2024 Y6 H2 Chemistry Preliminary Exams Paper 3 – Suggested Solutions

Section A

1(a)(i) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ $mol^{-1}\ dm^3$

1a(ii) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

$= \frac{(\frac{4.60}{1.00})^2}{(\frac{0.500}{1.00})^2(\frac{0.100}{1.00})}$

$= 846.4\ mol^{-1}\ dm^3$

$=$ <u>$846\ mol^{-1}\ dm^3$</u> (3 s.f.)

1(a)(iii) pV = nRT

$p = \frac{(0.5+0.1+4.6)(8.31)(273+450)}{\frac{1}{1000}} = 31.24 \times 10^6$ Pa

p = <u>31.2 MPa</u>

1(a)(iv) Partial pressure of SO_3

$= \frac{4.60}{0.5+0.1+4.6} \times (31.24 \times 10^6) =$ <u>27.6 MPa</u>

1(a)(v) Let y be the amount of O_2 added into the system

	$2\ SO_2$	+	O_2	$\rightleftharpoons$	$2\ SO_3$
Initial amt / mol	0.500		0.1 + y		4.6
Change in amt / mol	−0.1		−0.05		+0.1
Equilibrium / mol	0.400		0.05 + y		4.7

K_c is a constant as temperature remained constant

At equilibrium, $\frac{(\frac{4.70}{1.00})^2}{(\frac{0.400}{1.00})^2(\frac{0.05+y}{1.00})} = 846.4\ mol^{-1}\ dm^3$

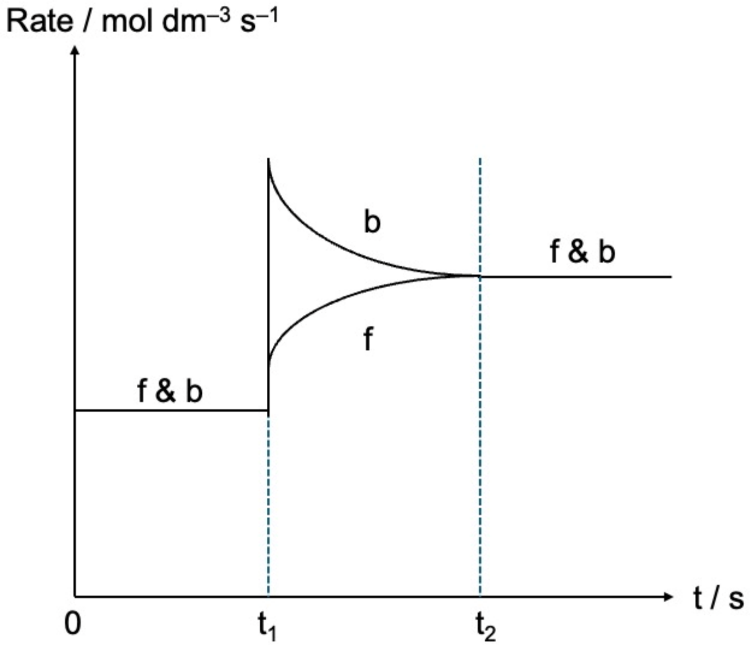
$4.7^2 = 846.4(0.4)^2(0.05 + y)$

$0.05 + y = 0.1631$

y = <u>0.113 mol</u>

1(b)(i) When temperature increases, equilibrium position shifts left to favour <u>the backward endothermic reaction</u> to counteract the increase in temperature. Hence, <u>the amount of SO_2</u> will <u>increase</u>.

1(b)(ii)



1(c)(i) 800 K

1(c)(ii) As temperature increases, ΔG_r of reaction 1 becomes more positive.

Thus, position of equilibrium of reaction 1 lies more to the left, causing the positions of equilibrium for both reactions 2 and 3 to shift to the left, which result in a lower proportion of H_2SO_4.

1(d)(i)

- An ideal gas consists of particles of negligible volume. The size of the gas particles is negligible compared to the volume of the container.
- The gas particles exert negligible attractive forces on one another.
- Collisions between gas particles are perfectly elastic.

1(d)(ii) At moderately high pressure, the gas particles come closer together and intermolecular attractive forces between the gas particles become significant.
OR
At very high pressure, the gas particles are much closer together and the gas occupies a smaller volume. As such, the volume of the gas particles is not negligible as compared to the volume of the container.

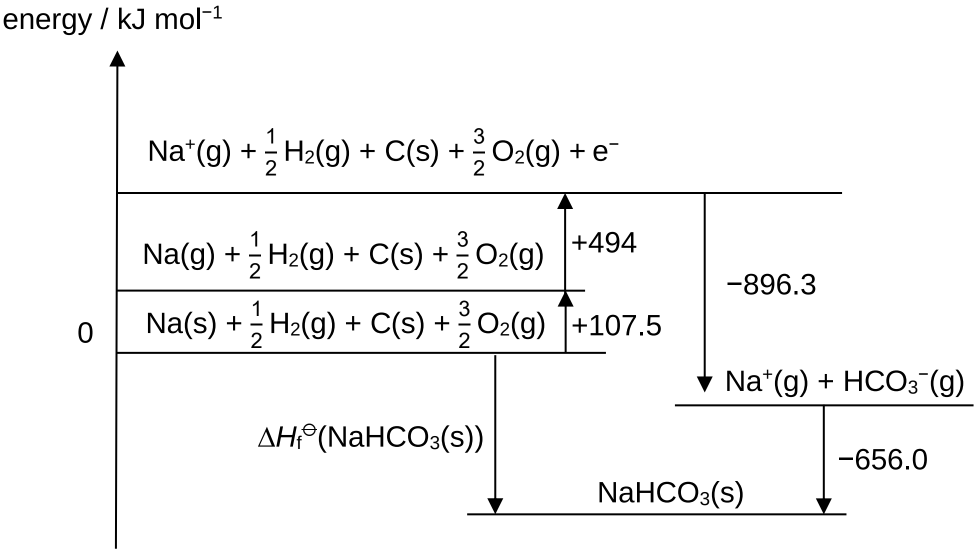
1(e)(i) Above T_c, kinetic energy of the gas particles is so high such that the intermolecular forces of attraction are overcome at all pressures.

1(e)(ii) The intermolecular forces of attraction present in steam are stronger hydrogen bonds compared to the weaker instantaneous dipole-induced dipole interactions (id-id) between carbon dioxide molecules.

More energy is required to overcome the stronger hydrogen bonds as compared to weaker id-id, hence steam has a higher critical temperature.

2(a)(i) Standard enthalpy change of formation is the energy change when 1 mole of the pure substance in a specified state is formed from its constituent elements in their standard states under standard conditions of 1 bar and 298 K.

2(a)(ii)



By Hess' Law,

$(+107.5) + (+494) + (-896.3) + (-656.0) = \Delta H_f^\ominus(NaHCO_3(s))$

$\Delta H_f^\ominus(NaHCO_3(s)) = -951 \text{ kJ mol}^{-1}$ (3 s.f.)

2(a)(iii) amount of sodium hydrogencarbonate = $\frac{11.2}{84.0}$ = 0.1333 mol

q = −(+18.7 x 0.13333) = −2.493 kJ

$\Delta T = \frac{-2.493 \times 1000}{(100)(4.18)} = -5.96$ °C or K

2(a)(iv) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Since $\Delta G_{solution}^\ominus < 0$, and $\Delta H_{solution}^\ominus > 0$, $-T\Delta S_{solution}^\ominus$ must be less than 0. Hence, the sign for $\Delta S_{solution}^\ominus$ is also positive.

2(a)(v) The hydroxide ion is smaller than hydrogencarbonate ion, while having the same charge. Therefore, the hydroxide ion has a higher charge density.

Hence, the standard enthalpy change of hydration of hydroxide is more exothermic.

2(b)(i) $K_{sp} = [Cu^{2+}][CO_3^{2-}]$ units = mol^2 dm^{-6}

2(b)(ii) $[CO_3^{2-}]$ to precipitate $PbCO_3 = \frac{7.40 \times 10^{-14}}{\frac{1}{2}(0.1)} = 1.48 \times 10^{-12}$ mol dm^{-3}

$[CO_3^{2-}]$ to precipitate $CuCO_3 = \frac{1.40 \times 10^{-10}}{\frac{1}{2}(0.2)} = 1.40 \times 10^{-9}$ mol dm^{-3}

Since $[CO_3^{2-}]$ needed to precipitate $PbCO_3 < CuCO_3$, $PbCO_3$ will be precipitated first.

2(b)(iii) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)$ – (1)

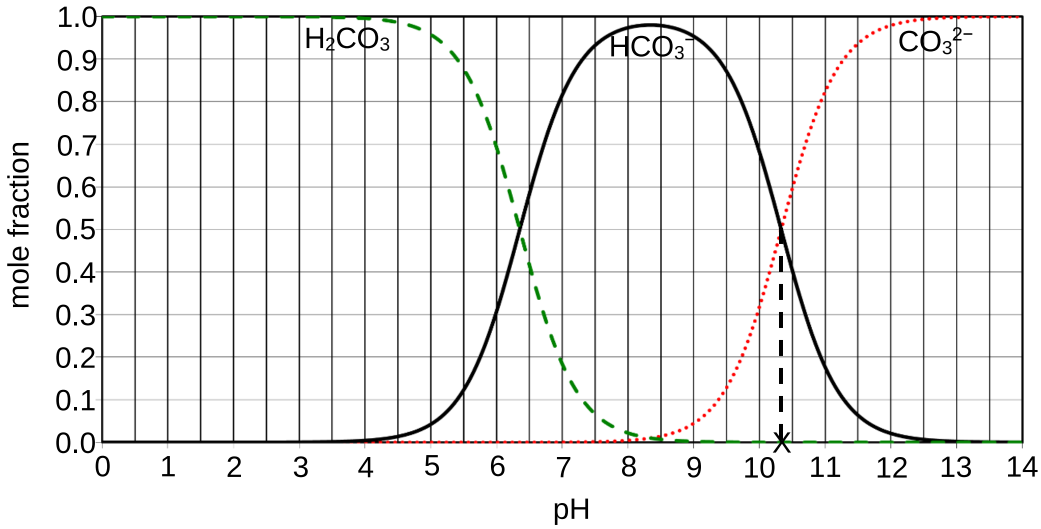
Upon addition of aqueous ammonia, a weak base, $[OH^-]$ increases and shift the position of equilibrium of (1) to the right, resulting in the formation of a light blue precipitate of $Cu(OH)_2$ since ionic product of $Cu(OH)_2 > K_{sp}(Cu(OH)_2)$.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$ – (2)

Upon addition of excess aqueous ammonia, $[NH_3]$ increases and shifts the position of equilibrium of (2) shifts to the right and decreases the concentration of $[Cu(H_2O)_6]^{2+}$. Hence, the position of equilibrium of (1) shifts to the left, causing the blue precipitate of $[Cu(OH)_2(H_2O)_4](s)$ to dissolve since ionic product $Cu(OH)_2 < K_{sp}(Cu(OH)_2)$, giving a dark blue solution.

2(c)(i) When mole fraction of $CO_3^{2-} = 0.05$, pH is about 9 – 9.25.
$[H^+] = 1.00 \times 10^{-9}$ mol dm^{-3}

2(c)(ii)

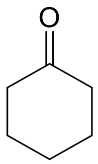


2(c)(iii) As carbon dioxide emission increases, concentration of H_2CO_3 in seawater increases. pH of seawater decreases.

From Fig. 2.1, the mole fraction of carbonate ions decreases with decreasing pH, Hence, it is more difficult for the marine creatures to build their shells.

3(a) Since C*l* is more electronegative than I, the C*l* atom is more electron-withdrawing than the I atom and the negative charge is dispersed to a greater extent in $CH_3CHC\mathit{l}COO^-$ ion than in $CH_3CHICOO^-$ ion. Hence $CH_3CHC\mathit{l}COO^-$ ion is more stable. The greater stability of the conjugate base anion explains the higher acidity of $CH_3CHC\mathit{l}COOH$.

3(b)(i)



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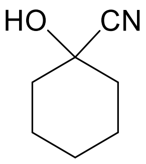


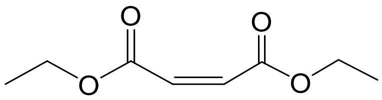
Q

3(b)(ii) Step 1: H_2SO_4(aq), $K_2Cr_2O_7$(aq) and heat

Step 2: HCN with trace KCN

Step 3: H_2SO_4(aq), heat

3(c)



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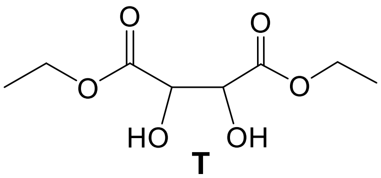
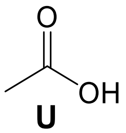


T

trans isomer acceptable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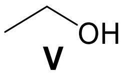
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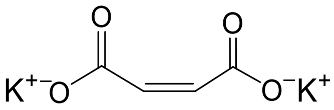
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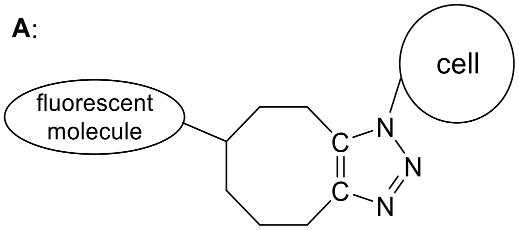
3(d) The $C\equiv C$ group in alkynes do not have a partial positive charge to attract nucleophiles.
OR
The alkyne is electron rich and repels electron rich nucleophiles.

3(e)(i) **A**:



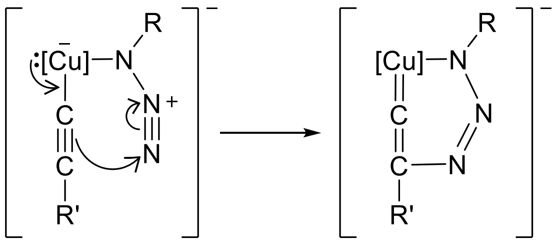
3(e)(ii) Due to ring strain/ bond strain, making cyclooctyne less stable and lowering the activation energy required for reaction.

Note: The alkyne $-C\equiv C-$ carbon atoms are sp hybridized and the ideal VESPR bond angle to minimise repulsion is 180°. In the ring structure of cyclooctyne, the bond angles from the $-C\equiv C-$ are less than 180°.

3(f)(i) The azide group has a net positive charge OR lost electron density coordinating to Cu Thus, it is more electron deficient and a better electrophile.

The alkyne group is next to the Cu and sideways overlap between the Cu orbital with the lone-pair electrons is possible with the alkyne π electron cloud. Hence the Cu lone pair electrons can be delocalised with the alkyne group, making it more electron rich and susceptible to electrophilic attack.

3(f)(ii) and 3(f)(iii)



complex **B** **C**

Section B

4(a) Aqueous Cu^{2+} exists as $[Cu(H_2O)_6]^{2+}$ complex and Cu^{2+} has an electronic configuration of $[Ar]3d^9$. The presence of H_2O ligands split the 3d orbitals into two sets of slightly different energy levels.

Since the 3d subshell in Cu^{2+} is partially filled, electrons in 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 transition). The colour observed is the complement of the colour absorbed.

Even though aqueous Zn^{2+} exists as $[Zn(H_2O)_6]^{2+}$ complex, Zn^{2+} has an electronic configuration of $[Ar]3d^{10}$. Hence, Zn^{2+} has a full 3d subshell and d-d transitions cannot occur. Thus, visible light is not absorbed and aqueous solution containing Zn^{2+} is colourless.

4(b) React bromine and iodine separately with aq $Na_2S_2O_3$.

$S_2O_3^{2-}(aq) + 4Br_2(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq)$

The average oxidation state of S increases from +2 to +6.

$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

The average oxidation state of S increases from +2 to +2.5.

I_2, being a weaker oxidising agent than Br_2, oxidises $S_2O_3^{2-}$ to a lesser extent.

OR

React bromine and iodine separately with aqueous iron(II) sulfate.

Fe^{2+} is oxidised to Fe^{3+} by Br_2 but no reaction occurs between Fe^{2+} and I_2.

$2Fe^{2+} + Br_2 \longrightarrow 2Fe^{3+} + 2Br^-$

(This example shows that Br_2 can be shown to be a stronger oxidising agent (OA) than iodine by reacting the two halogens separately with a reducing agent which has $E^\ominus$ greater than +0.54 V but less than +1.07 V.)

OR

React bromine with aqueous potassium iodide.

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

Br_2 is a stronger oxidising agent than I_2 as Br_2 is able to oxidise I^- but I_2 is unable to oxidise Br^-.

4(c)(i) The standard cell potential, $E^\ominus_{cell}$, is the potential difference between two half-cells under standard conditions (298 K, 1 bar of gases and 1 mol dm^{-3} of aqueous species).

4(c)(ii) $2VO_2^+ + 4H^+ + Cu \longrightarrow 2VO^{2+} + 2H_2O + Cu^{2+}$

$E^\ominus_{cell} = +1.00 - 0.34 = +0.66$ V

$\Delta G^\ominus = -nFE^\ominus_{cell} = -2 \times 96500 \times 0.66 = -127380 \text{ J mol}^{-1} = -127 \text{ kJ mol}^{-1}$

4(c)(iii) ① Solid sodium carbonate is added to the Cu^{2+}/ Cu half-cell

$E^\ominus_{cell} = E^\ominus(VO_2^+/VO^{2+}) - E^\ominus(Cu^{2+}/Cu)$

$Na_2CO_3(s)$ dissolves to form $CO_3^{2-}(aq)$ which reacts with $Cu^{2+}(aq)$ to form $CuCO_3(s)$. This causes the $[Cu^{2+}(aq)]$ to decrease.

$Cu^{2+} + 2e^- \rightleftharpoons Cu$
Hence position of equilibrium shifts left and $E(Cu^{2+}/Cu)$ will then be less positive than $E^{\ominus}(Cu^{2+}/Cu)$.
Hence, $E_{cell} = E^{\ominus}(VO_2^+/VO^{2+}) - E(Cu^{2+}/Cu)$ is more positive than $E^{\ominus}_{cell}$

② Water is added to the VO_2^+/VO^{2+} half-cell.
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$
Addition of water dilutes the mixture and favours the direction of reaction to produce more aqueous ions**.**
Hence position of equilibrium shifts left and $E(VO_2^+/VO^{2+})$ becomes less positive than $E^{\ominus}(VO_2^+/VO^{2+})$.
Thus, $E_{cell} = E(VO_2^+/VO^{2+}) - E^{\ominus}(Cu^{2+}/Cu)$ is less positive than $E^{\ominus}_{cell}$.

4(d) To ensure that electrical neutrality is maintained.

4(e)(i) BCA is added to prevent the volatile/ toxic Br_2 formed from escaping.

4(e)(ii) Even though complex **A** is ionic, its ions have low charge density.

Hence, the ion-dipole interactions with water are weak and insufficient to overcome the strong hydrogen bonding between water molecules/ ionic bonds in **A**, causing complex **A** to be immiscible with the aqueous electrolyte.

4(f) $Zn^{2+} + 2e^- \rightarrow Zn$
$n(e^-) = 2 \text{ x } n(Zn) = 2 \times \frac{1000}{65.4} = 30.58 \text{ mol}$

Quantity of charge = 30.58×96500 C = $2.951 \text{ x } 10^6$ C

Since the process is only 80.0 % efficient,
Quantity of charge required = $2.951 \times 10^6 \times 100/80 = 3.689 \times 10^6$ C

Q = It,
$\text{Time} = \frac{Q}{I} = \frac{3.689 \times 10^6}{32} \text{ s} = \frac{1.153 \times 10^5}{60 \times 60} = 32.0 \text{ h}$

5(a) The 3d and 4s electrons in Ni are close in energy, hence both its 3d and 4s electrons are available for delocalisation into the sea of electrons. Thus, Ni has more delocalised electrons as compared to s-block elements.

5(b)(i) Ni(s) possesses a partially filled 3d subshell.

5(b)(ii) Ni(s) provides sites on which alkene(g) and H_2(g) can be adsorbed.

The adsorption leads to an increase in reaction rate as

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

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

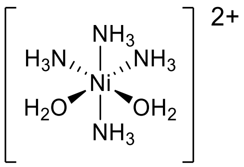
5(c)(i) Acid-base reaction

5(c)(ii) Down the group, cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations.

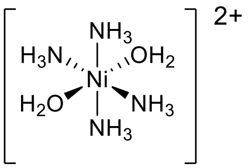
Consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion.

More heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature / thermal stability to increase down the group.

5(c)(iii)



cis



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5(c)(iv) NH_3 is added in excess to ensure that all H_2O ligands are exchanged with NH_3 ligands.

B is $[Ni(NH_3)_6]^{2+}$.

5(c)(v) Both $[Ni(H_2O)_6]^{2+}$ and **B** ($[Ni(NH_3)_6]^{2+}$) are complex ions with Ni^{2+} as the central metal ion with an electronic configuration of $[Ar]3d^8$. The presence of the ligands causes the splitting of the five originally degenerate 3d orbitals in the Ni^{2+} ion into two sets of slightly different energy levels.

Since the 3d subshell is partially filled, the 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. Such d-d transitions are responsible for the colour observed. The colour observed is the complement of the colour absorbed.

H_2O and NH_3 are different ligands of different strength. The d orbitals of Ni^{2+} are hence split into two sets of slightly different energy levels to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum for d-d transitions, thus displaying different colours.

5(d)(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

5(d)(ii) In an octahedral environment, the six ligands in octahedral complexes approach the central metal ion along the x, y and z axes.

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

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ 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 $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at a higher energy level while $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals are at a lower energy level

5(d)(iii) $3d_{x^2-y^2}$