Q1. a) $\underline{LiMnO_4}$

oxidation states. $Li +1, \underset{\text{The stable ones}}{\underbrace{Mn +3, \quad Mn +4}}$
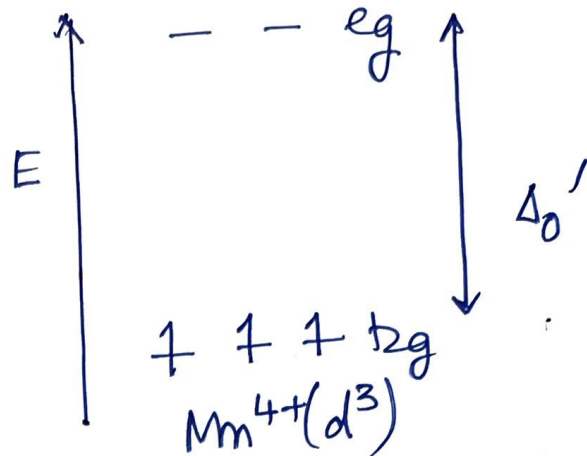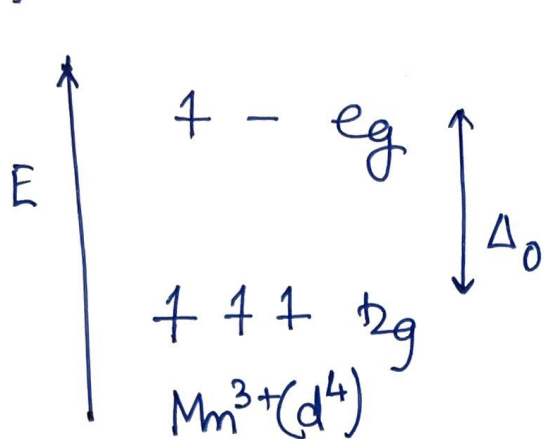
(CFSE)

1 Mark for each correct oxidation states

Q.1.b) Mn^{3+} & Mn^{4+} ions occupy the two

Octahedral (O_h) sites

Li^+ ion goes to Tetrahedral (T_d) site

$\Delta_o > \Delta_t$ & CFSE the prime reasons.

0.5 Mark for each O_h / T_d site identification

1. c) Mn^{3+} & Mn^{4+} at octahedral sites

$$E \uparrow \quad \underline{\uparrow} \; \underline{\;} \; e_g$$
$$\underline{\uparrow} \; \underline{\uparrow} \; \underline{\uparrow} \; t_{2g} \quad \updownarrow \Delta_0$$
$$Mn^{3+}(d^4)$$

$$E \uparrow \quad \underline{\;} \; \underline{\;} \; e_g$$
$$\underline{\uparrow} \; \underline{\uparrow} \; \underline{\uparrow} \; t_{2g} \quad \updownarrow \Delta_0'$$
$$Mn^{4+}(d^3)$$

$$CFSE = -0.4\Delta_0 \times 3 + 0.6\Delta_0 \times 1$$
$$= -0.6\Delta_0$$

$$CFSE = -0.4\Delta_0' \times 3$$
$$= -1.2\Delta_0'$$

$Li^+ \rightarrow$ no CFSE

$$Total \; CFSE = -0.6\Delta_0 - 1.2\Delta_0'$$

Marks are given for all other oxidation/spin states
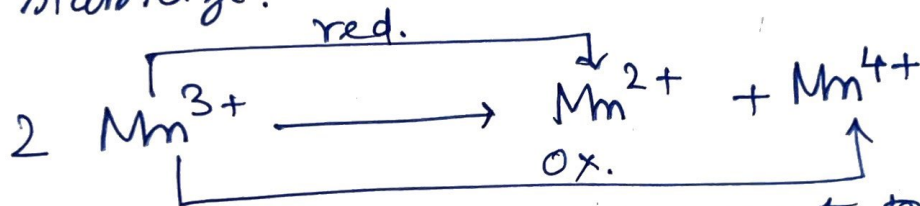used if they are calculated properly.

+1 Mark for each CFSE
Marks are deducted if $\Delta_0 \neq \Delta_0'$ is not considered
for different Mn states & if no energy
units are provided & if the sign (-ve) is not
correct for the CFSE calculation.

1. d) Mn^{3+} goes J-T distortion in the system.

Li^+ / Mn^{4+} can't exhibit any J-T distortion

$$E \uparrow \begin{cases} e_g \uparrow - \Big\langle \begin{matrix} - \\ \uparrow \end{matrix} \Big\} \begin{matrix} J\text{-}T \\ distortion \end{matrix} \\ \\ t_{2g} \uparrow \uparrow \uparrow \cdots \\ Mn^{3+}(d^4). \end{cases}$$

This J-T distortion leads to strain around Mn^{3+}

(50%) Mn^{3+} will disportionate to Mn^{2+} & Mn^{4+} all of to stabilize.
Mn-content

$$2\ Mn^{3+} \xrightarrow[\text{Ox.}]{\text{red.}} Mn^{2+} + Mn^{4+}$$

25% of Mn-content will convert to Mn^{2+}

1 Mark for the reasoning for the strain
1 Mark for the $Mn^{3+} \longrightarrow Mn^{2+}$ conversion via disproportionation

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1. e) Mn^{2+} in aqueous soln. identification

↳ optical spectroscopy
↳ magnetic moment
↳ appropriate chemical experiment

2 Marks for any proper reasonings

2. CO_2 transformed into supercritical liquid state under pressure in the sub-surface. At this condition, reactivity of CO_2 increases to drive mineralization rxn. further.

Any proper reasonings connecting the thermodynamics of the rxn. with the mineralization. $\longrightarrow$ 2 Marks.

Q.3. a) $Fe + S_{(s)} \longrightarrow FeS$ conversion has lower ΔG compared to $CO + S \longrightarrow COS$.

Hence, CO treatment directly cannot convert FeS to Fe.

1 Mark $\left[\begin{array}{l} Fe + O_2 \longrightarrow FeO \text{ line is lower than } Fe+S \rightarrow FeS \\ \text{Thus, the } FeS \text{ should be converted to } FeO \text{ first} \end{array}\right.$

1 Mark $\left[\begin{array}{l} CO + O_2 \longrightarrow CO \text{ line remains lower than} \\ Fe + O_2 \longrightarrow FeO \text{ below } 1000°C \end{array}\right.$

1 Mark $\longleftarrow$ So, we can ~~get~~ reduce FeO to Fe by $\boxed{CO \text{ below } 1000°C}$

whole process: 1. $FeS + O_2 \longrightarrow FeO$

2. $FeO + CO \longrightarrow Fe + CO_2$ (below 1000°C)

Q.3. b) The $H_2 + S \longrightarrow H_2S$ line lies higher than $Fe + S \longrightarrow FeS$

Hence, ~~H_2S is~~

$FeS + H_2 \longrightarrow Fe + H_2S$ will be having $\Delta G = +ve$ and thermodynamically unfavorable.

$\boxed{\begin{array}{l} H_2 \text{ can't} \\ \text{reduce} \\ \rightarrow 1 \text{ Mark} \\ \text{Reasoning} \\ \rightarrow 1 \text{ Mark} \end{array}}$

Q.4. a) Cr^{3+} is a d^3 system.

$E \uparrow$ $\quad -- \, eg \qquad\qquad \uparrow - eg$ $\qquad$ no J-T distortion

$\boxed{1 \text{ Mark}}$ $\quad \uparrow\uparrow\uparrow \, t_{2g} \qquad\qquad \uparrow\uparrow - t_{2g}$

$\longrightarrow$ only one absorbance peak is expected for d-d transition. $\therefore$

Q.4. b)

Absorbance at 520 nm (λ).

$Cr^{3+} (d^3)$
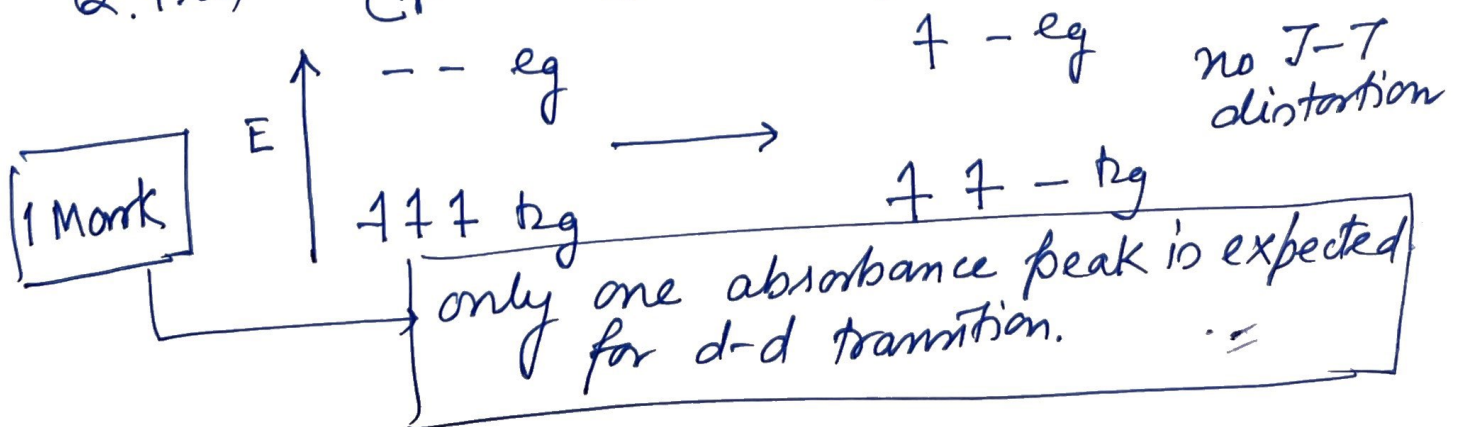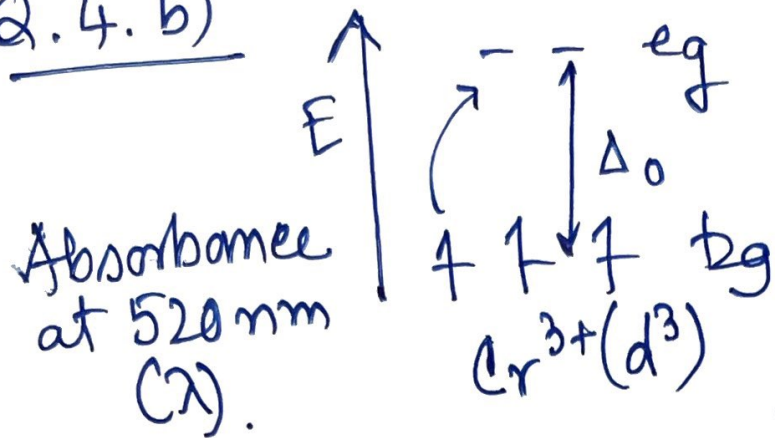
$$\boxed{\Delta_0 = E}$$

$$\boxed{\Delta_0 = \frac{hc}{\lambda}} \rightarrow \boxed{1 \text{ Mark}}$$

$$\Rightarrow \Delta_0 = \frac{6.63 \times 10^{-34} J.s. \times 3 \times 10^8 ms^{-1}}{520 \times 10^{-9} m}$$

$$= 0.03825 \times 10^{-17} J$$

converting it to $kJ/mol. \rightarrow$ need to divide by
Avogadro's number (N_A) **1 Mark**

Therefore, $\Delta_0 = \dfrac{0.03825 \times 10^{-17} J}{6.023 \times 10^{23} mol} = 230.4 \ kJ mol^{-1}$

1 Mark Answers between 210-250 kJ/mol will be accepted.

Q.4. c)

Total no. of unpaired $\bar{e}$ here is 3

so, $\mu_s = \sqrt{n(n+2)}$ B.M. $= \sqrt{3 \times 5}$ B.M. $= 3.87$ B.M.

1 Mark Answers between 3.8 - 3.95 B.M. will be accepted.

5. Myoglobin (Mb) & Hemoglobin (Hb) exhibit different O_2 binding behavior. due to the cooperativity effect present in Hb.

Thus, Hb → sigmoidal O_2 binding, while Mb → hyperbolic O_2 binding.

Under O_2-stressed conditions, the cellular pH decreases (increase in CO_2 → carbonic acid), which strengthens the cooperativity effect.

Also, the cells secrets 2,3-BPG, which stabilize the deoxy-Hb.

~~Either~~ Both these conditions ensures, Hb loses more O_2 under stressed condition (Hb-2) compared to standard conditions (Hb-1)

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1 Mark for difference in Hb/Mb (cooperativity effect)

1 Mark for difference between Hb-1/Hb2 (pH, 2,3-BPG)