Class 12 Chemistry · Chapter 4: The d- and f-Block Elements

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. The electronic configuration of the Co^{3+} ion (Z of cobalt = 27) is [1]

(a) $[Ar]3d^6$ (b) $[Ar]3d^5 4s^1$

(c) $[Ar]3d^4 4s^2$ (d) $[Ar]3d^7$

Answer: (a) Co is $[Ar]3d^7 4s^2$. On ionisation the two 4s electrons leave first, then one 3d electron: Co^{3+} is $[Ar]3d^6$, with no 4s electrons.

2. Which of these ions has an incomplete d subshell, so that its metal counts as a transition element? [1]

(a) Ag^{2+} (b) Cd^{2+}

(c) Zn^{2+} (d) Hg^{2+}

Answer: (a) A transition element has an incompletely filled d subshell in at least one of its common oxidation states. Zn^{2+}, Cd^{2+} and Hg^{2+} are all d^{10}; Ag^{2+} is $4d^9$, so silver, through Ag(II), qualifies while zinc, cadmium and mercury do not.

3. Which pair of elements has almost identical atomic radii? [1]

(a) Zr and Hf (b) Sc and Y

(c) Ti and Zr (d) Cu and Ag

Answer: (a) Because of the lanthanoid contraction the 4d and 5d members of a group have nearly the same radii: Zr 160 pm, Hf 159 pm. Down from 3d to 4d (Ti to Zr, Sc to Y, Cu to Ag) the radius increases.

4. Which set contains only ions that are colourless in aqueous solution? [1]

(a) Ti^{4+}, Cu^{2+}, Zn^{2+} (b) Ti^{3+}, Sc^{3+}, Zn^{2+}

(c) Sc^{3+}, Zn^{2+}, Fe^{3+} (d) Sc^{3+}, Ti^{4+}, Zn^{2+}

Answer: (d) Sc^{3+} and Ti^{4+} are $3d^0$ and Zn^{2+} is $3d^{10}$: none can have a d–d transition. Ti^{3+} ($3d^1$, purple), Fe^{3+} ($3d^5$, yellow) and Cu^{2+} ($3d^9$, blue) are coloured.

5. A tripositive ion M^{3+} of a 3d metal has a spin-only magnetic moment of 3.87 BM. The metal M is [1]

(a) vanadium (Z = 23) (b) iron (Z = 26)

(c) manganese (Z = 25) (d) chromium (Z = 24)

Answer: (d) 3.87 BM = $\sqrt{(3 \times 5)}$, so n = 3. M^{3+} has (Z − 21) d electrons: V^{3+} d^2 (2 unpaired, 2.84), Cr^{3+} d^3 (3 unpaired, 3.87), Mn^{3+} d^4 (4, 4.90), Fe^{3+} d^5 (5, 5.92). Only chromium fits.

6. Chromium(II) salts liberate hydrogen from dilute acids. Write the ionic equation and give the reason for this behaviour in terms of the electronic configuration of the product. [2]

$2Cr^{2+} + 2H^+ \rightarrow 2Cr^{3+} + H_2$. Cr^{2+} is a strong reducing agent: on oxidation it goes from d^4 to d^3 Cr^{3+}, which has a half-filled t_2g level and is stable in water.

- balanced ionic equation (1)
- Cr^{3+} d^3, half-filled t_2g, so Cr^{2+} is readily oxidised (1)

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7. Most Ln^{3+} ions are coloured, but La^{3+} and Lu^{3+} are colourless. Explain, and state whether these two ions are paramagnetic. [2]

Colour in Ln^{3+} comes from the f electrons. La^{3+} is $4f^0$ and Lu^{3+} is $4f^{14}$, so neither can absorb by an f–f transition, and both are colourless. With no unpaired electrons, both are diamagnetic, not paramagnetic.

- f^0 and f^{14}, no f–f transition (1)
- no unpaired electrons, so not paramagnetic (1)

8. The highest fluoride of manganese is MnF_4, but its highest oxide is Mn_2O_7. Explain. [2]

Oxygen can form multiple bonds to the metal while fluorine forms only single bonds. In Mn_2O_7 each Mn is tetrahedral, bonded to terminal O atoms by multiple bonds and joined through an Mn–O–Mn bridge, which lets manganese reach +7; fluorine cannot satisfy +7 with single bonds.

- oxygen forms multiple (π) bonds to the metal, fluorine does not (1)
- so oxygen stabilises +7 (Mn_2O_7) while fluoride stops at +4 (1)

9. Write balanced ionic equations for the reactions of permanganate with (i) nitrite ion in acidic solution, (ii) iodide ion in acidic solution, and (iii) iodide ion in neutral or faintly alkaline solution. [3]

(i) $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$. (ii) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$. (iii) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$.

- nitrite to nitrate, balanced (1)
- iodide to iodine in acid, balanced (1)
- iodide to iodate, MnO_2 formed, in neutral solution (1)

10. Write the electronic configurations of europium (Z = 63) and gadolinium (Z = 64). Use them to explain why europium shows a +2 oxidation state, and why the Gd^{3+} ion is especially stable. [3]

Eu: $[Xe]4f^7 6s^2$. Gd: $[Xe]4f^7 5d^1 6s^2$. Eu loses its two 6s electrons to give Eu^{2+}, $4f^7$, a half-filled f subshell, so +2 is reached (Eu^{2+} is, however, a strong reductant, returning to +3). Gd loses $6s^2$ and $5d^1$ to give Gd^{3+}, also $4f^7$, half-filled, so its +3 state is particularly stable.

- both configurations correct (1)
- Eu^{2+} is $4f^7$ after losing $6s^2$ (1)
- Gd^{3+} is $4f^7$, half-filled (1)

11. The standard electrode potentials $E°(M^{2+}/M)$ of some 3d metals are: V −1.18 V, Cr −0.90 V, Fe −0.44 V, Ni −0.25 V, Cu +0.34 V. (i) Judging by these values alone, which of these metals cannot liberate hydrogen from 1 M HCl? Give a reason. (ii) Arrange V, Fe and Ni in decreasing order of their tendency to form M^{2+} ions. (iii) State the general trend in $E°(M^{2+}/M)$ across the series and the quantity it follows. [3]

(i) Copper: its E° is positive (+0.34 V), so it cannot reduce H^+ to H_2; it dissolves only in oxidising acids. (ii) V > Fe > Ni, the order of increasingly less negative E°. (iii) $E°(M^{2+}/M)$ becomes less negative across the series, a decreasing tendency to form M^{2+}, following the rising sum of the first and second ionisation enthalpies.

- copper, positive E° (1)
- V > Fe > Ni (1)
- less negative across the series, tracking $IE_1 + IE_2$ (1)