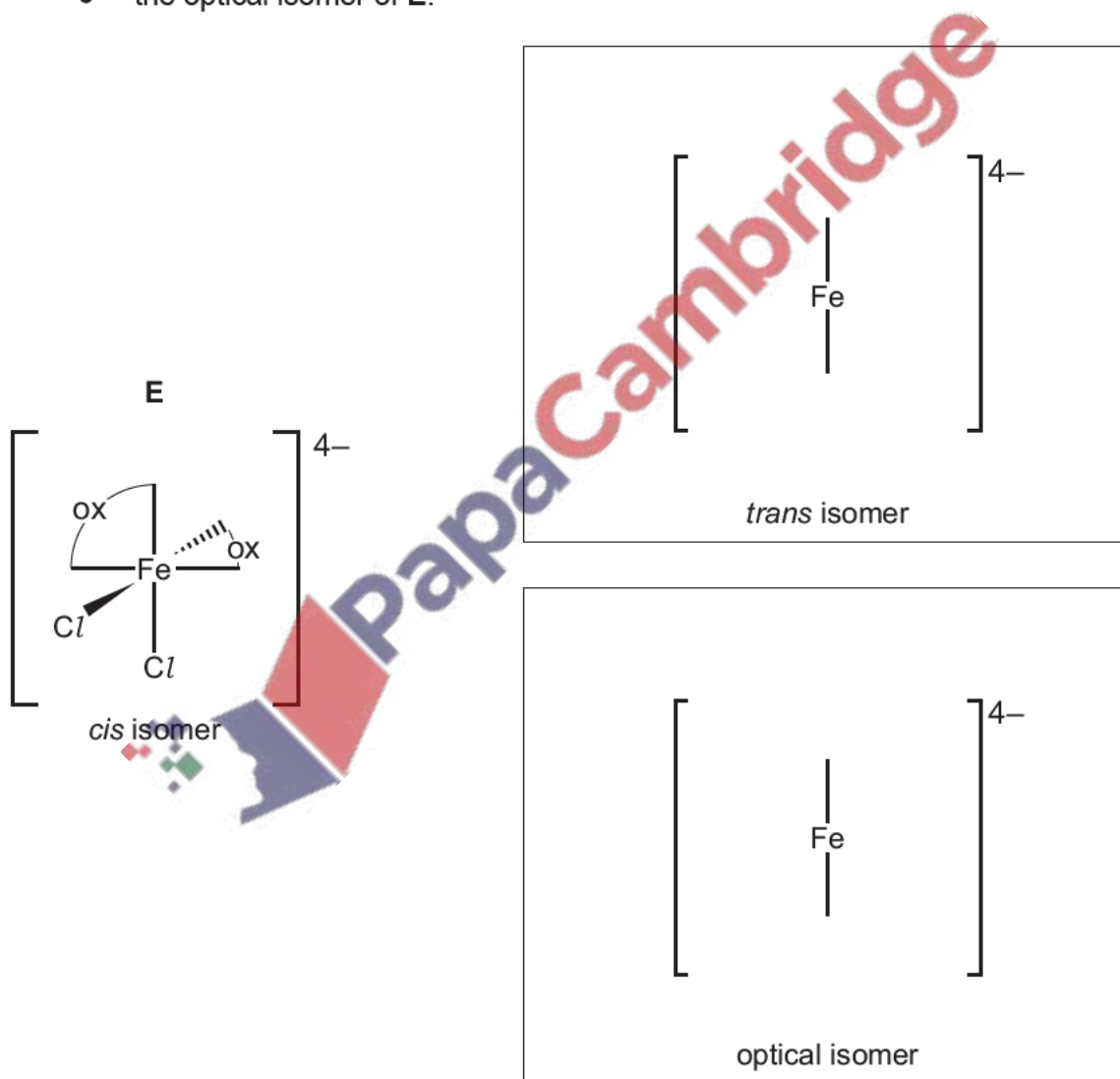
.....
..... [1]

(ii) **E** shows both optical isomerism and *cis-trans* isomerism.

One isomer of **E** is shown. The $\text{C}_2\text{O}_4^{2-}$ ion is represented as ox .

In the boxes, draw three-dimensional diagrams to show:

- the *trans* isomer of **E**
- the optical isomer of **E**.



[2]

(iii) $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$ contains ligands which are anions of ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$.

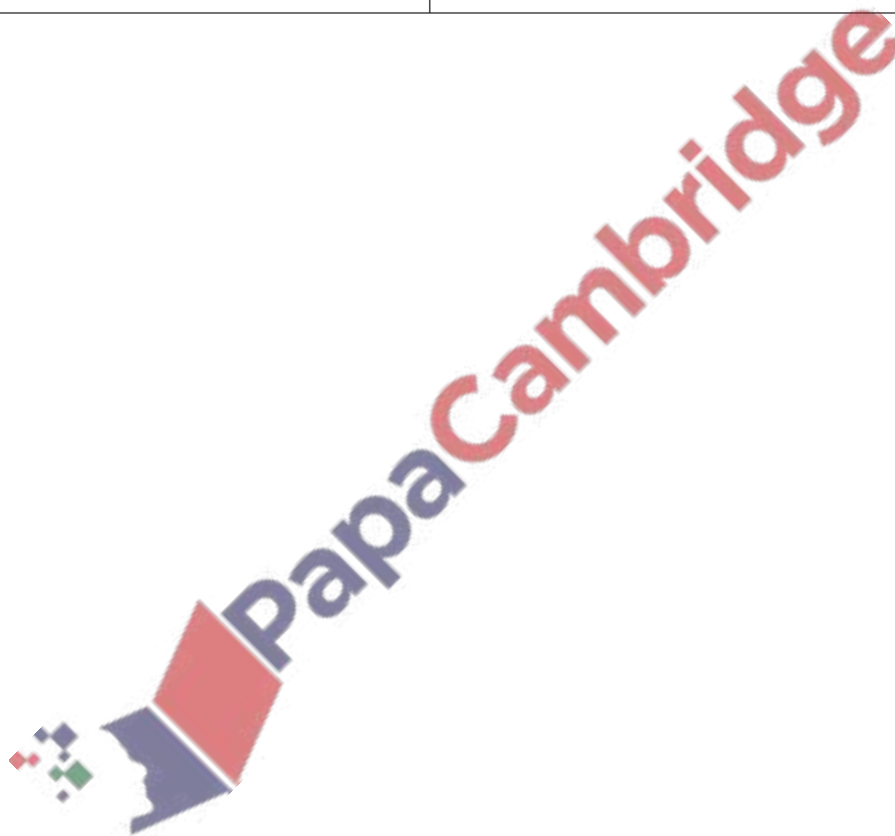
Complete the table to show any observations for the reactions of $\text{HO}_2\text{CCO}_2\text{H}$ with the named reagents.

Where no change is observed, write 'none'.

reagent	observations with $\text{HO}_2\text{CCO}_2\text{H}$
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

[2]

[Total: 20]



5. June/2020/Paper_41/No.10

(a) The electronic configuration of transition element Q is $[\text{Ar}] 3d^2 4s^2$.

Predict the likely oxidation states of element Q in compounds.

..... [1]

(b) Suggest why transition elements often show variable oxidation states in their compounds, but typical s-block elements such as calcium do not.

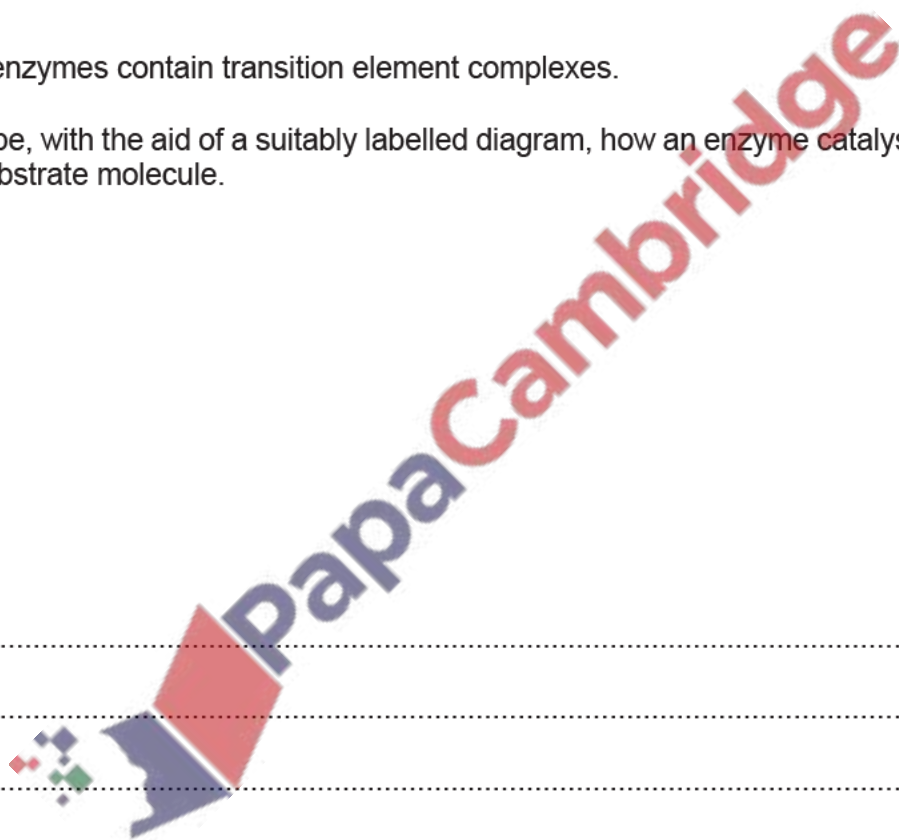
.....
..... [1]

(c) Many enzymes contain transition element complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

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

[Total: 5]



6. June/2020/Paper_42/No.1

EDTA⁴⁻, is a polydentate ligand.

(a) (i) Explain what is meant by the term *polydentate ligand*.

.....

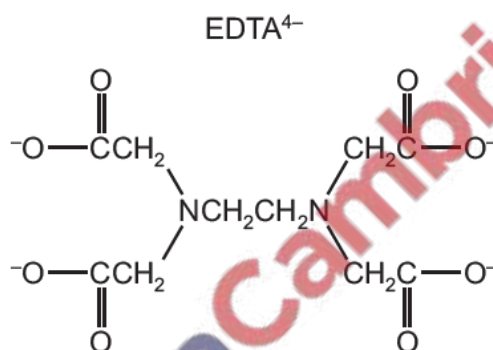
.....

..... [2]

(ii) When a solution containing EDTA⁴⁻ is added to a solution containing [Cd(H₂O)₆]²⁺ a new complex is formed, [CdEDTA]²⁻.



Circle, on the structure of EDTA⁴⁻, the **six** atoms that form bonds with the metal ion.



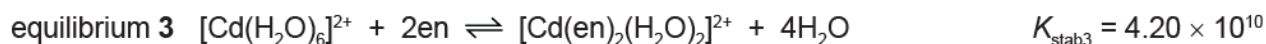
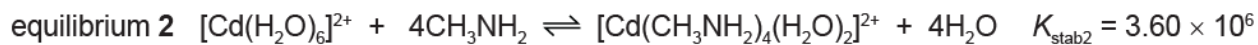
[1]

(iii) Write an expression for the stability constant, K_{stab1} , for equilibrium 1, and state its units.

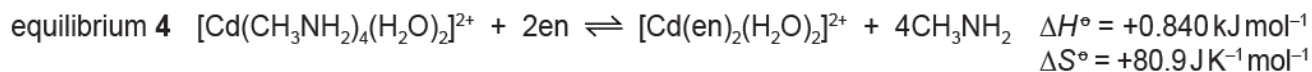


units = [2]

(b) Cadmium ions form complexes with methylamine, CH_3NH_2 , and with 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, as shown in equilibria 2 and 3. 1,2-diaminoethane is shown as en.



An equilibrium is set up between these two complexes as shown in equilibrium 4.



(i) $K_{\text{eq}4}$ is the equilibrium constant for equilibrium 4.

Write an expression for $K_{\text{eq}4}$ in terms of $K_{\text{stab}2}$ and $K_{\text{stab}3}$.

$K_{\text{eq}4} =$

[1]

(ii) Calculate the value of the standard Gibbs free energy change, ΔG° , for equilibrium 4 at 298 K.

$\Delta G^\circ = \dots\dots\dots \text{ kJ mol}^{-1}$ [2]

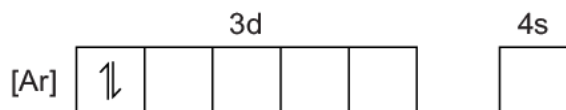
(iii) State how the value of ΔG° changes as the temperature increases. Explain your answer.

.....

[1]

[Total: 9]

(a) Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni²⁺.



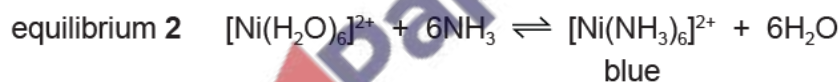
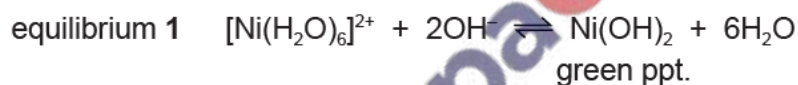
[1]

(b) Explain the origin of colour in transition element complexes.

.....

 [4]

(c) Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH⁻, in equilibrium 1 and a blue complex with ammonia, NH₃, in equilibrium 2.



Use Le Chatelier's principle to suggest explanations for the following observations.

(i) Explain why when aqueous NH₃ is added dropwise to [Ni(H₂O)₆]²⁺ a green precipitate is formed.

.....

 [1]

- (ii) Explain why when a large excess of aqueous NH_3 is added to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

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

- (d) The complex ion $[\text{NiBr}_2(\text{CN})_2]^{2-}$ shows stereoisomerism.

Draw diagrams to show the two isomers of $[\text{NiBr}_2(\text{CN})_2]^{2-}$. Name the type of stereoisomerism.

isomer 1	isomer 2
----------	----------

type of stereoisomerism

[2]

[Total: 9]

