Unit 6 · Transition Metals

ANSWER KEY · FOR TEACHERS

Full marks 33

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

K · 4

1. ligand → **b.** an atom, ion or molecule that gives a lone pair to a central metal in a complex
2. coordination number → **a.** the number of donor atoms bonded to the central metal
3. chelating ligand → **g.** a ligand that holds the metal in a ring through two or more donor atoms
4. paramagnetic → **c.** drawn into a magnetic field, because of unpaired electrons
5. diamagnetic → **j.** with all its electrons paired, and not drawn into a magnetic field
6. degenerate orbitals → **e.** orbitals of the same energy
7. crystal field splitting energy → **i.** the energy gap between the t_{2g} and e_g sets of d orbitals
8. spectrochemical series → **f.** ligands in order of the splitting they cause

Each carries 0.5 mark.

2 Label the diagram

K · 2

1. eg
2. +0.6 Δo
3. −0.4 Δo
4. t2g

Each carries 0.5 mark.

3 Multiple choice

i. **b.** +2 — A · 1

Four K^+ give +4, so the complex ion is $[Fe(CN)_6]^{4-}$. Six CN^- give −6: x − 6 = −4, so **x = +2**, as the (II) in its name says.

ii. **c.** 6 — U · 1

Each en is **bidentate**, bonding through both its nitrogens: 3 × 2 = **6** donor atoms round the cobalt. Counting the ligands instead of the donor atoms gives 3.

iii. **b.** 2.83 BM — A · 1

V is [Ar] $3d^3\,4s^2$; V^{3+} is [Ar] $\mathbf{3d^2}$, two unpaired electrons: $\mu = \sqrt{2 \times 4} = \sqrt{8} = \mathbf{2.83\ BM}$.

iv. **a.** Cl^- — U · 1

In the spectrochemical series, $I^- < Br^- < \mathbf{Cl^-} < F^- < OH^- < H_2O < NH_3 <$ en $< NO_2^- < CN^- <$ CO, chloride comes first of these four: the weakest field and the smallest Δ_o.

v. **c.** vanadium(V) oxide, V_2O_5 — K · 1

V_2O_5 catalyzes $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$. Iron is the catalyst of the Haber process, nickel of hydrogenation and $TiCl_4$ (Ziegler–Natta) of making polythene.

4 Short answers

a. MARKING SCHEME — U · 2

- ✓ Hexaamminecobalt(III) chloride.
- ✓ Potassium tetrachloridonickelate(II).

b. MARKING SCHEME — U · 2

- ✓ High spin: weak-field ligand, Δ_o < P, most electrons unpaired (an example).
- ✓ Low spin: strong-field ligand, Δ_o > P, electrons paired in t_{2g} (an example).

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c. MARKING SCHEME A · 3

- ✓ The four configurations.
- ✓ d^5 (half-filled) is especially stable.
- ✓ Mn^{2+} is already d^5; Fe^{2+} becomes d^5 by losing one electron.

5 Long answer

ANSWER U · 4

A **complex** is a central metal atom or ion bonded to surrounding molecules or ions (ligands) by coordinate bonds.

In $[Cu(NH_3)_4]SO_4$ the **central metal ion** is Cu^{2+}. The **ligands** are the four NH_3 molecules, each giving the lone pair on its nitrogen. The **coordination number** is 4, the number of donor atoms bonded to copper. The **coordination sphere** is the part in square brackets, $[Cu(NH_3)_4]^{2+}$; the sulphate ion is outside it.

Monodentate ligands bond through one donor atom (NH_3, H_2O, Cl^-); **bidentate** through two (ethane-1,2-diamine, oxalate); **tridentate** through three (diethylenetriamine); **polydentate** through more (EDTA, six).

MARKING SCHEME

- ✓ A complex: a central metal with ligands bonded by coordinate bonds.
- ✓ Central ion Cu^{2+}, ligands NH_3 (lone pair on N).
- ✓ Coordination number 4; coordination sphere $[Cu(NH_3)_4]^{2+}$, sulphate outside it.
- ✓ Mono-, bi-, tri- and polydentate ligands, an example of each.

6 Numerical problems

a. ANSWER A · 4

i. Mn is **+2** in both (water is neutral: $x = +2$; 6 CN^-: $x - 6 = -4$). Mn^{2+} is **$3d^5$**.

ii. $[Mn(H_2O)_6]^{2+}$, high spin: $t_{2g}^{\ 3}\, e_g^{\ 2}$, **5** unpaired. $[Mn(CN)_6]^{4-}$, low spin: $t_{2g}^{\ 5}$, **1** unpaired.

iii. $\mu = \sqrt{5 \times 7} =$ **5.92 BM** and $\sqrt{1 \times 3} =$ **1.73 BM**.

iv. High spin: $3(-0.4\ \Delta_o) + 2(+0.6\ \Delta_o) =$ **0**. Low spin: $5(-0.4\ \Delta_o) + 2P =$ **$-2.0\ \Delta_o + 2P$** (two more pairs than the free ion).

MARKING SCHEME

- ✓ +2 and $3d^5$ in both.
- ✓ 5 and 1 unpaired electrons.
- ✓ 5.92 BM and 1.73 BM.
- ✓ CFSE 0 and $-2.0\ \Delta_o + 2P$.

b. ANSWER A · 4

i. $E = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34} \times 3.00 \times 10^{8}}{575 \times 10^{-9}} =$ **3.46×10^{-19} J**.

ii. For a mole of photons: $3.46 \times 10^{-19} \times 6.022 \times 10^{23} = 2.08 \times 10^{5}$ J/mol, so $\Delta_o \approx$ **208 kJ/mol**.

iii. Cr^{3+} is $3d^3$, three electrons in t_{2g}: CFSE $= 3 \times (-0.4\ \Delta_o) = -1.2 \times 208 =$ **−250 kJ/mol**.

iv. Three unpaired electrons: $\mu = \sqrt{3 \times 5} = \sqrt{15} =$ **3.87 BM**.

MARKING SCHEME

- ✓ 3.46×10^{-19} J a photon.
- ✓ $\Delta_o \approx 208$ kJ/mol.
- ✓ CFSE = −250 kJ/mol.
- ✓ 3.87 BM.

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7 Think

ANSWER HA · 3

NH_3 comes after F^- in the spectrochemical series, so **$[Co(NH_3)_6]^{3+}$** has the larger Δ_o. $[CoF_6]^{3-}$, with the smaller gap, absorbs light of lower energy, the **longer wavelength** (orange-red), and looks blue, its complement; the ammonia complex absorbs shorter, bluer light and looks yellow-orange.
With fluoride, $\Delta_o <$ P: high spin, $t_{2g}^4\, e_g^2$, four unpaired electrons, so **$[CoF_6]^{3-}$ is paramagnetic**.
Ammonia is strong enough to pair cobalt(III)'s electrons, t_{2g}^6, so $[Co(NH_3)_6]^{3+}$ is diamagnetic.

MARKING SCHEME

- ✓ NH_3 is the stronger-field ligand: $[Co(NH_3)_6]^{3+}$ has the larger Δ_o.
- ✓ $[CoF_6]^{3-}$ absorbs the longer wavelength (lower energy), and so looks blue.
- ✓ $[CoF_6]^{3-}$ is high spin with four unpaired electrons: paramagnetic.

8 Activity: Colors of metal salts

(not marked)

WHAT STUDENTS SHOULD FIND

Cu^{2+} ($3d^9$) blue; Zn^{2+} ($3d^{10}$) colorless; Ni^{2+} ($3d^8$) green; Co^{2+} ($3d^7$) pink in water; MnO_4^- (manganese +7, $3d^0$) deep purple. Zn^{2+} is colorless because a full d subshell leaves no empty place for a d–d transition. Permanganate's color comes from charge transfer, an electron jumping from the oxygens to the manganese, not a d–d transition.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	7	10	13	3	**33**

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