

Chemistry of transition elements A2

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Read first: [Atomic structure](#), [Equilibria](#), [Electrochemistry](#)

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What you need to know

By the end of this topic you should be able to:

General properties (titanium to copper)

1. **Define a transition element:** a d-block element that forms one or more stable ions with incomplete d orbitals.
2. **Sketch the shapes** of a $3d_{xy}$ orbital and a $3d_{z^2}$ orbital.
3. **State the four typical properties:** variable oxidation states, catalytic activity, complex ion formation and coloured compounds.
4. **Explain variable oxidation states:** the 3d and 4s sub-shells are close in energy.
5. **Explain catalytic activity:** more than one stable oxidation state, and vacant d orbitals that are energetically accessible and can form dative bonds with ligands.
6. **Explain complex formation:** vacant d orbitals that are energetically accessible.

Complexes and their reactions

7. **Describe the reactions of transition element ions with ligands**, in particular copper(II) and cobalt(II) ions with water, ammonia, hydroxide ions and chloride ions.
8. **Define a ligand:** a species with a lone pair of electrons that forms a dative covalent bond to a central metal atom or ion.
9. **Use the terms monodentate** (H_2O , NH_3 , Cl^- , CN^-), **bidentate** (1,2-diaminoethane, en, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, and ethanedioate, $\text{C}_2\text{O}_4^{2-}$) and **polydentate** (EDTA).
10. **Define a complex:** a molecule or ion made of a central metal atom or ion surrounded by one or more ligands.
11. **Describe the shapes and bond angles** of linear, square planar, tetrahedral and octahedral complexes.
12. **Say what a coordination number is**, and **work out a complex's formula and overall charge** when you are told which metal ion (and its charge) and which ligand are involved, and how many bonds or what shape it has.
13. **Explain ligand exchange** qualitatively, using the copper(II) and cobalt(II) examples.
14. **Use $E^\ominus$ values** to predict whether redox reactions of transition elements and their ions are feasible.

15. **Know the reactions and do titration calculations** for acidified manganate(VII) with ethanedioate ions or with iron(II) ions, and for copper(II) ions with iodide ions; handle any **other redox reaction** the question gives you data for.

Colour

16. **Define degenerate and non-degenerate** d orbitals.
17. **Show how ligands separate the five d orbitals** into two groups at different energies, ΔE apart: an octahedral complex has a pair on top and a trio below; a tetrahedral one is the other way round.
18. **Explain the colour** of transition element compounds: an electron jumps from a lower d orbital to a higher one, taking in light of one particular frequency.
19. **Say in words how swapping ligands alters ΔE** , so which frequency is taken in and which colour we see, with the copper(II) and cobalt(II) ligand swaps as the examples.

Stereoisomerism

20. **Describe geometrical (cis/trans) and optical isomerism** in complexes, including those with bidentate ligands, for example square planar $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, octahedral $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$.
21. **Deduce whether each complex is polar.**

Stability constants

22. **Define the stability constant K_{stab}** : the equilibrium constant for forming the complex ion in a solvent from its constituent ions or molecules.
23. **Write K_{stab} expressions** (without $[\text{H}_2\text{O}]$) and **calculate** with them.
24. **Explain ligand exchange using K_{stab}** : a large K_{stab} means a stable complex.

Understand it

What makes an element a transition element

Across Period 4 from scandium to zinc, electrons go into the 3d sub-shell. The **4s** fills before the 3d, but once the 3d holds electrons the 4s is the **outermost** sub-shell, so **4s electrons are lost first** when an ion forms. Two atoms break the simple pattern because a half-full or full 3d sub-shell is extra stable: chromium is $[\text{Ar}] 3d^5 4s^1$ and copper is $[\text{Ar}] 3d^{10} 4s^1$.

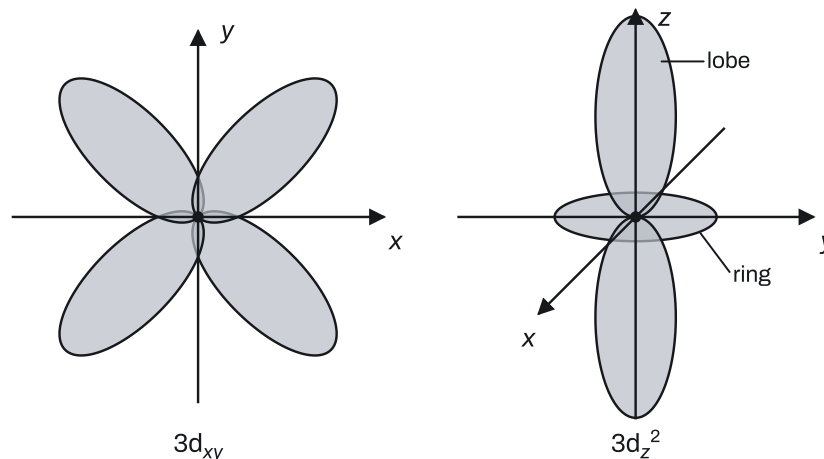
Species	Configuration	Unpaired electrons
Fe	$[\text{Ar}] 3d^6 4s^2$	4
Fe^{2+}	$[\text{Ar}] 3d^6$	4
Fe^{3+}	$[\text{Ar}] 3d^5$	5
Cu	$[\text{Ar}] 3d^{10} 4s^1$	1 (in 4s)

Species	Configuration	Unpaired electrons
Cu^{2+}	$[\text{Ar}] 3d^9$	1 (in 3d)

To count unpaired electrons, put one electron in each of the five 3d boxes before pairing any (Hund's rule).

A **transition element** forms at least one **stable ion with an incomplete d sub-shell**. Copper counts because Cu^{2+} is $3d^9$. Zinc does not: its only ion, Zn^{2+} , is $3d^{10}$. The definition is about the **ion**, not the atom.

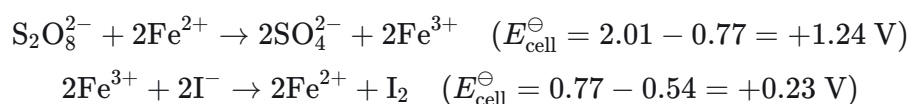
The five 3d orbitals have different shapes and directions. Two are drawn in exams:



The four typical properties and why they happen

- **Variable oxidation states.** The 3d and 4s sub-shells are **similar in energy**, so it costs little extra energy to remove (or use in bonding) different numbers of electrons. Iron forms +2 and +3; manganese ranges from +2 to +7 (in MnO_4^-).
- **Complex ions.** The ions have **vacant d orbitals that are energetically accessible**, so they can accept lone pairs from ligands.
- **Catalysts.** They have **more than one stable oxidation state**, so they can accept and give back electrons; and their **vacant d orbitals are energetically accessible and can form dative bonds** with reactant molecules (ligands), which holds reactants on a surface. Iron in the Haber process and platinum, palladium and rhodium in catalytic converters are **heterogeneous** catalysts (different phase from the reactants). Fe^{2+} or Fe^{3+} ions in the reaction between peroxodisulfate and iodide ions are a **homogeneous** catalyst (same phase).
- **Coloured compounds.** Explained below, under "Why complexes are coloured".

The iron catalysis works because the $E^\ominus$ of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (+0.77 V) lies between those of $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ (+2.01 V) and I_2/I^- (+0.54 V), so both steps are feasible:



The uncatalysed reaction is slow because two negative ions repel each other; each catalysed step is between oppositely charged ions. Fe^{2+} comes back at the end, so it is a catalyst.

Ligands and complexes

A **ligand** is a species with a **lone pair** that forms a **dative covalent (coordinate) bond** to a central metal atom or ion. A **complex** is the metal atom or ion with its ligands. The **coordination number** is the number of dative bonds the metal forms, not the number of ligands.

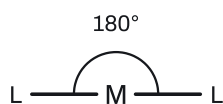
- **Monodentate** ligands form one dative bond: H_2O and NH_3 (lone pair on O or N), Cl^- , CN^- (through C), CO (through C).
- **Bidentate** ligands have **two lone pairs** on different atoms that form **two dative bonds** to the same metal: en (both N atoms) and ethanedioate, $\text{C}_2\text{O}_4^{2-}$ (one O from each end).
- **Polydentate** ligands form several: EDTA^{4-} forms **six** (two N and four O).

So $[\text{Ni}(\text{en})_3]^{2+}$ has three ligands but coordination number 6.

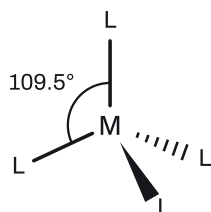
To find which atoms bond in an unfamiliar ligand, look for N atoms with lone pairs (amines), O atoms (carboxylates, alkoxides) and lone pairs placed so that a 5- or 6-membered ring can form with the metal. A carboxylic acid usually bonds after losing H^+ (its conjugate base, $-\text{COO}^-$).

Shapes and bond angles

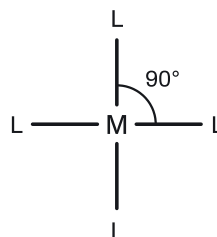
The shape depends on the coordination number (and, for 4, on the metal):



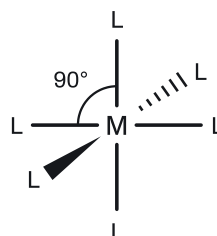
linear
coordination number 2



tetrahedral
coordination number 4



square planar
coordination number 4



octahedral
coordination number 6

Coordination number	Shape	Angle	Examples
2	linear	180°	$[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{CuCl}_2]^-$
4	tetrahedral	109.5°	$[\text{CuCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$
4	square planar	90°	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
6	octahedral	90° (and 180° across)	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$

Large ligands such as Cl^- usually give four-coordinate complexes: only four fit round the metal. Inside a ligand the angles follow electron-pair repulsion: in a coordinated NH_3 the N has four bonding pairs, so H–N–metal is 109.5° ; in a coordinated H_2O one of the O's lone pairs has become a bonding pair, so H–O–H opens from 104.5° to about 107° .

Predicting a formula and charge

Charge of the complex = charge of the metal ion + the sum of the ligand charges. Water, ammonia, en and CO are neutral; Cl^- , CN^- and OH^- are -1 ; $\text{C}_2\text{O}_4^{2-}$ is -2 ; EDTA^{4-} is -4 . Each bidentate ligand fills **two** positions.

- Iron(III) with six cyanide ions: $3 + 6(-1) = -3$, so $[\text{Fe}(\text{CN})_6]^{3-}$.
- Cobalt(III) with three ethanedioate ions (octahedral, $3 \times 2 = 6$ positions): $3 + 3(-2) = -3$, so $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$.
- Working backwards, the oxidation state of Co in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ is $x - 1 = +2$, so $x = +3$.

A **bridging** ligand bonds to two metal ions at once, so it counts once in the formula but fills a position on each metal. Two chromium(III) ions joined by two OH^- bridges, each octahedral, need four more ligands each; with water that is $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ (charge $2 \times 3 - 2 = +4$).

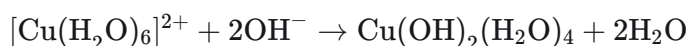
Which ions are ligands and which are not? Chloride ions outside the square brackets are free ions and precipitate straight away with Ag^+ ; chloride ligands do not. The compound $\text{CoCl}_3 \cdot 5\text{NH}_3$ gives 2 mol of AgCl per mole, so two Cl^- are free and one is a ligand: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, containing the ion $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.

Reactions of copper(II) and cobalt(II) aqua ions

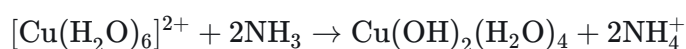
In water both ions are octahedral hexaaqua ions. Three reagents are tested:

Reagent	Copper(II), $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, blue solution	Cobalt(II), $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, pink solution	Type of reaction
OH^- (aq), or a few drops of NH_3 (aq)	pale blue precipitate, $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$	blue precipitate, $\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4$	precipitation (acid–base, deprotonation)
excess NH_3 (aq)	precipitate dissolves: deep blue solution, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	straw (yellow-brown) solution, $[\text{Co}(\text{NH}_3)_6]^{2+}$	ligand exchange
concentrated HCl	yellow solution, $[\text{CuCl}_4]^{2-}$ (tetrahedral)	blue solution, $[\text{CoCl}_4]^{2-}$ (tetrahedral)	ligand exchange

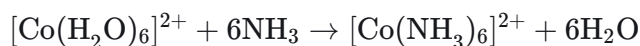
With hydroxide ions, two water ligands each lose H^+ to OH^- , leaving a neutral complex that precipitates:



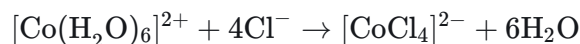
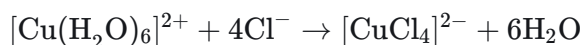
A few drops of ammonia do the same, because NH_3 acts as a base:



In **excess** ammonia, ammonia molecules replace ligands (**ligand exchange**, also called ligand substitution):



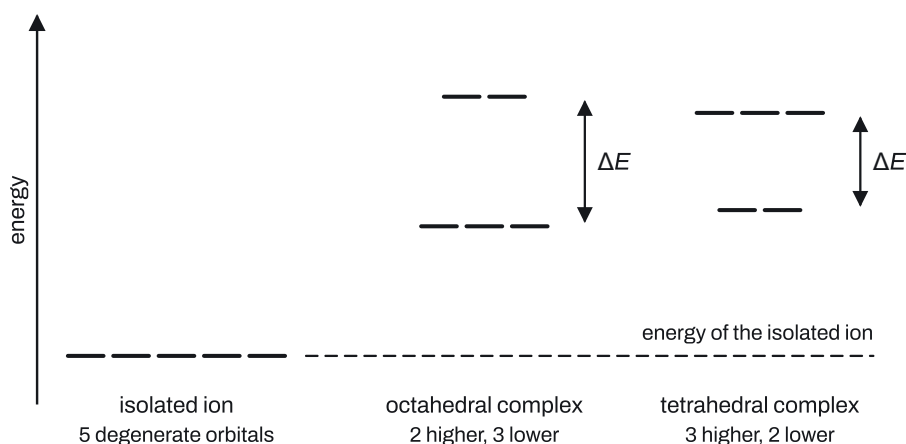
With concentrated HCl, the high $[\text{Cl}^-]$ drives exchange; the shape changes from octahedral to tetrahedral because only four Cl^- fit:



Ligand exchanges are **equilibria**: adding water to the yellow chloro-copper solution turns it back to blue, and adding excess ammonia to $[\text{CuCl}_4]^{2-}$ gives the deep blue ammine complex, releasing 4Cl^- . The cobalt hydroxide precipitate follows the same idea as copper's; for any other metal ion you meet, use the same patterns.

Why complexes are coloured

In an isolated gaseous ion the five 3d orbitals are **degenerate**: they have the same energy. In a complex, the ligands' lone pairs repel the d electrons. Orbitals pointing at the ligands are pushed up more than the others, so the d orbitals **split** into two **non-degenerate** sets (sets of different energy). All of them end up higher than in the isolated ion.



- **Octahedral**: 2 higher, 3 lower.
- **Tetrahedral**: 3 higher, 2 lower (the other way round).

When white light passes through, an electron in a lower d orbital absorbs a photon whose energy matches the gap and is **promoted** to a higher d orbital. Light of that frequency is **absorbed**: the bigger the gap, the higher the frequency. The light that is not absorbed passes through, and we see the **complementary colour**.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs mainly red-orange light and looks blue.

Different ligands split the d orbitals by different amounts. A different ΔE means a different frequency is absorbed, so a different colour is seen. This is why ligand exchange changes the colour: in the deep blue ammine complex of copper the gap is larger than in the aqua ion, so higher-frequency light is absorbed.

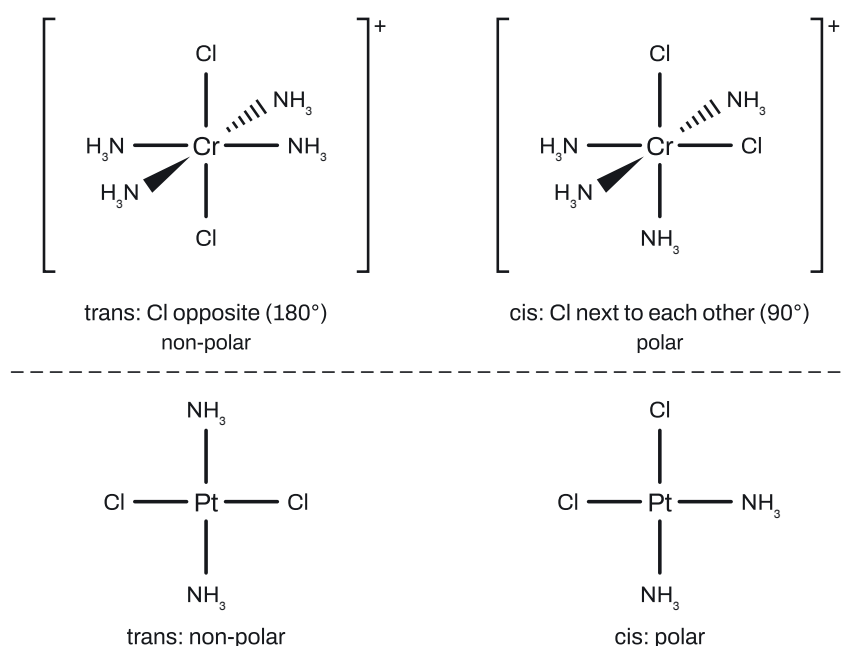
Changing the oxidation state of the metal also changes ΔE (so Fe^{2+} and Fe^{3+} complexes with the same ligand differ in colour).

No colour when no d–d promotion is possible: d^{10} ions (Cu^+ in white CuI , Zn^{2+} , Ag^+) have no space in the upper orbitals, and d^0 ions (titanium(IV)) have no d electrons to promote.

Stereoisomerism in complexes

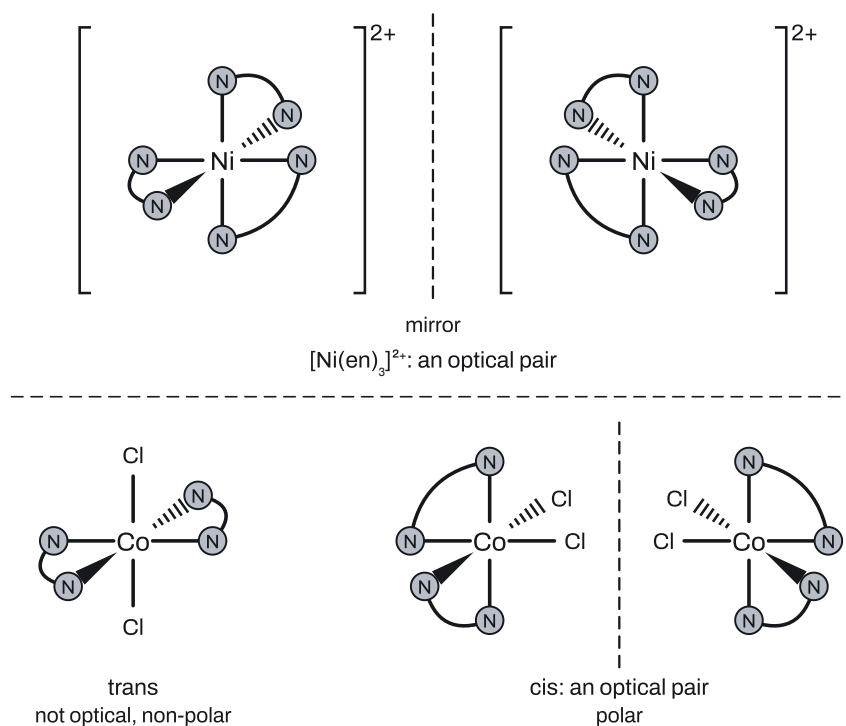
Stereoisomers have the same atoms bonded in the same order but arranged differently in space.

Geometrical (cis/trans). In a square planar $[\text{MA}_2\text{B}_2]$ or octahedral $[\text{MA}_4\text{B}_2]$ complex the two B ligands can be next to each other (**cis**, 90° apart) or opposite (**trans**, 180° apart). Tetrahedral complexes do not show cis/trans isomerism, because every position is next to every other.



Optical. A complex that is not superimposable on its mirror image exists as two optical isomers. The usual cases have bidentate ligands:

- $[\text{M}(\text{bidentate})_3]$, such as $[\text{Ni}(\text{en})_3]^{2+}$: two optical isomers (a left- and right-handed "propeller").
- $[\text{M}(\text{bidentate})_2\text{X}_2]$, such as $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$: **three** stereoisomers. The trans isomer (X opposite X) has a mirror plane, so it is not optical. The cis isomer is not superimposable on its mirror image, so it comes as a pair. It shows **both** geometrical and optical isomerism.



Polarity. Metal–ligand bonds are polar. In a **trans** isomer with identical ligands opposite each other the bond dipoles **cancel**, so it is **non-polar**. In a **cis** isomer they **do not cancel**, so it is **polar**. $[\text{M}(\text{en})_3]$ complexes, with three identical ligands spread evenly round the metal, are non-polar.

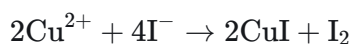
Redox reactions and $E^\ominus$

A reaction between an oxidising agent and a reducing agent is **feasible** if

$$E^\ominus_{\text{cell}} = E^\ominus(\text{half-equation that is reduced}) - E^\ominus(\text{half-equation that is oxidised}) > 0.$$

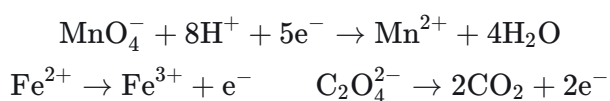
The more positive the $E^\ominus$, the better the species on the left of that half-equation is at oxidising. The half-equation with the less positive $E^\ominus$ runs backwards. Changing the ligands round a metal changes its $E^\ominus$, so always use the value for the exact species in the question.

"Feasible" says nothing about the rate, and it only applies at standard concentrations. Copper(II) ions oxidise iodide ions even though $E^\ominus(\text{Cu}^{2+}/\text{Cu}^+) = +0.15 \text{ V}$ is below $E^\ominus(\text{I}_2/\text{I}^-) = +0.54 \text{ V}$ ($E^\ominus_{\text{cell}} = 0.15 - 0.54 = -0.39 \text{ V}$): the Cu^+ formed is removed as a CuI precipitate, so $[\text{Cu}^+]$ stays tiny, which makes the electrode potential of $\text{Cu}^{2+}/\text{Cu}^+$ much more positive, above $+0.54 \text{ V}$.

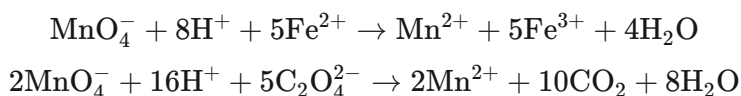


Redox titrations

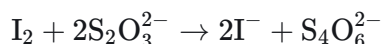
Three systems are named in the syllabus. Their half-equations are:



giving



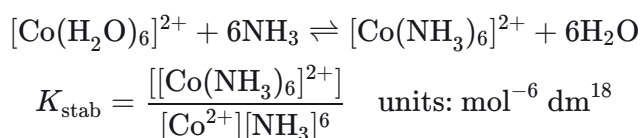
- **Manganate(VII)** is its own indicator: the purple colour disappears while the other reagent is in excess, and the end-point is the first **permanent pale pink**. The flask goes from **colourless to pale pink**. The ethanedioate titration is done warm (about 60 °C) because it is slow at room temperature.
- **Copper(II) and iodide**: excess KI gives a white CuI precipitate and iodine (brown). The iodine is titrated with sodium thiosulfate, adding starch near the end (blue-black, which disappears at the end-point):



Since 2Cu^{2+} give I_2 , which needs $2\text{S}_2\text{O}_3^{2-}$, **moles of Cu^{2+} = moles of $\text{S}_2\text{O}_3^{2-}$** .

Stability constants

The **stability constant**, K_{stab} , is the equilibrium constant for forming the complex ion in a solvent from its constituent ions or molecules. For



Water is the solvent, so $[\text{H}_2\text{O}]$ is left out. $[\text{Co}^{2+}]$ means the aqua ion, and you may write it either way. The charge goes **inside** the outer concentration bracket. With n ligand particles on the bottom, the units are $\text{mol}^{-n} \text{ dm}^{3n}$.

- **A larger K_{stab} means a more stable complex.** When two ligands compete for a metal ion at similar concentrations, the complex with the larger K_{stab} forms in the higher concentration.
- A ligand exchange from complex A to complex B has $K = \frac{K_{\text{stab}}(\text{B})}{K_{\text{stab}}(\text{A})}$. If this is large, the exchange goes almost completely.
- Complexes of bidentate and polydentate ligands usually have much larger K_{stab} than similar ones with monodentate ligands, which is why en or EDTA displace water and ammonia easily.

Key facts and formulas

"Given" means the question or the exam paper prints it (the Periodic Table with A_{r} values, the $E^\ominus$ values a question needs, and any K_{stab} values). "Learn it" means you must remember it. Colours, reagents and equations are never printed.

Formula	Status
A_{r} values; $E^\ominus$ values for the half-equations in a question; K_{stab} values	Given

Formula	Status
Transition element: forms one or more stable ions with incomplete d orbitals	Learn it
Ions lose 4s electrons before 3d; Cr is $[\text{Ar}] 3d^5 4s^1$, Cu is $[\text{Ar}] 3d^{10} 4s^1$	Learn it
Charge of complex = charge of metal ion + sum of ligand charges	Learn it
Coordination number = number of dative bonds to the metal (en and $\text{C}_2\text{O}_4^{2-}$ count 2, EDTA counts 6)	Learn it
Linear 180° ; square planar 90° ; tetrahedral 109.5° ; octahedral 90°	Learn it
Octahedral splitting: 2 higher, 3 lower; tetrahedral: 3 higher, 2 lower	Learn it
Larger ΔE means higher-frequency light absorbed (no equation needed)	Learn it
$E^\ominus_{\text{cell}} = E^\ominus(\text{reduced}) - E^\ominus(\text{oxidised})$; feasible if > 0	Learn it
$\text{MnO}_4^- : \text{Fe}^{2+} = 1 : 5$; $\text{MnO}_4^- : \text{C}_2\text{O}_4^{2-} = 2 : 5$; $\text{Cu}^{2+} : \text{S}_2\text{O}_3^{2-} = 1 : 1$	Learn it
$K_{\text{stab}} = \frac{[\text{complex}]}{[\text{M}^{n+}][\text{L}]^x}$, no $[\text{H}_2\text{O}]$; units $\text{mol}^{-x} \text{ dm}^{3x}$	Learn it
K for exchange $\text{A} \rightarrow \text{B} = K_{\text{stab}}(\text{B}) \div K_{\text{stab}}(\text{A})$	Learn it

How to do it

In the Paper 4 questions we have tagged for this topic (79 questions, 2021–2025, of which 23 are repeats on a second paper variant), the types came up this often. 75 of the 79 questions mix several types, so the counts add up to more than 79.

Question type	Questions
Stereoisomers and polarity	37
Reactions of copper(II) and cobalt(II) aqua ions	34
Ligands, complexes and donor atoms	33
Formula, charge, oxidation state and coordination number	30
Explaining colour	28

Question type	Questions
Shapes and bond angles	26
Explaining variable oxidation states, catalysis and complex formation	23
Stability constants	20
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Feasibility from electrode potentials	19
Splitting of d orbitals	14
Defining a transition element	13
Other equations and oxidation numbers	13
Electronic configurations	11
Sketching 3d orbitals	11
Transition elements as catalysts	7

1. Stereoisomers and polarity (37 questions)

1. **Work out the shape** from the coordination number (a bidentate ligand fills two positions).
2. **Decide which isomers exist:**
 - $[\text{MA}_2\text{B}_2]$ square planar or $[\text{MA}_4\text{B}_2]$ octahedral: cis and trans (2).
 - $[\text{M}(\text{bidentate})_3]$: an optical pair (2).
 - $[\text{M}(\text{bidentate})_2\text{X}_2]$: trans, plus a cis optical pair (3).
 - Tetrahedral: no cis/trans.
3. **Draw in 3D** as in the diagrams: two bonds in the plane of the paper, one wedge, one dashed bond, plus up and down for octahedral. Put the metal symbol in the middle and draw every bond to the donor atom: water bonds through O, so write OH_2 on the left of the metal and H_2O on the right. Never write O_2H , and never draw a bond to an H atom.
4. **A bidentate ligand spans two adjacent (cis) positions**, never opposite ones.
5. **Optical pair:** draw the first isomer, then draw its exact reflection in a vertical mirror. Check the two are not the same when rotated.
6. **Charges:** give the overall charge on each complex if the formula has one.

Variations you will meet:

- **"Name the types of stereoisomerism":** geometrical (cis/trans), optical, or both for the $[\text{M}(\text{bidentate})_2\text{X}_2]$ type.
- **"Which isomer is polar?":** the cis isomer, because the dipoles do not cancel. Say "dipoles do not cancel", not just "it is not symmetrical".

- **Which shapes can show isomerism** with some ligands swapped for different ones: exchanging two ligands for X and Y gives cis/trans in square planar and octahedral complexes only. Exchanging three for X, Y and Z gives a chiral complex for tetrahedral (four different groups, like a chiral carbon) and for octahedral.
- **Counting stereoisomers** of a complex with several different ligands: draw them systematically (fix one ligand at the top, move the others) and look for mirror images.

2. Reactions of copper(II) and cobalt(II) aqua ions (34 questions)

1. **Name the reagent's role:** OH^- or a little NH_3 removes H^+ (precipitate); excess NH_3 or concentrated HCl exchanges ligands.
2. **Give the observation:** colour **and** state (precipitate or solution), before and after if asked ("pink solution to blue solution").
3. **Write the formula** of the product from the table in "Understand it", with its charge.
4. **Write a balanced ionic equation;** check atoms and charges.
5. **Name the reaction type:** precipitation / acid–base / deprotonation for OH^- ; ligand exchange (substitution) for excess NH_3 and for Cl^- .

Variations you will meet:

- **The reverse exchange**, for example $[\text{CuCl}_4]^{2-} + 4\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{Cl}^-$. Balance by adding the water that the new complex needs.
- **An unfamiliar metal or ligand:** apply the same patterns. For example, Fe^{2+} with OH^- gives $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4$ by the same deprotonation.
- **Identify which ligands were exchanged** when an ion such as SCN^- or CN^- enters: compare the formulas before and after. The oxidation state is unchanged in ligand exchange.
- **Explain a precipitate dissolving or returning** using equilibrium (Le Chatelier): adding H^+ removes OH^- , adding excess ligand pushes the exchange forward.

3. Ligands, complexes and donor atoms (33 questions)

Learn the definitions word-perfect; each has two parts that both earn credit.

- **Ligand:** a species with a **lone pair** of electrons that forms a **dative covalent bond** to a **central metal atom or ion**.
- **Bidentate ligand:** a species with **two lone pairs** (on different atoms) that form **two dative bonds to the central metal atom or ion**.
- **Monodentate / polydentate:** one / more than two such bonds.
- **Complex:** a central metal atom or ion **surrounded by** (bonded to) one or more ligands.
- **Coordination number:** the number of dative (coordinate) bonds formed by the metal atom or ion.
- **Type of bond** between ligand and metal: dative covalent (coordinate).

Variations you will meet:

- **Classify ligands** as mono-, bi- or polydentate from a structure: count atoms with lone pairs that can reach the same metal.
- **"Suggest how this ligand forms three dative bonds"**: name the atoms (for example "two O⁻ and one N each donate a lone pair to the metal ion").
- **Explain why a molecule is only monodentate**: it has only one atom with a lone pair that can bond (for example, the N in an amine such as CH₃NH₂).
- **Circle the donor atoms** in EDTA: both N and the four O⁻.
- **Draw the ligand formed from an acid**: remove H⁺ from –COOH to get –COO⁻.

4. Formula, charge, oxidation state and coordination number (30 questions)

1. **Number of ligands** = coordination number ÷ dentate number (6 positions with en means 3 en).
2. **Charge** = metal ion charge + ligand charges.
3. Write the formula with square brackets and the charge outside: [Fe(C₂O₄)₃]³⁻.

Variations you will meet:

- **Oxidation state from a formula**: subtract the ligand charges from the overall charge. Watch for peroxide (O₂²⁻), amide (NH₂⁻) and hydroxide ligands, which carry a charge.
- **Metal atoms** (oxidation state 0) with neutral ligands such as CO: the complex is neutral, for example a tetrahedral nickel(0) complex with four CO is Ni(CO)₄.
- **Two metal centres** joined by bridging ligands: count the bridge once in the formula, but let it fill a position on each metal (see [Cr₂(OH)₂(H₂O)₈]⁴⁺ in "Understand it").
- **Formula from moles of AgCl precipitated**: that number of Cl⁻ are outside the brackets; the rest are ligands.
- **A new ligand of unknown charge** (for example a dianion): use the charge you are told, –2 per ligand.

5. Explaining colour (28 questions)

The three-mark answer, in order:

1. The **d orbitals split** into two sets of different energy (non-degenerate) because of the ligands.
2. An **electron is promoted** from a lower d orbital to a higher d orbital.
3. **Light of a particular frequency (visible) is absorbed**, and the colour seen is the **complementary** colour (the light that is transmitted).

Variations you will meet:

- **"Why are these two complexes different colours?"** (2 marks): different ligands (or oxidation state) → different ΔE (d–d energy gap) → **different frequency (wavelength) of visible light absorbed**. Say "d orbital energy gap", not just "energy gap".
- **"Why is this compound colourless or white?"**: d^{10} (full: no space to promote into) or d^0 (no d electrons), so no d–d transition and no visible light absorbed.

- **Coloured compound of a non-complex ion** (for example a chromate(VI) salt): answer with the same three points if the question asks why it is coloured; the mark scheme accepts them. (Strictly, chromium(VI) is d^0 , so its colour comes from a different process, charge transfer, which is beyond the syllabus; you are not expected to know it.)

6. Shapes and bond angles (26 questions)

1. Coordination number → shape: 2 linear, 4 tetrahedral or square planar, 6 octahedral.
2. **Label one angle** by drawing an arc from **bond to bond** (not to a ligand label) and write the value: 180° , 90° , 109.5° , 90° .
3. Draw 3D bonds (wedge and dashed) for tetrahedral and octahedral shapes.

Variations you will meet:

- **Angles within ligands:** H–N–M in a coordinated ammonia is 109.5° ; H–O–H in a coordinated water is about 107° , larger than 104.5° in free water, because a lone pair has become a bonding pair and bonding pairs repel less.
- **The angle between two named ligands** in a cis or trans isomer: trans 180° , cis 90° (octahedral or square planar).
- **Four-coordinate: which shape?** The question usually tells you; chloro complexes of copper(II) and cobalt(II) are tetrahedral, platinum(II) complexes are square planar.

7. Explaining variable oxidation states, catalysis and complex formation (23 questions)

One-line answers, learnt exactly:

- **Variable oxidation states:** the 3d and 4s sub-shells (orbitals) are similar in energy.
- **Complex formation:** vacant d orbitals that are energetically accessible (they can accept lone pairs from ligands).
- **Catalysis (2 marks):** (1) more than one stable oxidation state; (2) vacant d orbitals that are energetically accessible **and** can form dative bonds with ligands.

Don't mix them up: examiners see the complex-formation reason given for variable oxidation states, and the definition of a transition element given for complex formation.

8. Stability constants (20 questions)

1. **Define:** the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules.
2. **Expression:** complex on top; metal aqua ion times $[\text{ligand}]^x$ below, where x is the number of ligand particles in the equation; no $[\text{H}_2\text{O}]$.
3. **Units:** $\text{mol}^{-x} \text{ dm}^{3x}$.
4. **Calculate** by substituting and rearranging for the unknown.

Variations you will meet:

- **Missing concentration:** $[\text{complex}] = K_{\text{stab}}[\text{M}^{n+}][\text{L}]^x$, or rearrange for $[\text{M}^{n+}]$.
- **Exchange constant:** $K = K_{\text{stab}}(\text{new}) \div K_{\text{stab}}(\text{old})$. Its units are those of the new constant divided by the old one (for example $\text{mol}^{-2} \text{dm}^6 \div \text{mol}^{-4} \text{dm}^{12} = \text{mol}^2 \text{dm}^{-6}$); often just give the number if the question asks only for the value.
- **Rank or choose:** the larger K_{stab} is the more stable complex, which forms in higher concentration; the one with the smallest K_{stab} (often the aqua ion, K_{stab} taken as 1) is least stable.
- **Predict observations:** a ligand with a larger K_{stab} replaces one with a smaller value, so its colour appears; adding a ligand with a smaller K_{stab} afterwards changes nothing.
- **Combined with K_{sp}** (a precipitate dissolving in a ligand): multiply, $K = K_{\text{sp}} \times K_{\text{stab}}$, because the two equations add together.

9. Redox titrations (19 questions)

1. **Moles of titrant** $= c \times \frac{V}{1000}$.
2. **Ratio** from the equation: $\times 5$ for Fe^{2+} per MnO_4^- ; $\times \frac{5}{2}$ for $\text{C}_2\text{O}_4^{2-}$ per MnO_4^- ; $\times 1$ for Cu^{2+} per $\text{S}_2\text{O}_3^{2-}$; or the ratio in the equation given.
3. **Scale up** from the portion titrated to the whole solution (for example $\times 10$ for 25.0 cm^3 out of 250.0 cm^3).
4. **Convert** to what is asked: mass ($n \times M$), percentage purity, concentration, M_r , or an unknown in a formula.

For example, 1.390 g of hydrated iron(II) sulfate, $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$, is made up to 250.0 cm^3 , and 25.0 cm^3 needs 20.00 cm^3 of $0.00500 \text{ mol dm}^{-3} \text{ MnO}_4^-$. Moles $\text{MnO}_4^- = 1.000 \times 10^{-4}$; moles $\text{Fe}^{2+} = 5.000 \times 10^{-4}$ in 25.0 cm^3 , so 5.000×10^{-3} in total. $M_r = 1.390 \div 5.000 \times 10^{-3} = 278$. $\text{FeSO}_4 = 151.9$, so the water is $278 - 151.9 = 126.1$, and $x = 126.1 \div 18.0 = 7$.

Variations you will meet:

- **Unknown in a formula** (like x above, or n in FeCr_nO_4): find M_r from mass $\div$ moles, subtract the known part, and divide by the mass of the repeating part.
- **Water of crystallisation from a mass:** find moles of the salt, its anhydrous mass, then mass of water $\div 18.0$; $x = \text{moles of water} \div \text{moles of salt}$.
- **A back-step before the titration**, for example zinc reducing a vanadium or iron species first: use the species that is actually titrated.
- **A metal ion with more than one ligand to oxidise**, such as three $\text{C}_2\text{O}_4^{2-}$ in one formula unit: divide moles of ethanedioate by 3 to get moles of the compound.
- **Half-equations and the overall equation**, and the **colour change** at the end-point: colourless to pale pink with manganate(VII).

10. Feasibility from electrode potentials (19 questions)

1. Pick the half-equation for the species being reduced (its $E^\ominus$) and the one being oxidised.

2. $E_{\text{cell}}^{\ominus} = E^{\ominus}(\text{reduced}) - E^{\ominus}(\text{oxidised})$. Positive means feasible.
3. **Write the overall equation:** reverse the oxidation half-equation, multiply so the electrons cancel (never multiply $E^{\ominus}$), and add.

Variations you will meet:

- **"Explain why this precipitate turns brown in air"**: oxygen oxidises iron(II) to iron(III); show $E^{\ominus}(\text{O}_2) > E^{\ominus}(\text{Fe(III)/Fe(II)})$ and give the equation.
- **A species that can act as both oxidising and reducing agent** (such as H_2O_2): find one pair where it is reduced (it is on the left of a half-equation with a higher $E^{\ominus}$ than the partner) and one where it is oxidised (on the right of a half-equation with a lower $E^{\ominus}$).
- **Choose reagents** that can oxidise (or reduce) a given ion: any oxidising agent with a more positive $E^{\ominus}$ works.
- **Disproportionation**: the same ion is both oxidised and reduced; use its two half-equations.
- **Reactions that go despite a negative $E_{\text{cell}}^{\ominus}$** : a product is removed (a precipitate such as CuI), which shifts the electrode potential.

11. Splitting of d orbitals (14 questions)

1. Draw **five lines at one level** for the isolated ion.
2. Draw the complex's orbitals **higher** than all of those.
3. Split them: **octahedral 3 lower, 2 higher; tetrahedral 2 lower, 3 higher**. Mark ΔE if asked.

Variations you will meet:

- **"Define degenerate"**: orbitals of the same energy. **Non-degenerate**: orbitals of different energy.
- **"State the number of d orbitals at the higher and lower level"** for a described complex: decide octahedral or tetrahedral first; bridged or unusual ligands don't change the rule.

12. Defining a transition element (13 questions)

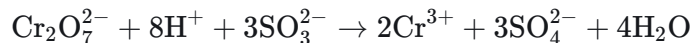
- **Definition** (both parts): a d-block element that forms **one or more stable ions** with **incomplete d orbitals**.
- **Properties** (any two, if asked): variable oxidation states; catalysts; complex ions; coloured compounds.
- **"Explain why silver (or copper) is a transition element"**: it forms a stable ion (such as Ag^{2+} , $4d^9$) with an incomplete d sub-shell, even though its common +1 ion is d^{10} .

13. Other equations and oxidation numbers (13 questions)

1. **Assign oxidation numbers** (O -2, H +1; the charges must add up) to find what is oxidised and what is reduced.
2. **Build half-equations** in acid: balance the metal, add H_2O to balance O, H^+ to balance H, and electrons to balance charge.

3. **Combine** so electrons cancel; check atoms and charge.

For example, dichromate(VI) oxidising sulfite: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ and $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$. Multiply the second by 3 and add:



Variations you will meet: thermal decompositions of transition element salts (balance atoms, then check oxidation numbers of the metal and of any gas formed); preparations described in words; disproportionation of an ion such as Cu^+ into Cu^{2+} and Cu .

14. Electronic configurations (11 questions)

1. Write the atom first, with 4s before 3d, remembering Cr ($3d^5 4s^1$) and Cu ($3d^{10} 4s^1$).
2. For the ion, **remove 4s electrons first**, then 3d.
3. Electrons-in-boxes: fill each 3d box singly before pairing; an ion like Cu^{2+} has empty 4s and 4p boxes.

Variation: "number of unpaired electrons in the 3d and 4s orbitals" of an atom and its ion (Cu atom: 0 in 3d, 1 in 4s; Cu^{2+} : 1 in 3d, 0 in 4s).

15. Sketching 3d orbitals (11 questions)

- $3d_{xy}$: four lobes in the xy plane, **between** the x and y axes (label the axes).
- $3d_{z^2}$: two lobes along the z axis and a ring around the middle in the xy plane.
- **Variation:** "one orbital from the lower set and one from the upper set" in an octahedral complex: $3d_{xy}$ is in the lower set (it points between the ligands); $3d_{z^2}$ is in the upper set (it points at them).

16. Transition elements as catalysts (7 questions)

- **Homogeneous** (same phase as reactants): write the two steps with Fe^{2+} and Fe^{3+} for $\text{S}_2\text{O}_8^{2-} + 2\text{I}^-$, as in "Understand it". The uncatalysed reaction is slow because both reactants are negative ions and repel.
- **Heterogeneous** (different phase): the mode of action is **adsorption** of reactants on the surface, **weakening of bonds** in them, and **desorption** of products. Iron in the Haber process; Pt, Pd and Rh in catalytic converters.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Chromium(III) ions form an octahedral complex ion, **T**, in which the chromium is bonded to two ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, and two water molecules.

(a) Give the electronic configuration of a Cr^{3+} ion, and state the number of unpaired electrons. **[2]**

(b) Give the formula and charge of **T**, and state the coordination number of chromium in it. **[2]**

(c) **T** has more than one stereoisomer. Deduce how many stereoisomers **T** has, name the types of stereoisomerism shown, and identify which of the isomers are polar. **[4]**

(a) Cr is $[\text{Ar}] 3d^5 4s^1$; removing the 4s electron and two 3d electrons gives $\text{Cr}^{3+} = [\text{Ar}] 3d^3$. **B1** Three electrons in three separate d orbitals: 3 unpaired. **B1**

(b) Charge = $+3 + 2(-2) + 0 = -1$, so **T** is $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$. **B1** Each ethanedioate forms two dative bonds: coordination number = $2 \times 2 + 2 = 6$. **B1**

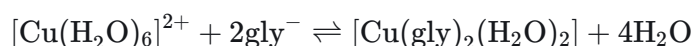
(c) This is the $[\text{M}(\text{bidentate})_2\text{X}_2]$ type, so there are **3** stereoisomers: one trans (the two water ligands opposite) and two cis (the waters adjacent) that are mirror images. **B1**

The isomerism is geometrical (cis/trans) **and** optical. **B1**

The two cis isomers are polar **B1** because their bond dipoles do not cancel; in the trans isomer the dipoles cancel, so it is non-polar. **B1**

Example 2

Copper(II) ions form a neutral complex with the bidentate glycinate ion, gly^- ($\text{H}_2\text{NCH}_2\text{COO}^-$):



K_{stab} of $[\text{Cu}(\text{gly})_2(\text{H}_2\text{O})_2]$ is 2.5×10^{15} and K_{stab} of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is 1.1×10^{13} .

(a) Write an expression for K_{stab} of $[\text{Cu}(\text{gly})_2(\text{H}_2\text{O})_2]$ and give its units. **[2]**

(b) A solution at equilibrium contains $0.050 \text{ mol dm}^{-3}$ $[\text{Cu}(\text{gly})_2(\text{H}_2\text{O})_2]$ and $0.010 \text{ mol dm}^{-3}$ gly^- . Calculate the concentration of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. **[1]**

(c) Glycinate ions are added to a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. Write an equation for the reaction, calculate its equilibrium constant, and explain what happens. **[3]**

(d) Suggest why the glycinate complex is a different colour from $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. **[2]**

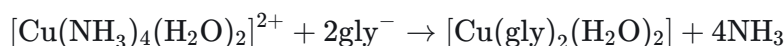
(a)

$$K_{\text{stab}} = \frac{[\text{Cu}(\text{gly})_2(\text{H}_2\text{O})_2]}{[\text{Cu}^{2+}][\text{gly}^-]^2}$$

B1 (no $[\text{H}_2\text{O}]$). Units: $\frac{\text{mol dm}^{-3}}{(\text{mol dm}^{-3})^3} = \text{mol}^{-2} \text{ dm}^6$. **B1**

(b) $[\text{Cu}^{2+}] = \frac{0.050}{2.5 \times 10^{15} \times 0.010^2} = 2.0 \times 10^{-13} \text{ mol dm}^{-3}$. **B1**

(c)



B1

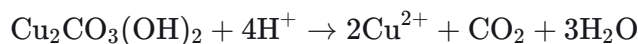
$$K = \frac{2.5 \times 10^{15}}{1.1 \times 10^{13}} = 227 = 2.3 \times 10^2$$
 B1

K is large (the glycinate complex has the larger K_{stab} , so it is more stable), so ammonia ligands are replaced by glycinate. **B1**

(d) Different ligands split the d orbitals by a different amount, so ΔE is different **B1**, and a different frequency of visible light is absorbed. **B1**

Example 3

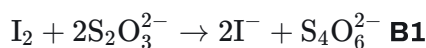
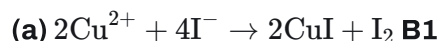
Malachite is a copper ore containing $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ($M_r = 221.0$). A 2.50 g sample of ore is dissolved in acid; the only copper-containing substance in the ore is malachite:



The solution is made up to 250.0 cm^3 . An excess of $\text{KI}(\text{aq})$ is added to 25.0 cm^3 of it, and the iodine formed needs 16.80 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate.

(a) Write equations for the reaction of Cu^{2+} with I^- and of iodine with thiosulfate ions. **[2]**

(b) Calculate the percentage by mass of malachite in the ore. **[4]**



(b) Moles $\text{S}_2\text{O}_3^{2-} = 0.100 \times \frac{16.80}{1000} = 1.680 \times 10^{-3} = \text{moles Cu}^{2+} \text{ in } 25.0 \text{ cm}^3$ (1 : 1). **M1**

In 250.0 cm^3 : $1.680 \times 10^{-2} \text{ mol Cu}^{2+}$. **M1**

Moles of malachite = $1.680 \times 10^{-2} \div 2 = 8.40 \times 10^{-3}$; mass = $8.40 \times 10^{-3} \times 221.0 = 1.856$ g. **M1**

Percentage = $\frac{1.856}{2.50} \times 100 = 74.3\%$. **A1**

Example 4

Use these values:

Half-equation	$E^\ominus / \text{V}$
$\text{Mn}^{3+} + \text{e}^- \rightleftharpoons \text{Mn}^{2+}$	+1.49
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{MnO}_2 + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Mn}^{3+} + 2\text{H}_2\text{O}$	+0.95

(a) Manganese(III) ions are unstable in aqueous solution: they disproportionate. Use the data to show that this is feasible and write an equation for the reaction. **[3]**

(b) Predict whether Mn^{3+} ions can oxidise chloride ions under standard conditions. Write an equation if they can. **[2]**

(c) Predict whether manganese(IV) oxide can oxidise chloride ions to chlorine, being reduced to Mn^{3+} , under standard conditions. **[1]**

(a) One Mn^{3+} is reduced to Mn^{2+} (+1.49 V) and one is oxidised to MnO_2 (the +0.95 V half-equation reversed). **M1**

$E_{\text{cell}}^\ominus = 1.49 - 0.95 = +0.54$ V, positive, so feasible. **A1**

$2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+$ **B1**

(b) $E_{\text{cell}}^\ominus = 1.49 - 1.36 = +0.13$ V, positive, so yes. **B1**

$2\text{Mn}^{3+} + 2\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + \text{Cl}_2$ **B1**

(c) $E_{\text{cell}}^\ominus = 0.95 - 1.36 = -0.41$ V, negative, so not feasible under standard conditions. **B1**

Common mistakes

- **Loose definitions.** "An element with an incomplete d sub-shell that forms ions" is wrong: it is the **stable ion** that must have incomplete d orbitals. A ligand definition must say the lone pair forms a **dative bond to the central metal atom or ion**; a bidentate one needs **two** lone pairs and **two** dative bonds.
- **Configurations of Cr, Cu and the ions.** $3d^4 4s^2$ for Cr and $3d^9 4s^2$ for Cu are wrong; so is keeping 4s electrons in an ion (remove 4s first).
- **Mixing up the three "explain why" answers.** Similar energy of 3d and 4s explains variable oxidation states; vacant accessible d orbitals explain complexes; both ideas together explain catalysis.

- **Splitting diagrams at the wrong height.** Most candidates get 3 : 2 or 2 : 3 right but draw the split levels at or below the isolated ion's. All complex levels must be **above**.
- **Colour answers without the key words.** Say "d orbitals", "electron promoted", "visible light absorbed" and "complementary colour". For two different colours, say ΔE is different **and** a different frequency is absorbed.
- **Weak 3D diagrams.** No wedges or dashed bonds, shapes that could not be octahedral, a bidentate ligand spanning opposite positions, two identical drawings offered as two isomers, or an optical "pair" that is not a mirror image. Bonds must go to the donor atom: OH_2 on the left of the metal is correct, but O_2H or a bond to H is not. Include charges on complex ions.
- **Polarity by "symmetry".** Say the cis isomer is polar because the **dipoles do not cancel**.
- **Coordination number = number of ligands.** $[\text{Fe}(\text{en})_3]^{3+}$ is 6, not 3. Chloride ligands are Cl^- , not Cl_2 or Cl.
- K_{stab} **slips**: not calling it an equilibrium constant; including $[\text{H}_2\text{O}]$; writing the charge outside the concentration bracket; dividing the wrong way for an exchange constant (new $\div$ old).
- **Observations missing the state.** "Blue" is not enough: say "pale blue precipitate" or "deep blue solution".
- **Not reversing the oxidation half-equation**, or multiplying $E^\ominus$ by the balancing number.

How to get the marks

- **Definitions** are marked point by point; learn them as written in "How to do it" type 3 and type 12.
- **"Explain"** a property: the one-line syllabus reason earns the mark; extra detail rarely adds anything, but a wrong idea can cost it.
- **"Describe"** observations: colour **and** state, and the starting colour when asked "from ... to ...".
- **"Draw" or "complete the diagram"**: 3D bonds, correct geometry, one mark per correct isomer. Draw the arc for a bond angle between two bonds.
- **Equations**: balanced ionic equations with correct formulas and charges; state symbols only when asked. Any correct multiple is accepted.
- **Calculations** earn method marks step by step (moles, ratio, scaling, final value) with error carried forward, so show every line. Give the final answer to the number of significant figures asked, or at least 3 s.f.
- **"Deduce" or "predict"** feasibility: quote the two $E^\ominus$ values or the $E_{\text{cell}}^\ominus$ with its sign, then conclude.
- **"Suggest"** means apply the patterns to an unfamiliar complex; any sensible answer using the right idea earns credit.
- K_{stab} **"give its units"**: work them out from the expression; don't guess.

Quick check

1. Give the electronic configurations of Mn^{2+} and V^{3+} as $[\text{Ar}] \dots$, and the number of unpaired electrons in each.
2. Platinum(IV) forms an octahedral complex with four ammonia molecules and two chloride ions. Give its formula and charge, name the type of stereoisomerism it shows, and say which isomer is polar.

3. Zinc is in the d-block. Explain why it is not a transition element and why zinc compounds are white.
4. A solution at equilibrium contains $0.012 \text{ mol dm}^{-3} [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, $0.20 \text{ mol dm}^{-3} \text{NH}_3$ and $6.8 \times 10^{-13} \text{ mol dm}^{-3} [\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Calculate K_{stab} for the ammine complex, with its units.
5. 25.0 cm^3 of a warm solution of ethanedioate ions needs 23.40 cm^3 of $0.0200 \text{ mol dm}^{-3}$ acidified MnO_4^- . Calculate the concentration of the ethanedioate ions and state the colour change at the end-point.

Answers

1. Mn is $[\text{Ar}] 3d^5 4s^2$, so $\text{Mn}^{2+} = [\text{Ar}] 3d^5$: 5 unpaired. V is $[\text{Ar}] 3d^3 4s^2$, so $\text{V}^{3+} = [\text{Ar}] 3d^2$: 2 unpaired.
2. Charge = $+4 + 4(0) + 2(-1) = +2$: $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$. Geometrical (cis/trans) isomerism. The cis isomer (Cl ligands at 90°) is polar because its dipoles do not cancel; the trans isomer is non-polar.
3. Zinc's only ion, Zn^{2+} , is $[\text{Ar}] 3d^{10}$: its d sub-shell is full, so it forms no stable ion with an incomplete d sub-shell. With all d orbitals full, no electron can be promoted from a lower to a higher d orbital, so no visible light is absorbed and the compounds are white (or colourless in solution).
4. $K_{\text{stab}} = \frac{0.012}{(6.8 \times 10^{-13})(0.20)^4} = \frac{0.012}{1.088 \times 10^{-15}} = 1.1 \times 10^{13} \text{ mol}^{-4} \text{ dm}^{12}$.
5. Moles $\text{MnO}_4^- = 0.0200 \times 23.40/1000 = 4.68 \times 10^{-4}$. Moles $\text{C}_2\text{O}_4^{2-} = 4.68 \times 10^{-4} \times \frac{5}{2} = 1.17 \times 10^{-3}$. Concentration = $1.17 \times 10^{-3} \div 0.0250 = 0.0468 \text{ mol dm}^{-3}$. Colourless to pale pink.

Past questions to try

- **9701/44/M/J/25 Q1**: configurations, a 3d orbital, bidentate ligands and the three isomers of a copper(II) complex.
- **9701/42/O/N/23 Q4**: EDTA, oxidation states and a K_{stab} calculation.
- **9701/43/O/N/21 Q6**: why copper(II) oxidises iodide ions, using electrode potentials.
- **9701/43/O/N/22 Q5**: orbital shapes, colour of nickel complexes and an iron titration.