Topic 15: Transition Metals

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

15.1 Know the definition of a transition metal as a d-block element that forms at least one stable ion with an incompletely filled d sub-shell.

A transition metal is a d-block element that forms at least one stable ion with a partially filled d sub-shell. Note: Sc and Zn are d-block elements but are NOT transition metals by this definition. Sc only forms Sc^{3+} (d^0); Zn only forms Zn^{2+} (d^{10}) – both have full or empty d sub-shells.

15.2 Be able to write electronic configurations of transition metal atoms and ions, using the 4s and 3d notation.

Atoms: fill 4s before 3d. E.g. Fe: [Ar] $3d^6$ $4s^2$; Cu: [Ar] $3d^{10}$ $4s^1$ (exception – full d sub-shell is especially stable); Cr: [Ar] $3d^5$ $4s^1$ (half-filled d sub-shell is especially stable).

Ions: remove 4s electrons first, then 3d. E.g. Fe^{2+}: [Ar] $3d^6$; Fe^{3+}: [Ar] $3d^5$; Cu^+: [Ar] $3d^{10}$; Cu^{2+}: [Ar] $3d^9$.

15.3 Know the characteristic properties of transition metals: variable oxidation state, complex ion formation, catalytic behaviour, and coloured ion formation.

Four key characteristic properties:

1. Variable oxidation states: transition metals can form stable ions in more than one oxidation state (e.g. Fe^{2+} and Fe^{3+}; Cu^+ and Cu^{2+}; Mn^{2+}, $Mn^{\prime+}$, Mn^{6+}, Mn^{7+}).
2. Complex ion formation: transition metal ions act as Lewis acids, accepting lone pairs from ligands to form complex ions.
3. Catalytic behaviour: transition metals and their compounds act as catalysts (e.g. Fe in the Haber process, MnO_2 for H_2O_2 decomposition, V_2O^5 in the Contact process).
4. Coloured ions: most transition metal ions are coloured in solution due to d-d electron transitions.

15.4 Understand why transition metals show variable oxidation states in terms of the energies of the 3d and 4s sub-shells.

The 3d and 4s sub-shells are very close in energy for transition metals. This means electrons can be removed from either the 4s or the 3d sub-shell without requiring a large amount of energy. As successive electrons are removed, the energy levels shift, allowing multiple stable oxidation states. This is unlike s-block metals (e.g. Na always forms Na^+ because removing a second electron requires far too much energy).

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15.5 Know what is meant by the term 'complex ion', including the terms 'ligand' and 'coordination number'.

Complex ion: a central metal ion surrounded by ligands, held together by dative (coordinate) covalent bonds.

Ligand: a molecule or ion that donates a lone pair of electrons to the central metal ion (Lewis base). E.g. H_2O, NH_3, Cl^-, CN^-, en (ethylenediamine), $EDTA^{4-}$.

Coordination number: the number of dative bonds formed between the central metal ion and its ligands. Most common: 6 (octahedral), 4 (tetrahedral or square planar), 2 (linear).

15.6 Be able to give the formula and name of common complex ions of Cu, Co, Fe and Cr.

Common complex ions:

Copper: $[Cu(H_2O)_6]^{2+}$ (blue, octahedral), $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (deep blue, octahedral), $[CuCl_4]^{2-}$ (yellow-green, tetrahedral), $[Cu(H_2O)_6]^{+}$ (not stable, very pale).

Cobalt: $[Co(H_2O)_6]^{2+}$ (pink, octahedral), $[CoCl_4]^{2-}$ (blue, tetrahedral), $[Co(NH_3)_6]^{3+}$ (yellow, octahedral).

Iron: $[Fe(H_2O)_6]^{2+}$ (pale green), $[Fe(H_2O)_6]^{3+}$ (pale violet/yellow-brown), $[Fe(CN)_6]^{4-}$ (hexacyanoferrate(II)), $[Fe(CN)_6]^{3-}$ (hexacyanoferrate(III)).

Chromium: $[Cr(H_2O)_6]^{3+}$ (violet/green), $[Cr(NH_3)_6]^{3+}$ (purple).

15.7 Be able to name complex ions and their compounds using IUPAC nomenclature.

Naming rules:

1. Name ligands first (alphabetical order), then the metal.
2. Ligand names: aqua (H_2O), ammine (NH_3), chloro (Cl^-), cyano (CN^-), hydroxo (OH^-), oxalato ($C_2O_4^{2-}$).
3. Number prefixes: di, tri, tetra, penta, hexa (or bis, tris for complex ligands).
4. Metal name: use English name for cations; add -ate suffix for anionic complexes (e.g. ferrate for Fe, cuprate for Cu).
5. Oxidation state in Roman numerals in brackets after the metal.

E.g. $[Cu(NH_3)_4(H_2O)_2]^{2+}$ = tetraammminediaquacopper(II) ion.

15.8 Be able to describe the shapes of complex ions with coordination numbers 2, 4 and 6.

Coordination number 6: octahedral (bond angles 90°). Most common for transition metal aqua complexes. E.g. $[Fe(H_2O)_6]^{3+}$.

Coordination number 4: tetrahedral (bond angles ~109.5°) or square planar (bond angles 90°). Tetrahedral: e.g. $[CoCl_4]^{2-}$, $[CuCl_4]^{2-}$. Square planar: e.g. $[Pt(NH_3)_2Cl_2]$ (cisplatin), $[Cu(NH_3)_4]^{2+}$.

Coordination number 2: linear (bond angle 180°). E.g. $[Ag(NH_3)_2]^{+}$, $[Ag(S_2O_3)_2]^{3-}$.

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15.9 Understand the origin of colour in transition metal complexes in terms of d-d electron transitions.

In a transition metal complex, the presence of ligands causes the five d orbitals to split into two groups of different energies (crystal field splitting). When white light passes through, photons of a specific energy are absorbed to promote an electron from the lower energy d orbital to the higher energy d orbital (d-d transition). The colour we observe is the complementary colour of the light absorbed.

E.g. $[Cu(H_2O)_6]^{2+}$ absorbs red/orange light → appears blue. A d^{10} ion (e.g. Zn^{2+}) cannot undergo d-d transitions and is therefore colourless.

15.10 Understand that the colour observed depends on the ligand and the metal ion.

The colour depends on the size of the d-orbital splitting, which is affected by:

- The identity of the ligand (spectrochemical series: CN^- causes large splitting → absorbs high energy/short wavelength light; Cl^- causes small splitting → absorbs low energy/long wavelength light).
- The identity and oxidation state of the metal ion (higher oxidation state → greater splitting).

This is why ligand substitution reactions cause colour changes.

15.11 Understand why transition metal ions are used as catalysts.

Transition metals and their compounds are effective catalysts because:

1. Variable oxidation states: they can gain and lose electrons easily, acting as intermediates in redox reactions (e.g. Fe^{2+}/Fe^{3+} in the Contact process, V^{+}/V^{5+} in the Contact process).
2. Complex ion formation: reactants can adsorb onto the metal surface, weakening bonds and lowering activation energy (heterogeneous catalysis).

Examples: Fe in Haber process, V_2O^5 in Contact process, MnO_2 for H_2O_2 decomposition, Pt/Pd in catalytic converters.

15.12 Know what is meant by the terms 'monodentate', 'bidentate' and 'multidentate' as applied to ligands.

Monodentate: donates one lone pair to the metal (one dative bond). E.g. H_2O, NH_3, Cl^-, CN^-.

Bidentate: donates two lone pairs (two dative bonds) from two donor atoms. E.g. ethylenediamine (en, $H_2NCH_2CH_2NH_2$), oxalate ($C_2O_4^{2-}$).

Multidentate (polydentate): donates multiple lone pairs. E.g. $EDTA^{4-}$ (hexadentate – 6 donor atoms, can replace all 6 water ligands in an octahedral complex).

15.13 Understand the chelate effect and why chelate complexes are more thermodynamically stable.

The chelate effect: complexes formed with bidentate or multidentate ligands are more thermodynamically stable than those with monodentate ligands. This is primarily an entropic effect: when a multidentate ligand replaces several monodentate ligands, the number of particles in solution increases, so ΔS_{system} increases. With ΔH being similar, this makes ΔG more negative, increasing stability. E.g. $[Cu(en)_2]^{2+}$ is more stable than $[Cu(NH_3)_4]^{2+}$.

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15.14 Know what is meant by the term 'isomerism' as applied to complex ions.

Two main types of isomerism in complex ions:

1. cis-trans (geometric) isomerism: occurs in square planar complexes with two different ligands (e.g. $[Pt(NH_3)_2Cl_2]$). cis: like ligands on the same side; trans: like ligands on opposite sides. Also in octahedral complexes with formula $[Ma_4b_2]$.
2. Optical isomerism: occurs in octahedral complexes with three bidentate ligands (e.g. $[Cr(en)_3]^{3+}$ or $[Fe(ox)_3]^{3-}$). Two non-superimposable mirror images (enantiomers). One rotates plane-polarised light clockwise (+), the other anticlockwise (–).

15.15 Know what is meant by the term 'ligand substitution' and understand that it can cause colour changes.

Ligand substitution: one ligand in a complex ion is replaced by another. The incoming ligand donates its lone pair to the metal, displacing the existing ligand. Because different ligands cause different d-orbital splitting, ligand substitution changes the energy of light absorbed and therefore the colour of the complex. E.g. adding NH_3 to $[Cu(H_2O)_6]^{2+}$ (blue) gives $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (deep blue/violet).

15.16 Know the use of cis-platin as an anti-cancer drug, including the reasons for its activity.

cis-Platin: cis-$[Pt(NH_3)_2Cl_2]$ is a square planar complex used as a chemotherapy drug. It works by entering cells and losing its Cl^- ligands (replaced by water in the low-Cl^- environment inside cells). The resulting complex then binds to two adjacent guanine bases on the same strand of DNA, forming a cross-link that distorts the DNA helix and prevents replication. The trans isomer is not effective because its geometry prevents it from forming this cross-link.

15.17 Know that haemoglobin contains Fe^{2+} in a complex with a porphyrin ring and that CO can bond to Fe^{2+} more strongly than O_2.

Haemoglobin contains Fe^{2+} at the centre of a porphyrin ring (a large, planar, multidentate ligand). O_2 binds reversibly to Fe^{2+} as a ligand, allowing oxygen to be transported around the body. CO binds to the same site as O_2 but with ~200× greater affinity. CO cannot be easily displaced, blocking O_2 transport and causing CO poisoning. CO acts as a competitive ligand for the Fe^{2+} site.

15.18 Know the reactions of $Cu^{2+}(aq)$ ions with NaOH(aq) and $NH_3(aq)$.

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$ [blue precipitate]

Excess NaOH: $Cu(OH)_2$ does not dissolve (no reaction with excess NaOH).

$NH_3(aq)$ – limited: same blue $Cu(OH)_2$ precipitate.

$NH_3(aq)$ – excess: $Cu(OH)_2$ dissolves to form the deep blue/violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex (ligand substitution: NH_3 replaces H_2O and OH^-).

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15.19 Know the reactions of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ ions with NaOH(aq) and $NH_3(aq)$.

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$ [green precipitate; turns rust-brown on standing as it oxidises to $Fe(OH)_3$]

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$ [rust-brown precipitate]

Both precipitates are insoluble in excess NaOH.

With $NH_3(aq)$: same precipitates form on addition of limited NH_3 (acts as a base). Neither $Fe(OH)_2$ nor $Fe(OH)_3$ dissolves in excess NH_3 (no complex ion formation).

15.20 Know the reactions of $Cr^{3+}(aq)$ ions with NaOH(aq) and $NH_3(aq)$.

$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$ [grey-green precipitate]

Excess NaOH: $Cr(OH)_3$ dissolves to form $[Cr(OH)_6]^{3-}$ (dark green solution) – $Cr(OH)_3$ is amphoteric.

Excess NH_3: $Cr(OH)_3$ dissolves to form $[Cr(NH_3)_6]^{3+}$ (purple solution) – ligand substitution.

15.21 Know the reactions of $Co^{2+}(aq)$ ions with NaOH(aq) and $NH_3(aq)$.

$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$ [blue/green precipitate]

Excess NaOH: $Co(OH)_2$ does not dissolve.

Excess NH_3: $Co(OH)_2$ dissolves to give $[Co(NH_3)_6]^{2+}$ (pale yellow/brown solution) which oxidises in air to $[Co(NH_3)_6]^{3+}$ (orange/yellow – Co^{3+} complex).

15.22 Know the use of EDTA in complexometric titrations to determine the concentration of metal ions.

$EDTA^{4-}$ (ethylenediaminetetraacetate) is a hexadentate ligand that forms very stable 1:1 complexes with almost all metal ions. In a complexometric titration: EDTA is added from a burette to a solution of the metal ion using a suitable metallochromic indicator (e.g. Eriochrome Black T). At the end point, all metal ions are complexed by EDTA and the indicator changes colour (e.g. wine red to blue). Used to determine water hardness (Ca^{2+} and Mg^{2+}).

15.23 Know the redox reactions of transition metal ions: the reduction of $Cr_2O_7^{2-}$ by Fe^{2+} and the oxidation of Fe^{2+} by MnO_4^-.

$Cr_2O_7^{2-}$ (orange, Cr^{6+}) + $6Fe^{2+}$ + $14H^+ \rightarrow 2Cr^{3+}$ (green) + $6Fe^{3+}$ + $7H_2O$

$Cr_2O_7^{2-}$ is the oxidising agent; Fe^{2+} is the reducing agent.

MnO_4^- (purple, Mn^{7+}) + $5Fe^{2+}$ + $8H^+ \rightarrow Mn^{2+}$ (nearly colourless) + $5Fe^{3+}$ + $4H_2O$

MnO_4^- is the oxidising agent; Fe^{2+} is the reducing agent. Used in titrations – MnO_4^- is self-indicating (purple → colourless at end point).

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15.24 Know the disproportionation of Cu^+ ions in aqueous solution.

Cu^+ ions are unstable in aqueous solution and undergo disproportionation – simultaneous oxidation and reduction of the same species:

$2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$

Cu^+ is both oxidised (to Cu^{2+}, +1 → +2) and reduced (to Cu, +1 → 0). This occurs because the $E^{\ominus}$ values favour the reaction: $E^{\ominus}(Cu^+/Cu) > E^{\ominus}(Cu^{2+}/Cu^+)$. Cu^+ compounds are stable in the solid state (e.g. Cu_2O, CuCl) but not in solution.

15.25 Know the reactions of metal ions with carbonate ions.

Transition metal ions react with $Na_2CO_3(aq)$ to form insoluble metal carbonates or metal hydroxide carbonates:

$Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$ [green/blue precipitate; often forms basic carbonate $Cu_2(OH)_2CO_3$]

$Fe^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3(s)$ [pale green precipitate]

$Fe^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow$ does NOT form $Fe_2(CO_3)_3$; instead hydrolysis occurs to form $Fe(OH)_3(s) + CO_2(g)$ [because $Fe_2(CO_3)_3$ is too unstable].

15.26 Know the reactions of transition metal ions with iodide ions, and use these in iodometric titrations.

Cu^{2+} ions oxidise I^- ions:

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s)$ [white ppt] + $I_2(aq)$ [brown solution]

The liberated I_2 is then titrated with sodium thiosulfate:

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

Starch indicator is added near the end point: starch turns blue-black with I_2; decolourises at the end point. Used to determine Cu^{2+} concentration. Fe^{3+} also oxidises I^-: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$.

15.27 Know the interconversion of chromate(VI) and dichromate(VI) ions.

CrO_4^{2-} (chromate(VI), yellow) $Cr_2O_7^{2-}$ (dichromate(VI), orange)

In acidic conditions (add H^+): equilibrium shifts right → $Cr_2O_7^{2-}$ forms (orange).

$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

In alkaline conditions (add OH^-): equilibrium shifts left → CrO_4^{2-} forms (yellow).

$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$

This is a pH-dependent equilibrium, NOT a redox reaction.

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15.28 Know the reduction of dichromate(VI) ions by ethanol and primary alcohols.

$Cr_2O_7^{2-}$ (orange) is reduced to Cr^{3+} (green) when it oxidises primary alcohols or ethanol:

Primary alcohols → aldehydes → carboxylic acids (with excess $Cr_2O_7^{2-}/H^+$).

E.g. $CH_3CH_2OH + Cr_2O_7^{2-}/H^+ \rightarrow CH_3CHO$ (aldehyde) then → CH_3COOH (with excess).

Colour change: orange → green. This reaction is used in breathalysers to detect ethanol.

15.29 Know the reactions of vanadium species and the use of vanadium in the Contact process.

Vanadium exists in oxidation states +2, +3, +4, and +5 in aqueous solution:

+5: VO_2^+ (yellow); +4: VO^{2+} (blue); +3: V^{3+} (green); +2: V^{2+} (violet).

Reduction with zinc and dilute H_2SO_4 proceeds stepwise through all states.

Contact process: V_2O^5 catalyst oxidises SO_2 to SO_3.

$V_2O^5 + SO_2 \rightarrow V_2O_4 + SO_3$ (V^{5+} reduced to V^{4+})

$V_2O_4 + ½O_2 \rightarrow V_2O^5$ (V^{4+} re-oxidised to V^{5+})

The catalyst is regenerated: this shows variable oxidation state in catalysis.

15.30 Know the test for the presence of a transition metal ion using NaOH(aq), NH_3(aq) and Na_2CO_3(aq).

Summary of precipitate colours and behaviour:

Cu^{2+}: blue ppt with NaOH/NH_3; dissolves in excess NH_3 (deep blue); green ppt with Na_2CO_3.

Fe^{2+}: green ppt with NaOH/NH_3; turns rust-brown on standing; pale green ppt with Na_2CO_3.

Fe^{3+}: rust-brown ppt with NaOH/NH_3; no precipitate with Na_2CO_3 (gives $Fe(OH)_3 + CO_2$).

Cr^{3+}: grey-green ppt with NaOH; dissolves in excess NaOH (dark green); dissolves in excess NH_3 (purple).

Co^{2+}: blue/green ppt with NaOH; dissolves in excess NH_3 (brown, oxidises to Co^{3+} complex).

Mn^{2+}: off-white/cream ppt with NaOH; oxidises to brown MnO_2 on standing.

15.31 Know that the concentration of a coloured complex ion can be determined using colorimetry.

Colorimetry: measures the absorbance of a coloured solution at a specific wavelength. The wavelength used is complementary to the colour of the solution (the wavelength most strongly absorbed). Beer-Lambert Law: absorbance is directly proportional to concentration (A c). Method: (1) Prepare a calibration curve using standard solutions of known concentration. (2) Measure absorbance of the unknown solution. (3) Read off the concentration from the calibration curve.

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15.32

Know what is meant by the autocatalytic behaviour of Mn^{2+} in the reaction of MnO_4^- with $C_2O_4^{2-}$.

The reaction between MnO_4^- and oxalate ($C_2O_4^{2-}$) in acidic solution is initially slow because the reactants are both negatively charged and repel each other at the active site. However, Mn^{2+} produced during the reaction acts as a catalyst for the reaction itself (autocatalysis). The rate initially increases as Mn^{2+} builds up, before slowing as the reactants are consumed. Rate-time curve: starts slow, accelerates, then slows – an S-shaped (sigmoidal) curve.

15.33

Know the use of Fe^{3+} as a homogeneous catalyst in the reaction between I^- and $S_2O_8^{2-}$.

The reaction $I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$ is slow without a catalyst because both ions are negatively charged. Fe^{3+} acts as a homogeneous catalyst by providing an alternative two-step mechanism:

Step 1: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ (Fe^{3+} oxidises I^-)

Step 2: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ (Fe^{2+} reduces $S_2O_8^{2-}$)

Fe^{3+} is regenerated. Both steps involve oppositely charged ions – lower activation energy.

15.34

Be able to use standard electrode potentials to explain observations in transition metal reactions.

Use $E^{\ominus}$ values to predict and explain which species oxidises and which reduces in a transition metal reaction. E.g. whether Cu^+ disproportionates, whether Fe^{2+} can reduce $Cr_2O_7^{2-}$, whether I^- can reduce Fe^{3+}. Method: write the two half-equations, assign $E^{\ominus}$ values, calculate $E^{\ominus}cell = E^{\ominus}cathode - E^{\ominus}anode$. If $E^{\ominus}cell > 0$, the reaction is feasible. Always quote relevant $E^{\ominus}$ values in explanations.

15.35

Know the use of transition metals as heterogeneous and homogeneous catalysts, with examples.

Heterogeneous catalysts: different phase from reactants. E.g. Fe (solid) in the Haber process for $N_2 + H_2 \rightarrow NH_3$; Pt/Rh (solid) in catalytic converters for NOx and CO removal; V_2O^5 (solid) in the Contact process for $SO_2 \rightarrow SO_3$; MnO_2 (solid) for H_2O_2 decomposition. Mechanism: adsorption of reactants weakens bonds, lowers Ea.

Homogeneous catalysts: same phase as reactants (usually aqueous). E.g. Fe^{3+} in $I^-/S_2O_8^{2-}$ reaction; Mn^{2+} (autocatalysis) in $MnO_4^-/C_2O_4^{2-}$; Co^{2+}/Co^{3+} in decomposition of 2-hydroxypropanedioic acid.

Qualitative Analysis of Transition Metal Ions Using NaOH(aq) and NH(aq)

ABOUT THESE NOTES

Notes written by Chloe Archard (MSc Biochemistry, Oxford-trained chemist, 20+ years teaching experience at top UK independent schools). For 1-1 tuition, revision courses, and more free resources: chemistrywithchloe.com

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