Chemistry of transition elements

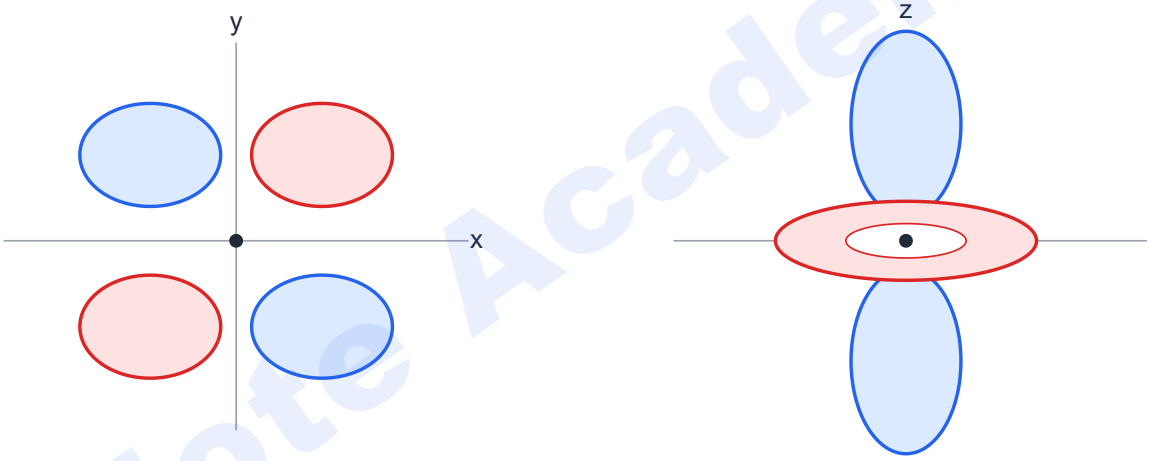
Transition element properties, ligands and complex ions, geometry and coordination number, ligand exchange, redox titrations, d-orbital splitting and colour, stereoisomerism of complexes, and stability constants.

28.1 General physical and chemical properties of the first row of transition elements, titanium to copper

A **transition element** is a d-block element which forms **one or more stable ions with incomplete d orbitals**. Scandium and zinc are not transition elements: Sc^{3+} has no d electrons and Zn^{2+} has a full $3d^{10}$.

The shapes of two of the five $3d$ orbitals: the $3d_{xy}$ has four lobes lying **between** the x and y axes; the $3d_{z^2}$ has two lobes along the z axis and a ring (torus) in the xy plane.

Two d-orbital shapes: schematic probability surfaces



3dxy: lobes lie between x and y axes **3dz²: axial lobes and an equatorial ring**

Colours distinguish phase, not electrical charge. Drawings are not to scale.

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Properties

1. **Variable oxidation states**, because the $3d$ and $4s$ sub-shells are **close in energy**, so electrons from both can be lost.
2. **Catalysts**, because they have **more than one stable oxidation state** (they can gain and lose electrons easily) and have **vacant d orbitals** that are energetically accessible, so reactants can form **dative bonds** with them (adsorption).
3. **Complex ions**, because of vacant low-energy d orbitals that accept lone pairs from ligands.
4. **Coloured compounds** (see 28.3).

Common oxidation states: Ti +4, V +2 to +5, Cr +3 and +6, Mn +2, +4 and +7, Fe +2 and +3, Co +2 and +3, Ni +2, Cu +1 and +2.

Apply the definition to the ions actually formed

Being in the d block and being a transition element are related but not identical criteria. Apply the syllabus definition to stable ions with incomplete d sub-shells. Zinc commonly forms Zn^{2+} with $3d^{10}$, while scandium commonly forms Sc^{3+} with $3d^{0}$. Copper qualifies because Cu^{2+} has $3d^{9}$, even though neutral copper has a filled 3d sub-shell.

Worked example: neutral iron is $[Ar]3d^{6}4s^{2}$. Its 2+ ion is $[Ar]3d^{6}$ and its 3+ ion is $[Ar]3d^{5}$: remove 4s electrons before 3d. Both ions have incomplete d sub-shells. This configuration work connects directly to variable oxidation states, magnetism and the simplified d–d explanation of colour.

Transition metals commonly have relatively high densities and melting points because of their structures and metallic bonding, but the detailed values are not perfectly uniform. When explaining catalysis, distinguish changing oxidation states in a redox cycle from adsorption on a metal surface; both can provide a lower-barrier route through different mechanisms.

> TRY IT
>
> Why does Cu^{+} being $3d^{10}$ not exclude copper from the transition-element definition?

Answer: Copper also forms stable Cu^{2+} ions with an incomplete $3d^{9}$ sub-shell. The definition requires at least one suitable stable ion, not every ion to be incomplete.

28.2 General characteristic chemical properties of the first set of transition elements, titanium to copper

Complex ions and ligands

- A **ligand** is a species with a **lone pair of electrons** that forms a **dative covalent bond** to a central metal atom or ion.
- A **complex** is a molecule or ion with a central metal atom or ion surrounded by ligands.
- The **coordination number** is the number of dative bonds to the metal.
- **Monodentate** ligands donate one pair: H_2O, NH_3, Cl^{-}, CN^{-}. **Bidentate** ligands donate two pairs: 1,2-diaminoethane (en, $H_2NCH_2CH_2NH_2$) and the ethanedioate ion $C_2O_4^{2-}$. **Polydentate** ligands donate more: $EDTA^{4-}$ (six).

The charge on a complex is the sum of the metal charge and the ligand charges. $[Fe(CN)_6]^{3-}$: Fe is +3 with six CN^{-}. $[CuCl_4]^{2-}$: Cu is +2 with four Cl^{-}.

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Geometry

Coordination number	Shape	Angle	Example
2	linear	180°	$[Ag(NH_3)_2]^+$
4	tetrahedral	109.5°	$[CuCl_4]^{2-}$
4	square planar	90°	$[Pt(NH_3)_2Cl_2]$
6	octahedral	90°	$[Cu(H_2O)_6]^{2+}$

Ligand exchange

One ligand is replaced by another. For copper(II) and cobalt(II) ions:

Reaction	Observation
$[Cu(H_2O)_6]^{2+}$ + a little NH_3 or OH^-	pale blue precipitate of $Cu(OH)_2$
... then excess NH_3	deep blue solution, $[Cu(NH_3)_4(H_2O)_2]^{2+}$
$[Cu(H_2O)_6]^{2+}$ + concentrated HCl	yellow-green solution, $[CuCl_4]^{2-}$
$[Co(H_2O)_6]^{2+}$ (pink) + a little NH_3 or OH^-	blue precipitate of $Co(OH)_2$
... then excess NH_3	brown or straw-coloured solution, $[Co(NH_3)_6]^{2+}$ (darkens in air as Co^{2+} is oxidised)
$[Co(H_2O)_6]^{2+}$ + concentrated HCl	blue solution, $[CoCl_4]^{2-}$

In these examples, chloride replacement can change coordination number from six to four and produce a tetrahedral complex. Ligand size contributes, but geometry is not determined by size alone. The water ligands in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ are the two that remain after four waters have been replaced.

Redox reactions and titrations

Use $E^\ominus$ values to predict the feasibility of reactions of transition elements and their ions.

- MnO_4^- **with** Fe^{2+} in acid: $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$. **Self-indicating**: the purple MnO_4^- is added from the burette and decolourises until the end-point, where the first permanent pink appears.
- MnO_4^- **with ethanedioate** (warm, acid): $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$. The reaction is autocatalysed by Mn^{2+}.

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- Cu^{2+} **with** I^-**:** $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$. The iodine produced is titrated with sodium thiosulfate, $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, using starch added near the end-point (blue-black to colourless), so one mole of I_2 is formed per two moles of Cu^{2+}.

> **TRY IT**
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> 25.0 cm³ of Fe^{2+} solution requires 21.5 cm³ of 0.0200 mol dm⁻³ $KMnO_4$. Find $[Fe^{2+}]$.

Moles $MnO_4^- = 0.0215 \times 0.0200 = 4.30 \times 10^{-4}$; $Fe^{2+} = 5\times$ that $= 2.15 \times 10^{-3}$ mol; $[Fe^{2+}] = 2.15 \times 10^{-3}/0.0250 = 0.0860$ mol dm⁻³.

Distinguish precipitation, ligand exchange and redox

A little ammonia supplies hydroxide through its weak-base reaction with water, so a metal hydroxide can precipitate. In excess ammonia, some precipitates dissolve because ammine complexes form. These are different chemical steps. For copper, the deep blue solution is evidence of a changed coordination environment rather than a change from copper(II) to copper(I).

Useful simplified equations are $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2(s)$ and $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$. Charges and ligand counts are conserved. Chloride replacement can instead change coordination number: $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$.

Complex geometry is not decided by ligand size alone. Metal identity, oxidation state, ligand properties and electronic factors matter; square-planar four-coordinate examples demonstrate why “four ligands always means tetrahedral” is wrong. For chelating ligands count donor **atoms/bonds**, not ligand molecules. Three bidentate ligands can give coordination number six.

Worked example: $[Co(en)_3]^{3+}$ contains three neutral en molecules, each binding through two nitrogens. The coordination number is six and cobalt's oxidation number is +3. For $[Fe(C_2O_4)_3]^{3-}$, three 2− ligands contribute −6, so iron must be +3 to give total −3.

> **TRY IT**
>
> Find the oxidation number and coordination number of nickel in $[Ni(en)_2(H_2O)_2]^{2+}$.

Answer: Both ligand types are neutral, so nickel is +2. Two en ligands donate four pairs and two waters donate two more, giving coordination number six, not four.

Redox titrations: from endpoint to stoichiometry

Start with the balanced redox equation, not an assumed 1 : 1 volume ratio. Acidified manganate(VII) titrations require suitable acid conditions; sulfuric acid is commonly used because chloride can itself be

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oxidised in sufficiently oxidising mixtures. Add manganate(VII) until a faint permanent pink remains, showing a slight excess beyond consumption by the reducing agent.

In copper iodometry, excess iodide produces iodine and a white copper(I) iodide precipitate. The liberated iodine is measured with thiosulfate. Combining the two equations shows one mole Cu^{2+} corresponds to one mole thiosulfate overall, although iodine itself reacts with two moles thiosulfate. Derive this relationship rather than confusing the two stages.

Worked example: a sample liberates iodine requiring 18.0 cm^3 of 0.100 mol dm^{-3} thiosulfate. Thiosulfate amount is 0.00180 mol, iodine amount 0.000900 mol and original Cu^{2+} amount **0.00180 mol**. If the copper sample volume was 25.0 cm^3, its concentration was 0.0720 mol dm^{-3}. Starch is added near the endpoint, and loss of the blue-black colour indicates iodine has been consumed.

28.3 Colour of complexes

In an **isolated atom** the five $3d$ orbitals are **degenerate** (equal in energy). In a complex the ligands' lone pairs repel the d electrons, splitting them into two **non-degenerate** sets with an energy gap ΔE:

- **Octahedral: three lower** (d_{xy}, d_{xz}, d_{yz}) and **two higher** (d_{z^2}, $d_{x^2-y^2}$).
- **Tetrahedral: two lower** and **three higher**.

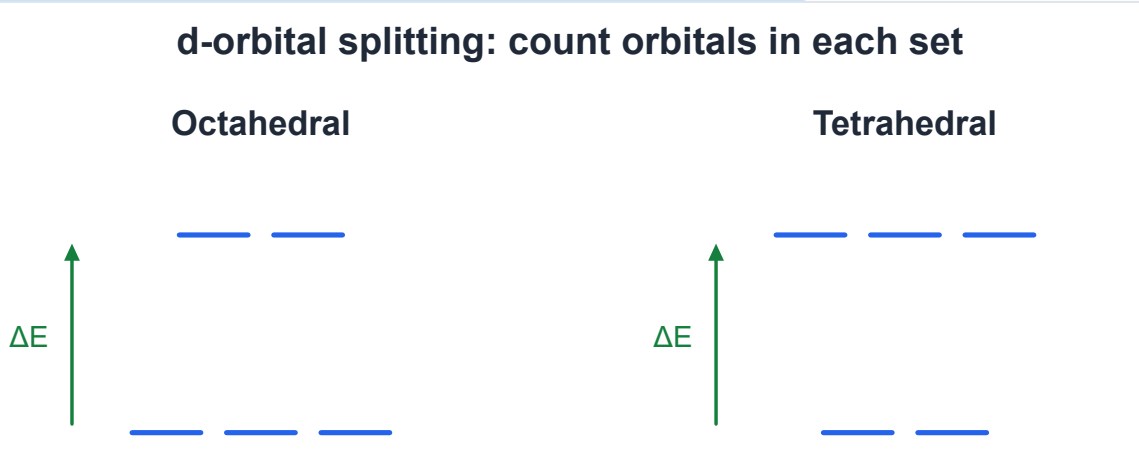
An electron absorbs light of energy $\Delta E = hv$ (frequency v) and is **promoted** from the lower to the higher set (a d–d transition). The light **not absorbed**, the **complementary colour**, is seen. A complex with an **empty or full d sub-shell** (Sc^{3+}, Zn^{2+}, Cu^{+}) has no d–d transition, so it is colourless.

> **The colour depends on ΔE, which depends on the metal ion, its oxidation state, the ligands (and the coordination number). A larger ΔE means higher-frequency (shorter-wavelength) light is absorbed.**

Changing the ligand changes ΔE, hence the colour: $[Cu(H_2O)_6]^{2+}$ is pale blue and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep blue (ammonia gives a larger ΔE, so it absorbs light of a higher frequency); $[CuCl_4]^{2-}$ is yellow.

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What the colour model does and does not predict



Absorbed photon: ΔE = hv. The complementary transmitted colour is seen.

Schematic level counts, not a comparison of equal splitting magnitudes.

Ligand interactions split otherwise equal-energy d orbitals. A suitable electron absorbs a photon matching the gap and is promoted between the split levels. The observed transmitted/reflected light is complementary to absorbed wavelengths. Changing the ligand can change the gap without changing the metal oxidation number; oxidising the metal can also change the gap and electron configuration.

Within the simple d–d model, d^0 and d^{10} ions lack the required partially filled levels for such transitions. This does **not** mean every compound containing them is colourless: charge-transfer processes or coloured ligands can produce colour by other routes. Likewise, coloured manganate(VII), with manganese(VII) formally d^0, should not be explained by a routine d–d transition.

Worked example: if a ligand change increases ΔE, then from $\Delta E = h\nu = hc/\lambda$, absorbed frequency increases and wavelength decreases. This statement concerns absorbed light, not a simplistic rule that the visible solution must become "more blue". A real colour depends on the absorption pattern.

> **TRY IT**
>
> Why can a copper(II) solution change colour on adding ammonia without electron transfer?

Answer: Ligand exchange changes the d-orbital splitting and wavelengths absorbed. Copper can remain in oxidation state +2 throughout, so colour change alone does not prove redox.

28.4 Stereoisomerism in transition element complexes

- **Geometrical (cis/trans):** the square planar $[Pt(NH_3)_2Cl_2]$ (cis has the two Cl adjacent at 90°, and trans opposite at 180°), and octahedral $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Ni(en)_2(H_2O)_2]^{2+}$ (the two water ligands cis or trans).
- **Optical:** an octahedral complex with **bidentate ligands**, for example $[Ni(en)_3]^{2+}$ and cis-$[Ni(en)_2(H_2O)_2]^{2+}$, has **non-superimposable mirror images** (enantiomers).

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Polarity: a symmetrical complex whose bond dipoles cancel is **non-polar** (trans-$[Pt(NH_3)_2Cl_2]$); a complex that has the dipoles in the same direction is **polar** (the cis isomer; this is the anti-cancer drug cisplatin).

Recognising geometrical and optical isomers

For square-planar $[Pt(NH_3)_2Cl_2]$, cis has the two chlorides adjacent and trans has them opposite. Rotating the whole diagram does not create a new isomer: compare relative positions of ligands. An octahedral complex with two distinguishable ligands among four others can similarly allow adjacent and opposite arrangements.

Optical isomers are mirror images that cannot be superimposed by rotation. Three bidentate ligands can wrap around an octahedral centre in two handed arrangements. The presence of a carbon atom with four different groups is not required: the entire coordination arrangement can be chiral. A drawing must make the three-dimensional arrangement clear with appropriate projection conventions.

> **TRY IT**
>
> Why are two drawings of a square-planar complex with the chlorides opposite one another not necessarily two different isomers?

Answer: They may simply be rotated drawings of the same trans arrangement. Isomerism requires a different arrangement that cannot be made identical by rotating the whole object.

28.5 Stability constants, Kstab

The **stability constant**, K_{stab}, is the **equilibrium constant for the formation of the complex ion** from its constituent ions or molecules in a solvent. The concentration of water is **not** included.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \qquad K_{stab} = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$$

units $mol^{-4}\ dm^{12}$.

- A **large** K_{stab} means the complex is **stable**, because the equilibrium lies to the right.
- **Ligand exchange** goes in the direction of the larger K_{stab}: ammonia replaces water in the copper complex because the ammine complex has the larger K_{stab}; EDTA replaces many ligands (a very large K_{stab}, aided by a gain in entropy as more particles are released).

> **TRY IT**
>
> For $[Cu(NH_3)_4]^{2+}$, equilibrium concentrations are complex 0.10, Cu^{2+} 1.0×10^{-13}, NH_3 0.20 (mol dm^{-3}). Find K_{stab}.

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$$K_{stab} = \frac{0.10}{(1.0 \times 10^{-13})(0.20)^4} = 6.3 \times 10^{14}\ \text{mol}^{-4}\ \text{dm}^{12}.$$

Using stability constants with equilibrium reasoning

Write the formation equilibrium before the expression, omit the pure solvent, and raise each free-ligand concentration to its coefficient. A large value favours complex formation under the specified conditions. Comparing constants is most direct for comparable equations and conventions; an observed ligand exchange also depends on concentrations, so a very large excess of one ligand can shift the balance.

Worked example: for $M^{2+} + 2L \rightleftharpoons ML_2^{2+}$, $K_{stab} = [ML_2^{2+}]/([M^{2+}][L]^2)$. If complex concentration is 0.0200, free metal concentration 1.00×10^{-6} and free ligand concentration 0.100 mol dm^{-3}, the constant is 2.00×10^{6} dm^6 mol^{-2}. Use **free ligand at equilibrium**, not total ligand originally added, when the difference matters.

Chapter check: count donor atoms, balance ligand-exchange equations, distinguish colour change from redox, and separate equilibrium stability from reaction speed. Link quantitative work to **equilibria** and **electrode potentials**.

References and further reading

Scope follows section 28 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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