Suggested Answers to Transition Elements Self-check questions

1(a) A **transition element** is a d-block element which can form one or more stable ions with a partially filled d subshell.

Note:
The definition should be in terms of partially filled d subshell (not orbitals). Partially filled d orbitals refer specifically to the d5 electronic configuration, where all the five d orbitals are partially/singly filled.

1(b) A **complex ion** is a charged species which consists of a central metal ion linked to one or more surrounding ions or molecules (called ligands) by dative covalent bonds.

1(c) A **ligand** is an ion or a molecule which contains at least one atom bearing a **lone pair of electrons** which can be donated into a low-lying vacant orbital of a central metal atom or ion forming a co-ordinate bond (or dative covalent bond), resulting in the formation of a complex.

1(d) In a complex, the **co-ordination number** of the central metal ion (or atom) is the total number of co-ordinate bonds that the central metal ion (or atom) has formed with ligands.

2a(i) Cu < Ni < V < Fe < Cr

2a(ii) $Zn^{2+} < Ti^{2+} < V^{2+} < Co^{3+} < Mn^{2+}$

2b(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

2b(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^2$

2c	*central metal ion or atom*	*oxidation state*	*electronic configuration of the transition metal atom/ion*
(i) $TiCl_2$	Ti^{2+}	+2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
(ii) $[V(H_2O)_6]^{3+}$	V^{3+}	+3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
(iii) $[Cr(NH_3)_6]Cl_3$	Cr^{3+}	+3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$
(iv) $[Fe(SCN)(H_2O)_5]^{2+}$	Fe^{3+}	+3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
(v) $[Fe(CN)_6]^{4-}$	Fe^{2+}	+2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
(vi) $[Ni(CO)_4]$	Ni	0	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

3 Answer: **D**

4 Answer: **D**

5 (a) Haemoglobin (denoted by Hb) acts as a transporter of oxygen in the human body. It carries out this function by having the oxygen molecule acting as a ligand forming a dative covalent bond to Fe(II) in its haem group. The resulting compound formed is called oxyhaemoglobin and it travels in the blood to places in the human body which requires oxygen. The H_2O ligand replaces the O_2 ligand when the oxygen is released to the oxygen-starved sites in the human body.

$$Hb\text{-}O_2 + H_2O \rightleftharpoons Hb\text{-}OH_2 + O_2$$

(b) In haemoglobin, a H_2O molecule acts as a ligand and forms a dative covalent bond with Fe(II) in the haem group. When converted into oxyhaemoglobin, a ligand exchange reaction occurs with the H_2O ligand being replaced by the O_2 ligand. There is no redox reaction and hence no change in the oxidation number of Fe(II) in the haem group.

(c) The interaction between CO and haemoglobin is that of a co-ordinate bond formed between the carbon atom of CO and the iron(II) in the haemoglobin. The CO acts as a monodentate ligand and donates the lone pair of electrons on the C atom into a vacant low-lying orbital in Fe(II) to form a co-ordinate bond.

CO is so much more toxic than CO_2 probably because the CO-haemoglobin complex is much more stable than the CO_2-haemoglobin complex. In other words, the CO ligand is much stronger than the CO_2 ligand and forms a stronger co-ordinate bond to Fe(II) such that it is very difficult for O_2 or H_2O ligand to displace it. This renders the haemoglobin ineffective in transporting oxygen and will result in death of the victim concerned.

(d) By using pure O_2, the equilibrium position of the reaction:

$$Hb\text{-}CO + O_2 \rightleftharpoons Hb\text{-}O_2 + CO$$

is shifted right due to the very high concentration of O_2. The formation of $Hb\text{-}O_2$ means that haemoglobin resumes its role as a transporter of O_2 and hence the patient can be revived.

Note: The pure O_2 administered does not oxidise CO to CO_2 but just displaces the CO.

(e) CN^- ion.
It also forms a very stable complex with haemoglobin. It does so by donating a lone pair of electrons from the carbon atom to a vacant low-lying orbital in Fe(II) of haemoglobin to form a strong co-ordinate bond. This renders the haemoglobin ineffective in performing its oxygen-transporting function.

- **6(a)(i)** Fe and Cu are first-row transition metals. Although Cu has a higher nuclear charge (greater proton number) than Fe, Cu has more 3d electrons which provide more shielding between the nucleus and the outer 4s shell of electrons. This increase in shielding effect offsets the increase in nuclear charge considerably and hence the electrostatic attraction between the nucleus and outer 4s electrons increases minimally, resulting in the atomic radii of Fe and Cu to be similar.

(a)(ii) $\text{Density} = \frac{\text{mass}}{\text{Volume}}$
The relative atomic mass of Fe and Cu are higher than that of Ca. Since the atomic radius of Fe and Cu are smaller than that of Ca, there are more Fe and Cu per unit volume than Ca. Hence, the densities of Fe and Cu are significantly greater than that of Ca.

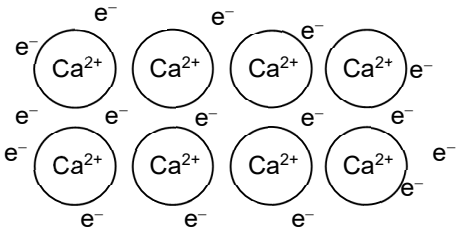
(a)(iii) Fe and Cu are first row transition metals with the general valence electronic configuration $3d^x\ 4s^y$. Due to the **close similarity in energy** between the 3d electrons and the 4s electrons, Fe and Cu can make use of different number of these electrons in bond formation (ionic or covalent) when they form compounds and hence they have a tendency to vary in their oxidation states.

Calcium, an s-block element, has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. It can only exist in the +2 oxidation state by losing 2 valence electrons to form Ca^{2+}.

+3 oxidation state of Ca is not favourable due to the very high 3rd ionisation energy required to remove the third electron from the inner quantum shell, n =3. Hence, too much energy is needed for its formation, which is not offset by the more exothermic lattice energy of ionic compounds containing Ca^{3+}.

Note:
Ca does not exhibit +1 oxidation state where it exists as Ca^+. This is because the lattice energy of an ionic compound in which calcium exists as Ca^+ would be much less exothermic compared to an ionic compound in which calcium exists as Ca^{2+}. Since the 2nd IE of Ca is not very high (as the second electron is removed from the valence 4s subshell), calcium loses the two valence electrons to form Ca^{2+} in its ionic compounds which have much more exothermic lattice energy.

(b) (i) As shown in the diagram, Ca has a giant metallic lattice structure with a regular array of positively charged Ca^{2+} ions surrounded by a 'sea of delocalised electrons'. Metallic bonding arises from the electrostatic forces of attraction between the metal cations held in the lattice and the delocalised electrons.



(b) (ii) Fe has a significantly higher melting point than Ca due to its stronger metallic bonding. The stronger metallic bonding in Fe arises because both the 3d and 4s electrons of Fe can contribute to the 'sea' of delocalised electrons (due to the small energy difference between these electrons). For Ca, only the two valence 4s electrons per atom can contribute to the 'sea' of delocalised electrons.

In addition, the contribution of more electrons for delocalisation makes the iron cations in the lattice smaller and more highly charged, resulting in stronger electrostatic attraction between

these cations and the delocalised electrons than in the case between calcium ions and the delocalised electrons. Hence Fe has a higher melting point than Ca.

(c) (i) Cu has a very <u>high density</u> and may <u>sag and deform</u> when used as overhead electrical cables.

(c) (ii) Electronic configuration:

Cu $1s^2 2s^2 2p^6 \underline{3s^2 3p^6 3d^{10} 4s^1}$; Cu^{2+} $1s^2 2s^2 2p^6 \underline{3s^2 3p^6 3d^9}$

(c) (iii) An electrolytic method is used to purify copper industrially.

The impure copper to be purified is used as the anode while pure copper is used as cathode. The electrodes are immersed in an electrolyte of copper(II) sulfate solution.

During electrolysis, Cu is oxidised at the anode and enters the solution as $Cu^{2+}(aq)$ while Cu^{2+} in the electrolyte is reduced to Cu at the pure copper cathode.

As the reaction proceeds, the impure Cu anode decreases in size while the pure Cu cathode increases in size, with pure Cu plating out onto the cathode, thus purifying Cu.

Metal impurities in anode with $E^{\ominus}$ values more positive than Cu, e.g. Ag, will not be oxidised but fall to the bottom as 'sludge'. Metal impurities in anode with $E^{\ominus}$ values less positive than Cu, e.g. Zn, will be oxidised and enter the electrolyte as ions but will remain in solution and not be reduced at the cathode.

7

			addition of excess NaOH(aq)		addition of excess NH_3(aq)	
cation	colour	formula of aqua complex ion	colour of complex ion formed	formula of complex ion formed	colour of complex ion formed	formula of complex ion formed
$Al^{3+}(aq)$	colourless	$[Al(H_2O)_6]^{3+}$	colourless	$[Al(OH)_4]^-$	*ppt is insoluble is excess NH_3*	
$Cr^{3+}(aq)$	violet/ green	$[Cr(H_2O)_6]^{3+}$	dark green	$[Cr(OH)_6]^{3-}$	*ppt is insoluble is excess NH_3*	
$Cu^{2+}(aq)$	blue	$[Cu(H_2O)_6]^{2+}$	*ppt is insoluble is excess NaOH*		dark blue	$[Cu(NH_3)_4]^{2+}$
$Fe^{2+}(aq)$	pale green	$[Fe(H_2O)_6]^{2+}$	*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
$Fe^{3+}(aq)$	pale violet (lilac) / yellow	$[Fe(H_2O)_6]^{3+}$	*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
$Mn^{2+}(aq)$	faint pink/ colourless (dilute solution)	$[Mn(H_2O)_6]^{2+}$	*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
$Zn^{2+}(aq)$	colourless	$[Zn(H_2O)_6]^{2+}$	colourless	$[Zn(OH)_4]^{2-}$	colourless	$[Zn(NH_3)_4]^{2+}$