3.2.5 Transition Metals

★ A-LEVEL ONLY — not examined at AS level

3.2.5.1 *Transition metal properties: complex formation, coloured ions, variable oxidation state, catalytic activity. Ligands and co-ordination number.*

Transition metal: d-block element forming at least one stable ion with an incomplete d sub-shell. Sc and Zn are NOT transition metals.

Characteristic properties: variable oxidation states, coloured compounds, catalytic activity, complex ion formation.

Ligand: molecule/ion with a lone pair donated to a metal ion (dative bond).

Complex: central metal ion surrounded by ligands.

Co-ordination number: number of dative bonds to the central ion.

3.2.5.2 *Ligand substitution reactions. Monodentate, bidentate, multidentate. Chelate effect. Haemoglobin and CO.*

H■O → NH■ exchange: no change in co-ordination number (both small, uncharged). May be incomplete: [Cu(NH■)■(H■O)■]²■.

H■O → Cl■ exchange: co-ordination number 6→4 (Cl■ is larger). Octahedral → tetrahedral.

Chelate effect: bidentate/multidentate ligands replace monodentate → more free particles → positive ΔS → more stable (more negative ΔG).

Haemoglobin: Fe²■ complex with multidentate porphyrin. O■ binds reversibly. CO binds more strongly than O■ (irreversible) → toxic (carboxyhaemoglobin).

3.2.5.3 *Shapes of complexes: octahedral, tetrahedral, square planar, linear. Isomerism: cis-trans and optical. Cisplatin.*

Octahedral: 6 ligands, 90° (e.g. [Cu(H■O)■]²■). Can show cis-trans or optical isomerism (with bidentate ligands).

Tetrahedral: 4 large ligands, 109.5° (e.g. [CoCl■]²■).

Square planar: 4 ligands, 90° (e.g. cisplatin [PtCl■(NH■)■]). Cisplatin (cis isomer) used in cancer treatment — binds to DNA, prevents replication.

Linear: 2 ligands, 180° (e.g. [Ag(NH■)■]■ in Tollens' reagent).

3.2.5.4 *Colour in transition metal complexes. ΔE = hν. Effect of oxidation state, co-ordination number and ligand on colour.*

Colour from d-d transitions: ligands split d-orbitals into two energy levels. Electrons absorb visible light of frequency ν where ΔE = hν = hc/λ. Colour seen = complementary colour of light absorbed.

Colour changes when ΔE changes due to: change in oxidation state, change in ligand, change in co-ordination number.

Ions with d■ or d¹■ are colourless (no d-d transition possible).

Colorimetry: absorbance ∝ concentration.

3.2.5.5 *Variable oxidation states. Vanadium (V to II). Redox titrations: Fe²■/MnO■■ and C■O■²■/MnO■■.*

Vanadium reduced by Zn in acid: VO■■ (yellow, +5) → VO²■ (blue, +4) → V³■ (green, +3) → V²■ (violet, +2).

MnO■■ + 8H■ + 5Fe²■ → Mn²■ + 5Fe³■ + 4H■O (1:5 ratio). Self-indicating: first permanent pink = end point.

2MnO■■ + 16H■ + 5C■O■²■ → 2Mn²■ + 10CO■ + 8H■O (2:5 ratio). Warm to ~60°C. Mn²■ autocatalyses.

Always acidify with H■SO■ (never HCl or HNO■).

3.2.5.6 *Catalysts: heterogeneous and homogeneous. V■O■, Fe, Fe²■, Mn²■ autocatalysis.*

Heterogeneous catalyst: different phase from reactants. Reaction at the surface. Can be poisoned (impurities block active sites).

V■O■ (Contact process): SO■ + V■O■ → SO■ + V■O■ (V: +5→+4), then V■O■ + ½O■ → V■O■ (regenerated).

Fe (Haber process): N■ + 3H■ ■ 2NH■.

Homogeneous catalyst: same phase as reactants. Works via intermediate.

Fe²■ catalyses I■/S■O■²■: Fe²■ → Fe³■ → Fe²■ (regenerated).

Mn²■ autocatalysis: MnO■■/C■O■²■ starts slow, speeds up as Mn²■ product catalyses the reaction.