Suggested Answers to Transition Elements Practice Questions

Question 1 N08/2/4

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

(b) (i) $[Ag(NH_3)_2]Cl$

> **Note:**
> The question requires the candidate to give the formula of **compound B**. Hence, $[Ag(NH_3)_2]^+$ is not acceptable. Do check if the question asks for the formula of compound or complex ion and give the answer accordingly.

(ii) Cation in $CuCl_2(aq)$: $[Cu(H_2O)_6]^{2+}$

Cation in **C**: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ or $[Cu(NH_3)_4]^{2+}$

(c) (i) $CuCl_2 + 2HCl \longrightarrow \underset{\textbf{D}}{H_2[CuCl_4]}$;

$CuCl_2 + Cu + 2HCl \longrightarrow \underset{\textbf{E}}{2H[CuCl_2]}$

(c) (ii) Complex ion in **D**: $[CuCl_4]^{2-}$

Complex ion in **E**: $[CuCl_2]^-$
(charged, thus soluble in water to give colourless solution)

(c) (iii) ligand exchange

(c) (iv) **D** is tetrahedral in shape. *Also accepted:* square planar **(c) (v)** +1

(d) (i) Reduction

Reduction: $[CuCl_4]^{2-} + e^- \rightarrow CuCl + 3\ Cl^-$
Oxidation: $SO_2 + 2\ H_2O \rightarrow SO_4^{2-} + 4\ H^+ + 2e^-$
Overall: $2[CuCl_4]^{2-} + SO_2 + 2\ H_2O \rightarrow 2\ CuCl + 6\ Cl^- + SO_4^{2-} + 4H^+$

(d) (ii) $CuCl$

(*Equation for conversion of **E** to **F**:* $H[CuCl_2](aq) + H_2O\ (l) \rightarrow CuCl(s) + H_3O^+(aq) + Cl^-(aq)$
*The expected answer for identity of **F** is CuCl, since it is stated in the question that **F** contains only Cu and Cl.*

Extra information:
*However the complex form, **F**, could be* $[CuCl(H_2O)]$*, a 2-coordinate neutral complex, thus insoluble in water. The addition of* H_2O *to* $[CuCl_2]^-$ *causes a shift in the position of equilibrium resulting in* Cl^- *being replaced by* H_2O: $[CuCl_2]^- + H_2O \rightleftharpoons [CuCl(H_2O)] + Cl^-$)

(e) (i) Molar ratio of Cu to F to K

$$= \frac{21.5}{63.5} : \frac{38.7}{19.0} : \frac{39.8}{39.1} = 0.338 : 2.036 : 1.018 = 1 : 6 : 3$$

Empirical formula of **G**: K_3CuF_6

(e) (ii) +3

(f) (i) Both **E** and **F** contain Cu(I) which has electronic configuration of $[Ar]3d^{10}$.
Cu(I) has a fully filled 3d subshell, i.e. absence of partially filled d subshell.
Consequently d-d transitions are not possible and hence both **E** and **F** are colourless.

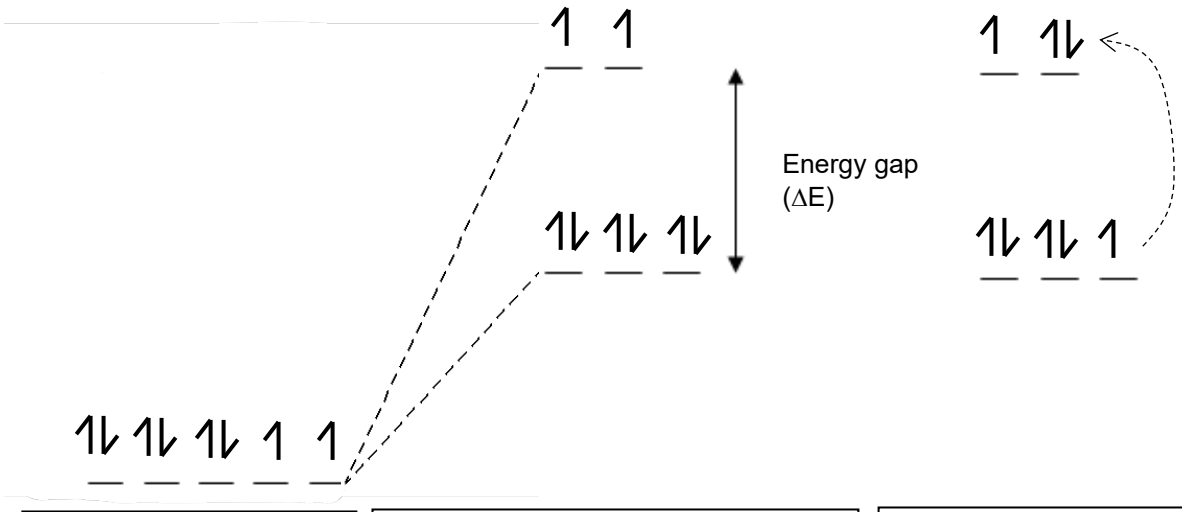
> **Note:**
> A colourless compound transmits all wavelengths of visible light while a white compound reflects all wavelengths of visible light.

(f) (ii) **G** contains CuF_6^{3-} with the central Cu(III) which has electronic configuration [Ar] $3d^8$.

L
S
P
E

C

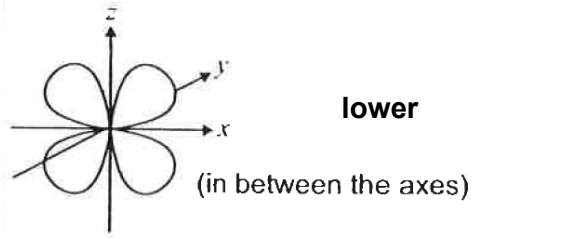
- presence of F^- **ligands** causes the
- **splitting** of the five 3d orbitals in Cu^{3+} ion into two sets of slightly different energy levels.
- Since the 3d subshell is **partially filled**,
- **electrons** from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals. (d-d transitions)
- The **colour observed** is the complement of the colour absorbed.
- This is illustrated in the diagrams below:



d-orbitals have the same energy in an isolated Cu^{3+} ion	In the presence of ligands, d-orbitals of Cu^{3+} are split into 2 sets of different energy, with energy gap corresponding to energies in the visible light spectrum.	An e^- in the lower energy level absorbs visible light energy corresponding to ΔE and is promoted to the higher energy level.

Question 2

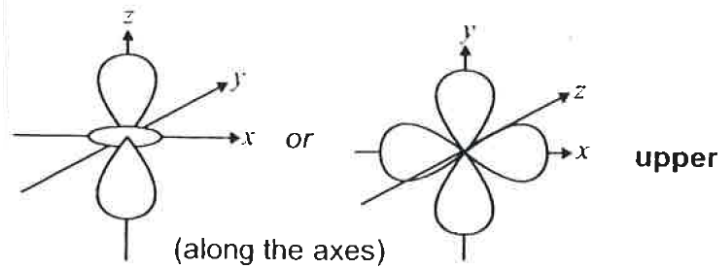
(i)



lower

(in between the axes)

d_{xz} (d_{xy}, d_{yz} are also acceptable)



or

upper

(along the axes)

d_{z^2} **$d_{x^2-y^2}$**

(ii) **$3d_{x^2-y^2}$ and $3d_{z^2}$** : These orbitals have their greatest electron density **along** the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be repelled by them.

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$: These orbitals have their greatest electron density **in between** the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be **less** compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

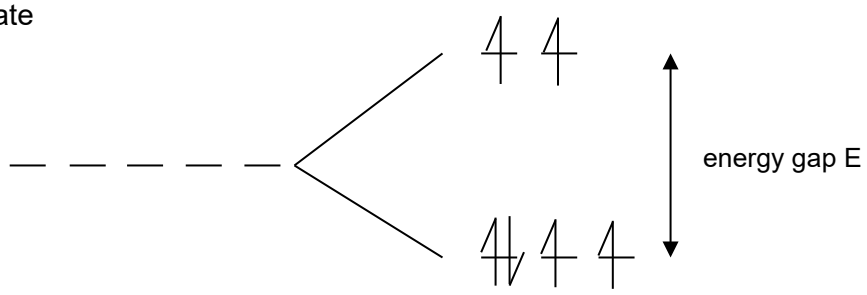
Hence the d-orbitals are split into two different energy levels.

(iii)

- Electronic configuration of Fe^{2+} : $[Ar]3d^6$
- As shown in Fig. 1, in haemoglobin, the presence of **ligands** causes the **splitting** of the five 3d orbitals in Fe^{2+} into two sets of slightly different energy levels.
- Since the 3d subshell in Fe^{2+} is **partially filled**,
- **electrons** from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals. (d-d transitions)
- The **colour observed** (red) is the complement of the colour absorbed (green).

(iv)

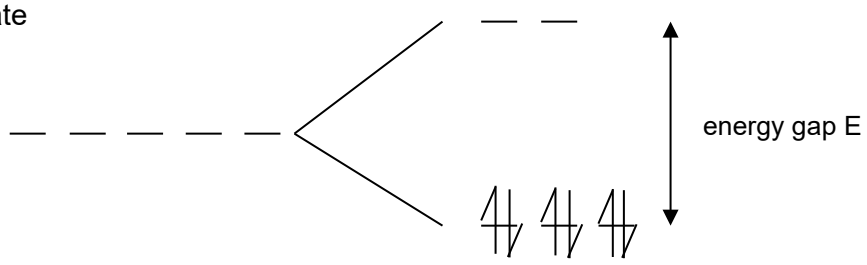
High Spin State



d orbitals of an isolated Fe^{2+} ion

d orbitals of Fe^{2+} in haemoglobin

Low Spin State



d orbitals of an isolated Fe^{2+} ion

d orbitals of Fe^{2+} in haemoglobin

(v) Electrons are negatively charged and experience electronic repulsion when paired together in the same orbital. Occupying an orbital singly minimises inter-electron repulsion.

(vi) Oxyhaemoglobin has a larger energy gap.

Due to the larger energy gap in oxyhaemoglobin, it is energetically more favourable for electrons to pair up in d-orbitals in the lower energy level (despite inter-electronic repulsion) than to occupy a d-orbital in the higher energy level singly. Hence electronic configuration of Fe^{2+} in oxyhaemoglobin is the low spin state.

(Conversely, the energy gap between the 2 different levels in deoxyhaemoglobin is small so that it is energetically more favourable for electrons to occupy d-orbitals in higher energy level singly before pairing up).

Question 3 (RI Prelim 2017/P3/Q1(c) and (d)

(i) A ligand exchange reaction has taken place.

$[Fe(H_2O)_6]^{2+} + 6\ CN^- \rightleftharpoons [Fe(CN)_6]^{4-} + 6\ H_2O$

Examiner's Comments
- Ligand exchange/ligand displacement were acceptable as possible answers.
- A handful of students who wrote the charge on the complex incorrectly were not given credit.
- Note that in the question, it was already stated that the complex was $[Fe(CN)_6]^{4-}$, thus ALL 6 H_2O ligands had to be exchanged for CN^- ligands and not only one of them.

(ii) The complexes contain <u>different ligands</u>, H_2O and CN^-, and these ligands <u>split the d-orbitals of Fe^{2+} to a different extent</u>. Thus, <u>different wavelengths of light are absorbed</u> to promote the electrons from the lower energy d-orbitals to the higher energy d-orbitals in the two complexes, leading to different complementary colours observed.

Examiner's Comments
- Students who only mentioned that a different wavelength of light was absorbed without explaining why were not awarded any credit for their answers.

(iii) $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +0.54 - (+0.36) = +0.18\ V > 0$.

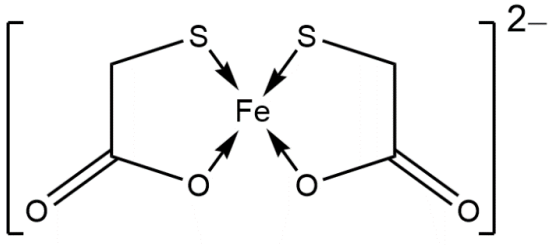
Oxidation of yellow $[Fe(CN)_6]^{4-}$ to red $[Fe(CN)_6]^{3-}$ by I_2 is <u>spontaneous</u>. Thus, I_2 can be used.

Examiner's Comments
- It was important to calculate the $E^{\ominus}_{cell}$ for the reaction AND conclude that it was spontaneous before concluding that I_2 can be used. A positive $E^{\ominus}_{cell}$ calculation is not sufficient to substantiate the possibility for the use of I_2 if there is no link provided that the reaction is spontaneous/feasible.
- A significant number of students used +0.77 instead of +0.36 and came to the incorrect conclusion that I_2 cannot be used. Note that the complex involved is $[Fe(CN)_6]^{4-}$ and not $[Fe(H_2O)_6]^{2+}$. The value of +0.77 which is for Fe^{3+}/Fe^{2+} is for the aqua complex.

Question 4

(a) Thioglycolic acid acts as a reducing agent as it reduces Fe^{3+} to Fe^{2+} as shown in equation 5.1.

(b)



, tetrahedral or square planar

(c) Ammonia was added to react with thioglycolic acid to form the corresponding anion, which can then complex with Fe^{2+} to form the pink-coloured complex, **M**.

OR

Ammonia was added to provide the basic conditions necessary for thioglycolic acid to complex with Fe^{2+} to form the pink-coloured complex, **M**.

(d) $Fe(SCH_2COOH)_2 + 2NH_3 \longrightarrow [Fe(SCH_2COO)_2]^{2-} + 2NH_4^+$

(e)(i) $[Fe(H_2O)_6]^{2+}(aq) + \underline{2}NH_3(aq) \longrightarrow \underline{\mathbf{[Fe(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)}}$

(e)(ii) Green ppt of $Fe(OH)_2$ is oxidised by O_2 in the air to form a brown ppt of $Fe(OH)_3$.

Question 5

(a) A catalyst increases the rate of a reaction by providing an alternative reaction pathway with a lower E_a and is regenerated at the end of the reaction.

From the mechanism, $[Fe(H_2O)_6]^{3+}$ is used up in step 1 and regenerated in step 3. In Test **1**, yellow **FA 2** (which contains $[Fe(H_2O)_6]^{3+}$) turned brown upon the addition of H_2O_2. The brown solution eventually turned back to yellow at the end of the reaction. Hence, both the mechanism and observations in Test 2 show the regeneration of $[Fe(H_2O)_6]^{3+}$.

Also in Test **1**, effervescence of oxygen gas that relighted a glowing splint is observed, showing that the addition of **FA 2** increased the rate of decomposition of **FA 1** (aqueous H_2O_2) to produce O_2.

Hence $[Fe(H_2O)_6]^{3+}$ acts as a catalyst for the decomposition of H_2O_2.

(b) $[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$

Due to its high charge and small size, the Fe^{3+} ion has high charge density and is hence strongly polarising. It distorts the electron cloud of the H_2O molecules bonded to it, weakening the O–H bonds and enabling these H_2O molecules bonded to it to become proton donors.
The Fe^{3+} ion consequently undergoes appreciable hydrolysis in aqueous solution. The slight excess of H_3O^+ ions in the solution causes the solution to be acidic, thus turning the universal indicator orange (pH 3), in test **2**.

Question 6

(a) $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

(b) $E^{\ominus}_{cell} = 2.01 - 0.54 = +1.47$ V
$E^{\ominus}_{cell} > 0$, reaction is thermodynamically favourable but because the reaction is between two negatively charged ions that repel one another, the activation energy is high, hence, reaction is slow when uncatalysed.

(c) The Fe^{2+} ions are in the same aqueous phase as the reactants and increases the rate of the reaction by enabling it to proceed via an alternative reaction pathway with lower activation energy which involves the following steps:

Step I **$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$**
$E^{\ominus}_{cell}$ = (2.01– 0.77) = +1.24 V > 0 V

Step II **$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$**
$E^{\ominus}_{cell}$ = (0.77 – 0.54) = +0.23 V > 0 V

- Each of these steps involves reaction between oppositely charged species and the activation energy for each of these steps is relatively lower than that of the uncatalysed reaction. Therefore, reaction rate is increased.
- The Fe^{2+} catalyst reacted to form an intermediate (Fe^{3+}) but is regenerated at the end of the reaction.

(d) One other example is Mn^{2+}.

Consider Mn^{2+} as the catalyst.

Relevant half-equation: $Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $\quad E^\ominus = +1.54$ V

Catalysed reaction:

1. $2Mn^{2+} + S_2O_8^{2-} \longrightarrow 2Mn^{3+} + 2SO_4^{2-}$

   $E^\ominus_{cell} = 2.01 - 1.54 = +0.47$ V > 0 V

2. $2Mn^{3+} + 2I^- \longrightarrow 2Mn^{2+} + I_2$

   $E^\ominus_{cell} = 1.54 - 0.54 = +1.00$ V > 0 V

Note:

Basically, any TM cation with $0.54\ V < E^\theta < 2.01\ V$ will work. (Do not use anionic species as they will also repel the anions!)

(Another example: Co^{2+})

Question 7

(a) Catalysis is the phenomenon in which the rate of a reaction is increased by the addition of a small amount of substance termed a catalyst. A catalyst increases the reaction rate by providing an alternative reaction pathway with lower activation energy.

'Heterogeneous catalysis' refers to catalysis in which the catalyst and the reactants are in different physical phases. (Most commonly, the catalyst is a solid and the reactants are gases.)

(b)

- Iron is used as a heterogeneous catalyst in Haber Process in the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \underset{}{\overset{\text{Fe (catalyst), 250 atm, 450 °C}}{\rightleftharpoons}} 2NH_3(g)$$

- Nickel is used as a heterogeneous catalyst for hydrogenation of unsaturated fats in the manufacture of margarine.

$$\underset{\text{unsaturated fats}}{R-CH=CH-R'} + H_2(g) \xrightarrow{\text{Ni, heat}} \underset{\text{margarine}}{R-CH_2CH_2-R'}$$

(c) Iron acts as a heterogeneous catalyst in the reaction between gaseous nitrogen and hydrogen in the Haber Process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

In this reaction, Fe(s) provides sites on which $N_2(g)$ and $H_2(g)$ can be adsorbed. The adsorption is possible because Fe(s) possesses a partially filled 3d subshell. It provides 3d electrons to form bonds with reactant molecules.

[Note: Fe ($[Ar]3d^64s^2$) has no empty low-lying vacant 3d orbitals to accept electron pairs from reactant molecules. This point should be included in the answer if the catalyst used has low-lying vacant 3d orbitals, e.g. V ($[Ar]3d^34s^2$) catalyst for Contact process.]

The adsorption leads to an increase in reaction rate

- it weakens the covalent bonds in N_2 and H_2 thus reducing the activation energy for the reaction.
- It increases the concentration of the reactant molecules at the Fe surface. Hence, the reactant molecules can come into close contact, with proper orientation, for reaction.

Once formed, NH_3 molecules can easily desorb from the Fe surface so that the active sites are exposed for further reaction (regeneration of catalyst).

Question 8

(a) $Cu^+ + e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.52$ V
$Cu^{2+} + e^- \rightleftharpoons Cu^+$ $\quad E^\ominus = +0.15$ V

Overall reaction:
$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$
$E^\ominus_{cell} = (0.52–0.15) = +0.37$ V > 0 V

The reaction is thermodynamically feasible under standard conditions as $E^\ominus_{cell} > 0$ V.

When Cu_2SO_4 is treated with water, a **disproportionation** reaction occurs leading to the formation of pink-coloured copper and blue $CuSO_4$ solution. $CuSO_4(aq)$ is blue because it contains the blue $[Cu(H_2O)_6]^{2+}$ ions.

$Cu_2SO_4(s) + 6H_2O(l) \longrightarrow [Cu(H_2O)_6]^{2+}(aq) + SO_4^{2-}(aq) + Cu(s)$
blue solution pink solid

(b) *Relevant data:* $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54$ V
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $\quad E^\ominus = +0.36$ V

When $FeCl_3(aq)$ is added to KI(aq), the following redox reaction occurs.

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$
$E^\ominus_{cell} = +0.77 – (+0.54) = +0.23$ V $> 0 \Rightarrow$ reaction is thermodynamically favourable

Fe^{3+} ion is strong enough an oxidising agent to oxidise the I^- to I_2. Hence a brown solution of I_2 is obtained.

When $K_3[Fe(CN)_6]$ (aq) is added to KI(aq), there is no reaction.

$2[Fe(CN)_6]^{3-} + 2I^-(aq) \rightarrow 2[Fe(CN)_6]^{4-}(aq) + I_2(aq)$
$E^\ominus_{cell} = +0.36 – (+0.54) = –0.18$ V $< 0 \Rightarrow$ reaction is not thermodynamically favourable

Unlike $Fe^{3+}(aq)$, $[Fe(CN)_6]^{3-}$ is not strong enough an oxidising agent to oxidise I^- to $I_2(aq)$. The difference in oxidising power between Fe^{3+} (i.e. $[Fe(H_2O)_6]^{3+}$) and $[Fe(CN)_6]^{3-}$ can be attributed to their different charges. It is easier for the positively charged Fe^{3+} ion to accept an electron than for the negatively charged $[Fe(CN)_6]^{3-}$ to do so since there will naturally be repulsion between like charges in the latter case. Hence, the CN^- ligand has stabilised the +3 oxidation state relative to the +2 oxidation state of Fe.

(c) Relevant data: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^\ominus = +1.23$ V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77$ V

Reaction:
$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(l)$ ……(1)
$E^\ominus_{cell} = 1.23 – 0.77 = +0.46$ V > 0 V $\Rightarrow$ reaction is thermodynamically favourable

An acidified solution of Fe^{2+} ions can be oxidised by O_2 in the air to form Fe^{3+} ions. However, this reaction is kinetically slow since it involves the loss of an electron from a **positively charged** Fe^{2+} ion which is energetically demanding.

Relevant data: $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $\quad E^\ominus = +0.40$ V
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $\quad E^\ominus = –0.56$ V

Reaction:
$4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s)$ ……(2)
$E^\ominus_{cell} = 0.40 – (–0.56) = + 0.96$ V $\Rightarrow$ reaction is thermodynamically favourable

The green ppt of $Fe(OH)_2$ obtained from the reaction between NaOH(aq) and Fe^{2+} ions is oxidised by O_2 in the air to form the brown ppt of $Fe(OH)_3$. Unlike reaction (1), this reaction involves the loss of an electron from the **neutral** $Fe(OH)_2$. Hence, it occurs more rapidly, compared to losing an electron from a positively charged Fe^{2+}.