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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

# Structure 3.1
# The Transition Elements

## Booklet 3 (HL) · Understandings 3.1.8 – 3.1.10

*What makes a transition element, their characteristic properties, complex ions, variable oxidation states, and why their complexes are coloured*

Complete revision notes & memory points · Higher Level

**How the level tags work in this booklet**

HL **Everything in this booklet is Higher Level only.** Understandings 3.1.8, 3.1.9 and 3.1.10 are not assessed at Standard Level. SL students do not need this booklet.

SL + HL Short reminder panels recap SL material from Booklets 1 and 2 (oxidation states, ionization energy, metallic bonding) that the HL work builds on.

**Inside this booklet**


1. What the syllabus actually asks of you
2. 3.1.8 — What a transition element is
3. 3.1.8 — Physical and magnetic properties
4. 3.1.8 — Catalysts and complex ions
5. 3.1.9 — Variable oxidation states
6. 3.1.10 — Why transition element complexes are coloured
7. 3.1.10 — Using colour: the colour wheel, calculations and colorimetry
8. Key points to memorise
9. Check yourself
10. Answers

# 1 What the syllabus actually asks of you

The elements in the middle of period 4, from scandium to copper, behave very differently from the s-block metals beside them. Sodium and calcium form one ion each, and their compounds are white. Iron forms $Fe^{2+}$ and $Fe^{3+}$, its compounds are green, yellow or brown, and it catalyses the industrial synthesis of ammonia. Every one of these differences can be traced to one feature: an **incomplete 3d sublevel**, whose electrons are close in energy to the 4s electrons.

| Understanding | What it says | What you must be able to do | Level |
|---|---|---|---|
| **3.1.8** Characteristic properties | Transition elements have incomplete d sublevels that give them characteristic properties. | Recognize properties including variable oxidation state, high melting points, magnetic properties, catalytic properties, formation of coloured compounds and formation of complex ions with ligands. Knowledge of different types of magnetism will not be assessed. | HL |
| **3.1.9** Variable oxidation states | The formation of variable oxidation states in transition elements can be explained by the fact that their successive ionization energies are close in value. | Deduce the electron configurations of ions of the first-row transition elements. | HL |
| **3.1.10** Coloured complexes | Transition element complexes are coloured because of the absorption of light when an electron is promoted between the orbitals in the split d sublevels. The colour absorbed is complementary to the colour observed. | Apply the colour wheel to deduce the wavelengths and frequencies of light absorbed and/or observed. Students are not expected to know the different splitting patterns and their relation to the coordination number. The colour wheel and $c = \lambda f$ are given in the data booklet. | HL |

### Linking questions and connections for 3.1.8 – 3.1.10

- **Nature of Science, Structure 2.3:** what are the arguments for and against including scandium as a transition element? → section 2.4
- **Reactivity 3.4:** what is the nature of the reaction between transition element ions and ligands in forming complex ions? → section 4.3
- **Tool 1, Inquiry 2:** how can colorimetry or spectrophotometry be used to calculate the concentration of a solution of coloured ions? → section 7.4
- **Structure 1.3:** electron configurations, Cr and Cu exceptions, successive ionization energies. **Structure 2.3:** metallic bonding in the d block. **Reactivity 2.2:** catalysts and activation energy.

### What the data booklet gives you — and what it does not

The data booklet gives the **colour wheel** (with wavelength boundaries), the equations **$c = \lambda f$** and **$E = hf$**, the **Planck constant**, the **speed of light** and the **Avogadro constant**, and successive ionization energies. It does **not** give the definition of a transition element, the colours of particular ions, the shapes of complexes, or which ions are colourless. These must be learned.

# 2 Structure 3.1.8 — What a transition element is HL

## 2.1 Electron configurations of the first-row d block

From scandium (Z = 21) to zinc (Z = 30), electrons are added to the **3d** sublevel, which lies just below the 4s in energy once it starts to fill. The outer 4s sublevel stays occupied throughout.

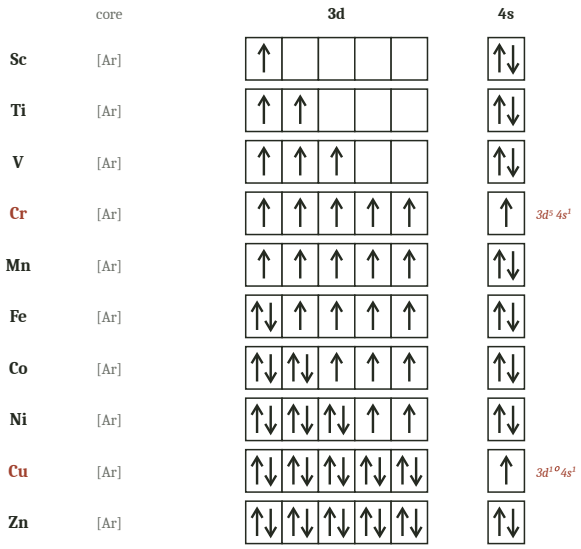



Figure 1 — Orbital diagrams for Sc to Zn. Chromium and copper (red) have only one 4s electron.

### Reminder from Structure 1.3

- Chromium is [Ar] $3d^5\ 4s^1$ and copper is [Ar] $3d^{10}\ 4s^1$. These arrangements give a lower total energy than $3d^4\ 4s^2$ and $3d^9\ 4s^2$.
- Hund's rule: electrons occupy separate orbitals of a sublevel singly, with parallel spins, before pairing.
- When writing configurations, 3d is usually written before 4s, because once it is occupied the 3d sublevel is lower in energy.

## 2.2 Forming ions: 4s electrons are lost first

### The rule for ions

Although 4s fills **before** 3d, the **4s electrons are removed first** when a transition element forms a positive ion. Once the 3d sublevel is occupied, the 4s electrons are the outermost and highest in energy. Only after both 4s electrons have gone are 3d electrons removed.

### Worked example — $V^{3+}$ and $Fe^{2+}$

**V** (Z = 23): [Ar] $3d^3\ 4s^2$. Remove the two 4s electrons, then one 3d electron: **$V^{3+}$ = [Ar] $3d^2$** (not [Ar] $3d^0\ 4s^2$).

**Fe** (Z = 26): [Ar] $3d^6\ 4s^2$. Remove the two 4s electrons: **$Fe^{2+}$ = [Ar] $3d^6$**. Remove one more, from 3d: **$Fe^{3+}$ = [Ar] $3d^5$**. Check: $Fe^{3+}$ has 26 − 3 = 23 electrons = 18 + 5 ✓.

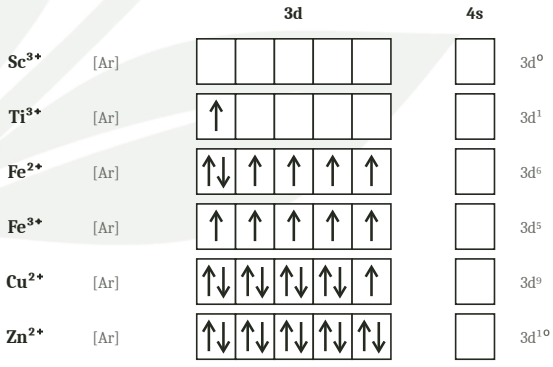



Figure 2 — Some first-row ions. No ion keeps 4s electrons.

### 2.3 The definition, and why zinc is not a transition element

**Definition to learn**

A **transition element** is an element whose atoms have an **incomplete d sublevel**, or which can give rise to **cations with an incomplete d sublevel**.

All transition elements are in the d block, but not all d-block elements are transition elements. **Zinc** is the clear exception. The Zn atom is [Ar] $3d^{10}$ $4s^2$, and its only ion, $Zn^{2+}$, is [Ar] $3d^{10}$: the d sublevel is **complete** in both. As a result, zinc shows none of the characteristic properties: it has only one oxidation state (+2) in its compounds, and its compounds are white and its solutions colourless. In the first row, the transition elements are therefore **scandium to copper**. Copper qualifies because, although the Cu atom ($3d^{10}$ $4s^1$) and $Cu^+$ ($3d^{10}$) have full d sublevels, $Cu^{2+}$ is $3d^9$.

### 2.4 Nature of Science: is scandium a transition element?

**Arguments for**

The scandium **atom** has an incomplete d sublevel ([Ar] $3d^1$ $4s^2$), so it fits the IUPAC definition used by the IB. It is in the d block and is a hard, high-melting metal like its neighbours.

**Arguments against**

Its only common ion, $Sc^{3+}$, is [Ar] $3d^0$. So scandium has **one** oxidation state (+3), forms **colourless** compounds, and shows few of the typical properties. Scandium(II) compounds are very rare. Some textbooks define a transition element by its **ions** only, which excludes scandium.

The disagreement shows that a classification is a human choice. A definition based on atoms includes scandium; one based on the properties that make the group useful excludes it. In the exam, use the IB definition in section 2.3, but be ready to discuss both sides.

**Examiner traps in 2.1 – 2.4**

- Remove the **4s electrons first**. $Fe^{2+}$ is [Ar] $3d^6$, not [Ar] $3d^4$ $4s^2$. This is the most common error in this topic.
- To explain why zinc is not a transition element, give the configurations of **both** the atom and the ion, and state that the 3d sublevel is complete in both.
- "Transition element" and "d-block element" are not the same thing. Zinc is d block but not transition.
- The definition says an incomplete d sublevel in the atom **or** in a cation. Quote both parts.

## 3 Structure 3.1.8 — Physical and magnetic properties HL

### 3.1 Physical properties

Transition elements are typical metals, but with stronger metallic bonding than the s-block metals. They have:

- **high melting and boiling points** (iron 1538 °C, compared with 842 °C for calcium and 63 °C for potassium);
- **high densities**, and high tensile strength (they can carry large loads without breaking);
- high **electrical and thermal conductivity**; they are malleable and ductile.

The reason is the energy of the electrons. The 3d and 4s electrons are **close in energy**, so both are involved in bonding and become part of the sea of delocalized electrons (Structure 2.3). More delocalized electrons per atom, attracted to smaller cations, give stronger metallic bonding: hence the high melting points and good conductivity. The smaller atomic radius, together with a

greater mass, also explains the higher density.

## 3.2 Why the atoms are so similar in size

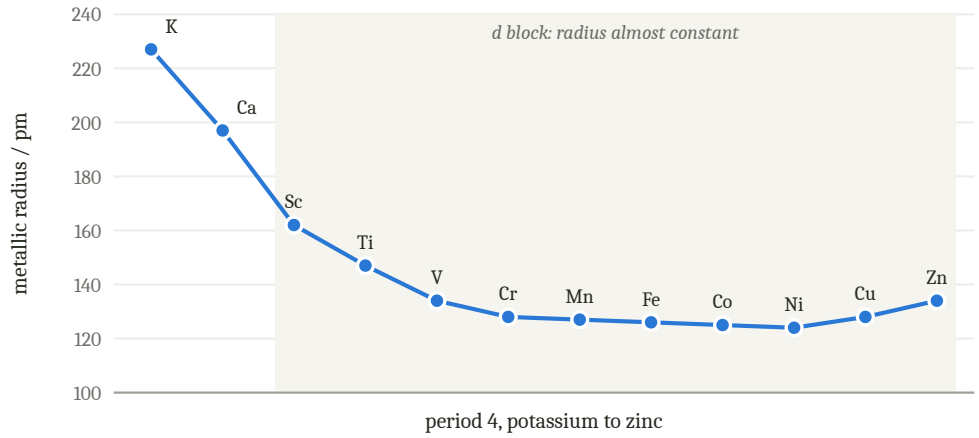



Figure 3 — Metallic radii across period 4 from K to Zn. The radius falls sharply from K to Sc, then changes very little across the d block.

Across the d block, each extra proton is matched by an extra electron in the **inner** 3d sublevel. The 3d electrons shield the outer 4s electrons quite effectively, so the effective nuclear charge felt by the 4s electrons rises only slightly, and the radius barely changes. This has two consequences:

- the first ionization energies across the d block are also very similar (Booklet 2, Figure 5);
- the atoms are almost the same size, so atoms of one transition metal can replace another in a metal lattice with little disruption. This is why transition metals form **alloys** so readily (Structure 2.4), for example the chromium and nickel in stainless steel.

## 3.3 Magnetic properties

Every electron behaves like a tiny magnet because of its spin. In an orbital containing **two** electrons the spins are opposite and the magnetic effects cancel. So a substance with **unpaired electrons** has a net magnetic effect and is **attracted** into a magnetic field; a substance whose electrons are all paired is not (it is very weakly repelled).

- Most s- and p-block substances have all their electrons paired. Transition metal atoms and ions often have several **unpaired 3d electrons**, so they and their compounds are attracted by a magnet.
- The **more unpaired electrons**, the stronger the attraction. Chromium atoms ($3d^5\ 4s^1$: six unpaired electrons) have the most in the first row; zinc atoms ($3d^{10}\ 4s^2$: none) are not attracted.
- **Iron, cobalt and nickel** are strongly magnetic as solid metals (they can be made into permanent magnets). The guide does not require the names of the different types of magnetism.

### Worked example — compare the magnetic properties of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$

$Fe^{2+}$ is [Ar] $3d^6$: by Hund's rule, one 3d orbital holds a pair and four hold one electron each, so there are **4 unpaired electrons**. $Fe^{3+}$ is [Ar] $3d^5$: all five 3d orbitals hold one electron, so there are **5 unpaired electrons**. Both are attracted by a magnetic field, but $Fe^{3+}(aq)$ is attracted **more strongly**. ($Zn^{2+}$, $3d^{10}$, and $Sc^{3+}$, $3d^0$, have no unpaired electrons and are not attracted.)

**Nature of Science and TOK**

Magnetic compasses were used for navigation for centuries before anyone could explain magnetism; the technology came before the science. Today the order is often reversed, with scientific understanding leading to new technologies. The puzzling "action at a distance" of magnets led early thinkers to compare magnetism with attraction between people, and traces survive in language: the French word for magnet, *aimant*, also means "loving". How does the vocabulary we inherit help or hinder the pursuit of knowledge?

# 4 Structure 3.1.8 — Catalysts and complex ions HL

The **chemical** properties of transition elements are very different from those of the s-block metals. Transition elements:

**The four characteristic chemical properties**

1. show **variable oxidation states** in their compounds (section 5);
2. act as **catalysts**, both as elements and as compounds (section 4.1);
3. form **complex ions** with ligands (section 4.2);
4. form **coloured compounds** (section 6).

Together with the physical properties (high melting point, magnetic properties), these are the properties you must be able to recognize. Each one comes from the incomplete d sublevel.

## 4.1 Transition elements as catalysts

A catalyst increases the rate of a reaction by providing an alternative pathway with a **lower activation energy**; it is not used up (Reactivity 2.2). Catalysts let industrial processes run at a reasonable rate at lower temperatures, saving energy and money.

| Catalyst | Reaction | Use |
|---|---|---|
| **Fe** (iron) | $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ | Haber process: ammonia for fertilizers, plastics, drugs and explosives |
| **Ni** (nickel) | C=C + $H_2$ → CH–CH (hydrogenation) | converting unsaturated vegetable oils into margarine |
| **Pt, Pd, Rh** | $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$ | catalytic converters remove CO and NO from car exhausts |
| **$V_2O_5$** (vanadium(V) oxide) | $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ | Contact process: making sulfuric acid |
| **$MnO_2$** (manganese(IV) oxide) | $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ | laboratory preparation of oxygen |

Most of these are **heterogeneous** catalysts: the solid catalyst is in a different phase from the gaseous or liquid reactants, and the reaction happens on its surface.

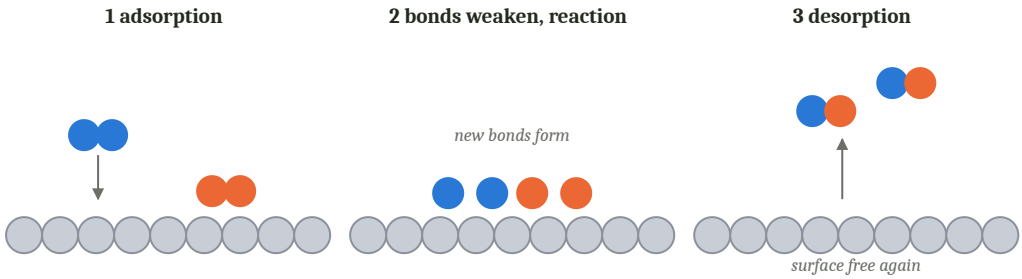



Figure 4 — On the surface of a metal catalyst, reactant molecules are adsorbed (bond to the surface), their bonds are weakened and they react; the products are then released (desorbed), freeing the surface for more reactants.

Transition metals are good at this because they can use their partly filled **3d** and their 4s orbitals to form **weak bonds** with reactant molecules. Adsorption concentrates the reactants on the surface, weakens bonds within them and holds them in a favourable orientation. The bonding must be just right: too weak (silver) and few molecules are adsorbed; too strong (tungsten) and the products cannot leave. Nickel and platinum are near the ideal. Transition metal **ions** can also catalyse reactions in solution (homogeneous catalysis), because they can switch easily between oxidation states, such as $Fe^{2+}$ and $Fe^{3+}$, accepting and then giving back electrons.

Platinum, palladium and rhodium are very expensive, but only small amounts are needed because a catalyst is not used up. The mining and trading of transition metals is important to the economies of many countries.

## 4.2 Complex ions

Transition metal ions are small and highly charged, so they strongly attract molecules or ions that have a **lone pair** of electrons. In water, for example, an $Fe^{3+}$ ion is surrounded by six water molecules, each forming a **coordination bond** to the metal ion by donating a lone pair from its oxygen atom.

### Definitions to learn

- A **ligand** is a molecule or ion that uses a lone pair of electrons to form a coordination bond with a metal ion. (From the Latin *ligandus*, "to bind".)
- A **coordination bond** (dative covalent bond) is a covalent bond in which both shared electrons come from the same atom.
- A **complex ion** is a central metal ion surrounded by ligands bonded to it by coordination bonds.
- The **coordination number** is the number of coordination bonds from the ligands to the central ion.

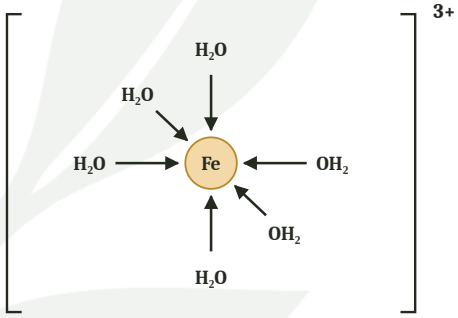



Figure 5 — $[Fe(H_2O)_6]^{3+}$. Each arrow is a coordination bond from an oxygen lone pair. Coordination number 6.

The square brackets show that the metal ion and its ligands form one unit, and the charge outside the brackets belongs to the whole complex. The charge of a complex is the charge of the metal ion plus the charges of the ligands, so $[Fe(CN)_6]^{3-}$ contains $Fe^{3+}$ and six $CN^-$ ligands: $+3 + 6(-1) = -3$.

| Common ligand | Charge | Atom donating the lone pair | Example complex |
|---|---|---|---|
| water, $H_2O$ | 0 | O | $[Cu(H_2O)_6]^{2+}$ |
| ammonia, $NH_3$ | 0 | N | $[Cu(NH_3)_4(H_2O)_2]^{2+}$, $[Ag(NH_3)_2]^{+}$ |
| chloride, $Cl^-$ | −1 | Cl | $[CuCl_4]^{2-}$, $[CoCl_4]^{2-}$ |
| cyanide, $CN^-$ | −1 | C | $[Fe(CN)_6]^{3-}$ |
| hydroxide, $OH^-$ | −1 | O | $[Cr(OH)_6]^{3-}$ |
| thiocyanate, $SCN^-$ | −1 | S | $[Fe(SCN)(H_2O)_5]^{2+}$ (blood red) |

Most complexes with small ligands such as $H_2O$ and $NH_3$ are **octahedral** (coordination number 6). Larger ligands such as $Cl^-$ often give **tetrahedral** complexes with coordination number 4, because only four fit around the metal ion. Some ligands (bidentate ligands, such as 1,2-diaminoethane) form two coordination bonds each; you are not required to know these.

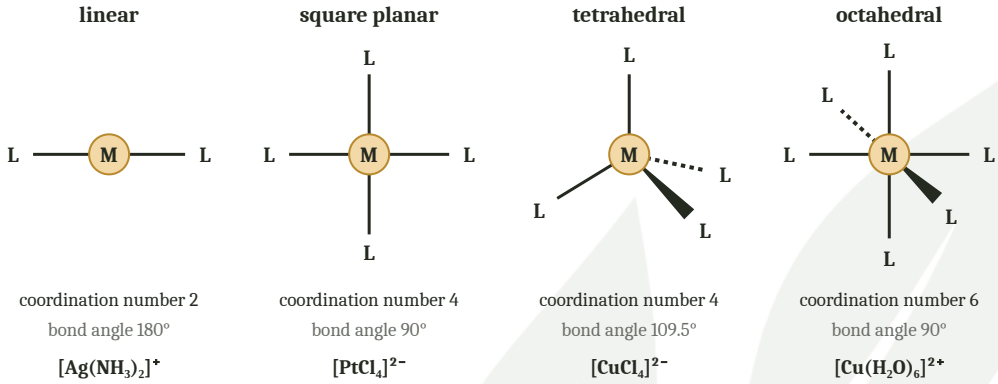



Figure 6 — Common shapes of complex ions. M is the metal ion and L a ligand. Wedges point towards you and dashes away from you.

**Ligands and counter ions are not the same**

In a compound containing a complex ion, ions **inside** the square brackets are ligands; ions **outside** are counter ions that balance the charge. In $[Cr(H_2O)_5Cl]Cl_2$, the complex ion is $[Cr(H_2O)_5Cl]^{2+}$, with five $H_2O$ ligands and one $Cl^-$ ligand (co-ordination number 6, Cr +3). The other two $Cl^-$ ions are counter ions, not ligands. In $K_2[CuCl_4]$, the $K^+$ ions are counter ions: a positive ion cannot be a ligand, because it has no lone pair to donate.

## 4.3 Complex formation is a Lewis acid–base reaction (link to Reactivity 3.4)

The ligand donates a pair of electrons and the metal ion accepts it. A **Lewis base** is an electron-pair donor and a **Lewis acid** is an electron-pair acceptor, so in forming a complex the ligand acts as a Lewis base and the metal ion as a Lewis acid. The metal ion can accept electron pairs because it has empty orbitals at low enough energy (3d, 4s, 4p). Ligands can also be exchanged: in **ligand substitution**, one ligand replaces another, which often changes the colour (section 6.4).

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l) \quad \text{blue} \rightarrow \text{yellow-green (with concentrated HCl)}$$

**Examiner traps in 3.1.8**

- When asked to "recognize" properties, list the specific ones from the guide: variable oxidation states, high melting points, magnetic properties, catalytic properties, coloured compounds, complex ions.
- A ligand needs a **lone pair**. State this in any definition, and say the bond formed is a **coordination** bond.
- Coordination number counts **bonds** to the metal, not ligands: it is not the same as the number of different kinds of ligand.
- Magnetic attraction depends on the number of **unpaired** electrons, not the total number of d electrons.
- Heterogeneous catalysts work by **adsorption** (on to a surface), not absorption (into the solid).

# 5 Structure 3.1.9 — Variable oxidation states HL

## 5.1 The explanation: successive ionization energies are close in value

An s-block metal shows only one oxidation state in its compounds: +1 for group 1, +2 for group 2. A transition element shows several. The difference is explained by the pattern of **successive ionization energies**.

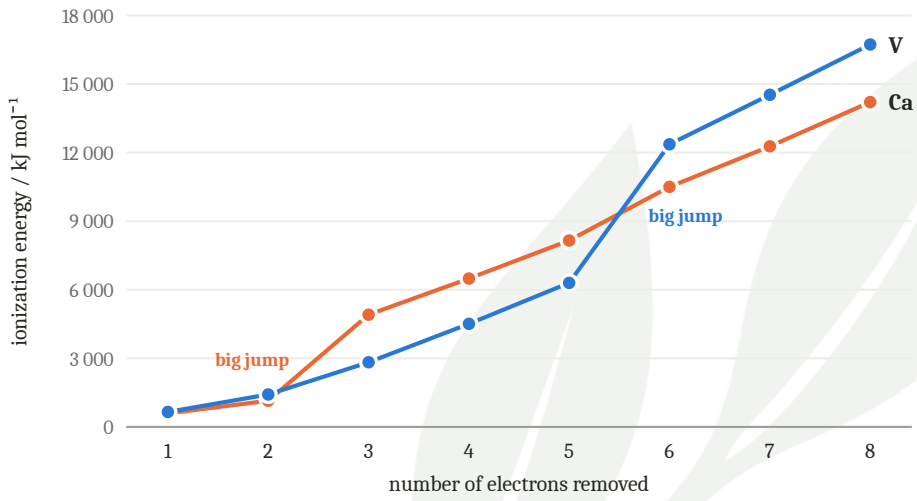



Figure 7 — The first eight ionization energies of calcium and vanadium.

**Calcium** ([Ar] $4s^2$) shows a very large jump between the 2nd and 3rd ionization energies (1145 to 4912 kJ $mol^{-1}$). The third electron would come from the inner 3p sublevel, which is much closer to the nucleus and much less shielded. The energy needed is far too large to be recovered when bonds form, so $Ca^{3+}$ compounds do not exist: calcium is always +2.

**Vanadium** ([Ar] $3d^3$ $4s^2$) shows a **gradual** increase for the first five ionization energies, because the 4s and 3d electrons are **close in energy**. Removing one more electron costs only a little more each time, so the energy released when compounds form can pay for any of these: V shows +2, +3, +4 and +5. The big jump comes after the fifth, when 3p electrons would be removed, so +6 is not possible.

**Model answer: "Explain why transition elements show variable oxidation states but calcium does not." (3 marks)**

In transition elements the 3d and 4s electrons are close in energy **[1]**, so successive ionization energies increase gradually and different numbers of electrons can be lost (or used in bonding) without a large jump in energy **[1]**. In calcium, after the two 4s electrons are removed the next electron comes from the inner 3p sublevel, which needs a very large amount of energy, so only +2 is found **[1]**.

## 5.2 The oxidation states of the first row

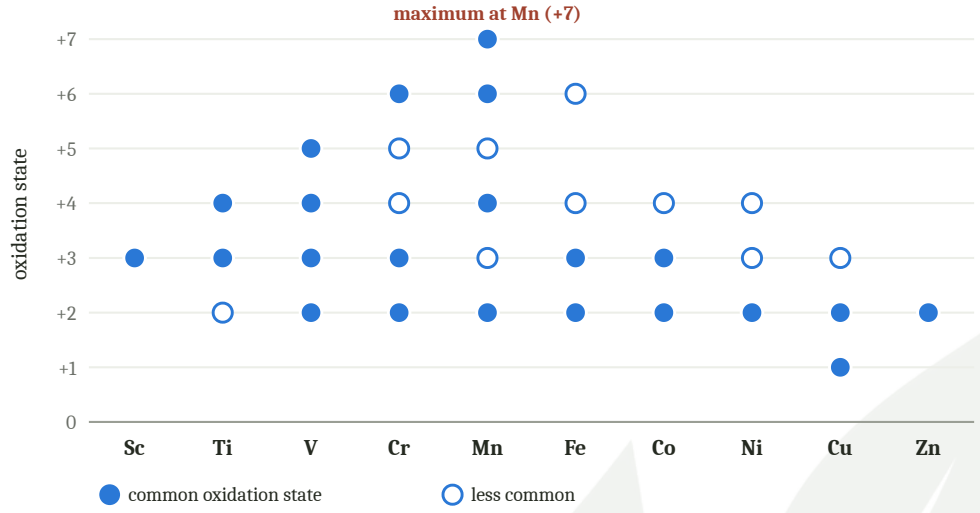



Figure 8 — Oxidation states shown by the first-row d-block elements in their compounds.

- **Nearly all show +2** (loss of the two 4s electrons), and most also show +3. $M^{3+}$ is the more stable state from Sc to Cr; $M^{2+}$ becomes more common for the later elements, whose greater nuclear charge makes a third electron harder to remove.
- **The maximum rises by +1 each step to manganese (+7)**, which equals the total number of 4s and 3d electrons. After manganese the maximum falls, because the extra nuclear charge holds the d electrons more tightly.
- **High oxidation states** (above about +3) are found in oxyanions and oxides with **covalent** character, such as $MnO_4^-$ (+7), $Cr_2O_7^{2-}$ (+6) and $V_2O_5$ (+5), not as simple ions: an ion such as $Mn^{7+}$ would be so small and highly charged that it would polarize any neighbouring anion. Compounds in high oxidation states are good **oxidizing agents**: acidified potassium dichromate(VI) and potassium manganate(VII) are used to oxidize alcohols and in redox titrations (Reactivity 3.2).

| Element | Common oxidation states | Examples |
|---|---|---|
| V | +2, +3, +4, +5 | $V^{2+}$(aq) violet, $V^{3+}$(aq) green, $VO^{2+}$(aq) blue, $VO_2^+$(aq) yellow |
| Cr | +3, +6 | $Cr^{3+}$, $Cr_2O_3$; $CrO_4^{2-}$ (yellow), $Cr_2O_7^{2-}$ (orange) |
| Mn | +2, +4, +6, +7 | $Mn^{2+}$, $MnO_2$, $MnO_4^{2-}$ (green), $MnO_4^-$ (purple) |
| Fe | +2, +3 | $FeSO_4$, $Fe_2O_3$, $FeCl_3$ |
| Cu | +1, +2 | $Cu_2O$ (red), $CuSO_4$, CuO (black) |

### 5.3 Deducing electron configurations of ions

1. Write the configuration of the atom, with 3d before 4s: e.g. Mn [Ar] $3d^5\ 4s^2$. Remember Cr ($3d^5\ 4s^1$) and Cu ($3d^{10}\ 4s^1$).
2. Remove electrons from **4s first**, then from 3d, until the charge is reached.
3. Check that the number of electrons left is Z minus the charge.

**Worked example — five ions**

| Ion | Atom | Electrons removed | Ion configuration | Unpaired $e^-$ |
|---|---|---|---|---|
| $Ti^{2+}$ | [Ar] $3d^2\ 4s^2$ | $4s^2$ | [Ar] $3d^2$ | 2 |
| $Cr^{3+}$ | [Ar] $3d^5\ 4s^1$ | $4s^1$ + two 3d | [Ar] $3d^3$ | 3 |
| $Mn^{2+}$ | [Ar] $3d^5\ 4s^2$ | $4s^2$ | [Ar] $3d^5$ | 5 |
| $Ni^{2+}$ | [Ar] $3d^8\ 4s^2$ | $4s^2$ | [Ar] $3d^8$ | 2 |
| $Cu^+$ | [Ar] $3d^{10}\ 4s^1$ | $4s^1$ | [Ar] $3d^{10}$ | 0 |

Shortcut for checking: the number of 3d electrons in a first-row transition metal ion = group number − charge. Mn (group 7) → $Mn^{2+}$ has 7 − 2 = 5; Cu (group 11) → $Cu^{2+}$ has 11 − 2 = 9.

**Comparing aluminium and chromium**

Both form 3+ ions, but aluminium (Al, [Ne] $3s^2\ 3p^1$) shows **only** +3: its fourth electron would come from the inner 2p sub-level, a huge jump in ionization energy. Chromium shows +2, +3 and +6 because its 3d and 4s electrons are close in energy, so its successive ionization energies rise gradually up to the sixth.

**Examiner traps in 3.1.9**

- The explanation must mention **successive ionization energies being close in value**, because the 3d and 4s sub-levels are close in energy. "They have lots of d electrons" is not enough.
- 4s electrons are lost **first**, even though 4s fills first.
- The maximum oxidation state in the first row is **+7 (Mn)**, equal to the number of 3d + 4s electrons.
- Do not write $MnO_4^-$ as containing an $Mn^{7+}$ ion. High oxidation states are found in covalent oxyanions and oxides.

## 6 Structure 3.1.10 — Why transition element complexes are coloured HL

### 6.1 Colour comes from light that is *not* absorbed

White light contains all the colours of the visible spectrum, from violet (about 400 nm) to red (about 700 nm). A substance looks coloured when it **absorbs** some wavelengths: a solution transmits the rest, a solid reflects the rest, and our eyes see the mixture of what is left. The colour seen is the **complementary colour** of the light absorbed.

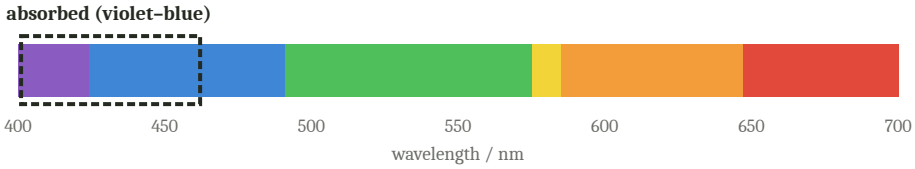



Figure 9 — Iron(III) solutions look yellow because they absorb light at the violet–blue end of the spectrum. The light that remains is seen as yellow.

## 6.2 The d sublevel splits into two levels

In an isolated transition metal atom or ion, the five 3d orbitals all have the **same energy** (they are *degenerate*). When ligands bond to the ion, their lone pairs create an electric field around it. The d electrons are repelled by the ligand electrons, but not equally:

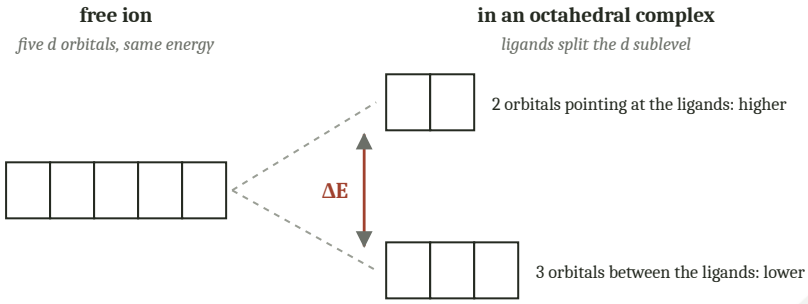



Figure 10 — In an octahedral complex, two of the d orbitals point directly at the six ligands and are raised in energy; the other three point between them and are lower. The energy gap is ΔE.

- In an octahedral complex, the ligands approach along the x, y and z axes. Electrons in the two d orbitals that point **along** the axes are repelled more strongly by the ligand lone pairs, so these orbitals are raised in energy.
- The three d orbitals that point **between** the axes are lower in energy.
- The energy gap ΔE between the two sets is small: it corresponds to a photon of **visible** light.

The pattern shown is for octahedral complexes. Other shapes, such as tetrahedral, give different splitting patterns, but the guide states you do not need to know them.

## 6.3 Promoting an electron absorbs a photon

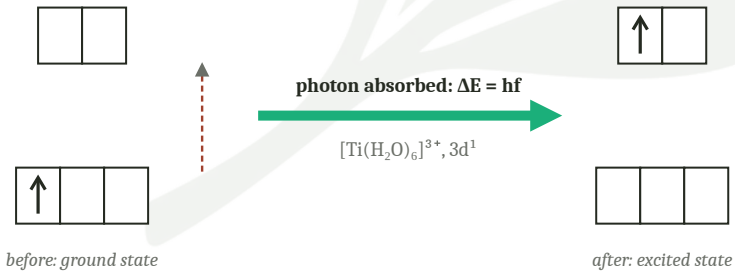



Figure 11 — In $[Ti(H_2O)_6]^{3+}$ ($3d^1$), absorbing a photon of green-yellow light (about 510 nm) promotes the single d electron to the upper level. The complex transmits red and blue light, so it looks violet-purple.

An electron in the lower d level can be **promoted** to the upper d level by absorbing a photon whose energy exactly matches the gap: **$\Delta E = hf = hc/\lambda$**. Light of that frequency is removed from the white light passing through, and the complementary colour is seen.

> **Explanation to learn: why transition metal complexes are coloured**
>
> (1) The ligands cause the d sublevel to **split** into two levels of different energy. (2) An electron in the lower level absorbs a photon of **visible light** and is **promoted** to the higher level; the energy of the photon equals ΔE. (3) The light that is not absorbed is transmitted or reflected, and we see the **complementary colour** of the light absorbed.

## 6.4 When there is no colour

For an electron to be promoted between d orbitals, there must be at least one d electron, and there must be a space for it in the upper level. Ions with an **empty** ($3d^0$) or a **full** ($3d^{10}$) d sublevel cannot absorb visible light in this way, so their compounds are **white** and their solutions **colourless**.

| Ion | Configuration | Colour in water | Ion | Configuration | Colour in water |
|---|---|---|---|---|---|
| $Sc^{3+}$ | [Ar] $3d^0$ | **colourless** | $Fe^{3+}$ | [Ar] $3d^5$ | yellow to orange-brown * |
| $Ti^{3+}$ | [Ar] $3d^1$ | violet | $Fe^{2+}$ | [Ar] $3d^6$ | pale green |
| $V^{3+}$ | [Ar] $3d^2$ | green | $Co^{2+}$ | [Ar] $3d^7$ | pink |
| $Cr^{3+}$ | [Ar] $3d^3$ | violet (often green) | $Ni^{2+}$ | [Ar] $3d^8$ | green |
| $Mn^{2+}$ | [Ar] $3d^5$ | very pale pink | $Cu^{2+}$ | [Ar] $3d^9$ | blue |
| $Cu^{+}$ | [Ar] $3d^{10}$ | **colourless** | $Zn^{2+}$ | [Ar] $3d^{10}$ | **colourless** |

* $[Fe(H_2O)_6]^{3+}$ itself is very pale violet; the familiar yellow-orange colour of iron(III) solutions comes from complexes in which a water ligand has been replaced by $OH^-$ or $Cl^-$. Chromium(III) solutions often look green for a similar reason. You will not be asked to recall these details, but they explain why textbooks give different colours.

## 6.5 What decides the colour?

Anything that changes the size of the energy gap ΔE changes the wavelength of light absorbed, and so changes the colour.

| Factor | Why ΔE changes | Example |
|---|---|---|
| **Identity of the metal** (nuclear charge) | different nuclear charge attracts the ligands differently, even with the same number of d electrons | $[Mn(H_2O)_6]^{2+}$ pale pink, $[Fe(H_2O)_6]^{3+}$ yellow: both $3d^5$ |
| **Oxidation state** of the metal | a higher charge pulls the ligands closer, so they interact more strongly with the d orbitals: usually a larger ΔE | $[Fe(H_2O)_6]^{2+}$ pale green, $[Fe(H_2O)_6]^{3+}$ yellow |
| **Identity of the ligand** | different ligands split the d orbitals by different amounts; $NH_3$ gives a larger split than $H_2O$ | $[Cu(H_2O)_6]^{2+}$ pale blue, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue-violet |
| **Coordination number and shape** | a different arrangement of ligands gives a different splitting pattern | $[Co(H_2O)_6]^{2+}$ pink (octahedral), $[CoCl_4]^{2-}$ blue (tetrahedral) |

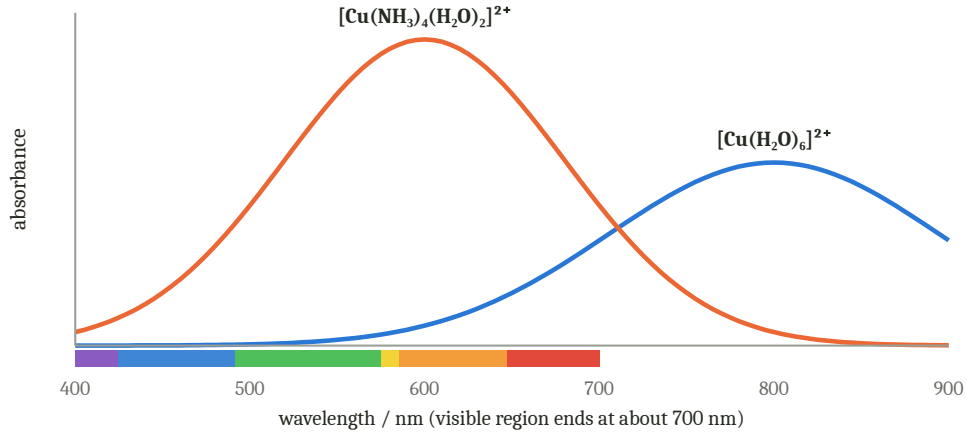



Figure 12 — Sketch of the visible absorption spectra of two copper(II) complexes. Replacing four water ligands with ammonia increases ΔE, so the peak moves to a shorter wavelength (higher energy). The deep blue complex absorbs yellow-orange light strongly.

### Two colour changes worth knowing

**Cobalt chloride paper** is blue when dry and turns pink with water. Blue tetrahedral $[CoCl_4]^{2-}$ becomes pink octahedral $[Co(H_2O)_6]^{2+}$: both the ligand and the coordination number change. **The test for iron(III)**: adding colourless thiocyanate ions to a yellow solution of $Fe^{3+}(aq)$ gives a deep blood-red colour, as one water ligand is replaced by $SCN^-$ to form $[Fe(SCN)(H_2O)_5]^{2+}$.

### Model answer: "Explain why $[Cu(H_2O)_6]^{2+}$ is coloured but $[Zn(H_2O)_6]^{2+}$ is colourless." (3 marks)

The water ligands split the 3d sublevel into two levels of different energy **[1]**. $Cu^{2+}$ is $3d^9$, so an electron can be promoted from the lower to the upper level by absorbing a photon of visible light, and the complementary colour is seen **[1]**. $Zn^{2+}$ is $3d^{10}$: the d sublevel is full, so no d–d transition is possible and no visible light is absorbed **[1]**.

### Examiner traps in 3.1.10 (theory)

- The colour is due to light being **absorbed**, and we see the **complementary** colour. Do not say the complex "emits" its colour or "gives off" light.
- Do not confuse this with **emission** spectra and flame tests (Structure 1.3), where excited electrons fall back and emit light.
- The transition is between **d orbitals** that have been split by ligands, not between the 3d and 4s sublevels.
- A blue solution absorbs **orange** light (the complementary colour), not blue light.
- Name the cause of splitting: the **ligands** (their lone pairs). Without ligands, the d orbitals are degenerate.

# 7 Structure 3.1.10 — Using colour: the colour wheel, calculations and colorimetry HL

## 7.1 The colour wheel

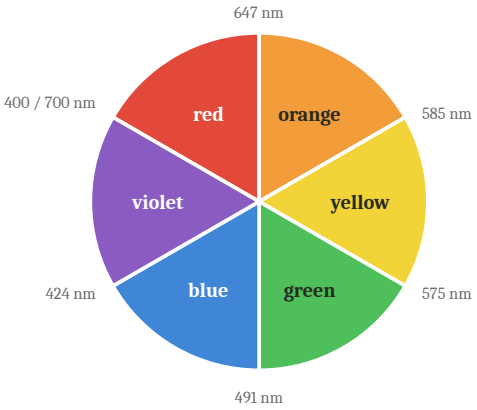



Figure 13 — A colour wheel with the wavelength boundaries used in the IB data booklet. Complementary colours are opposite each other.

Colours **opposite** each other on the wheel are complementary. To use it:

1. Find the colour **observed** on the wheel.
2. Go to the **opposite** segment: that is the colour **absorbed**.
3. Read off the wavelength range at the edges of that segment.

| Observed | Absorbed | λ absorbed / nm |
|---|---|---|
| red | green | 491–575 |
| orange | blue | 424–491 |
| yellow | violet | 400–424 |
| green | red | 647–700 |
| blue | orange | 585–647 |
| violet | yellow | 575–585 |

Different books use slightly different wheels and boundaries, so a textbook may say a yellow solution absorbs "blue" where the data booklet wheel gives violet. In the exam, always use the colour wheel **in the data booklet**, and quote a wavelength within the range it gives.

**Worked example — copper(II) sulfate solution is blue. Estimate the wavelength of light it absorbs.**

Blue is observed, so the complementary colour, **orange**, is absorbed. From the colour wheel, orange light has wavelengths of **585–647 nm**; any value in this range, such as 620 nm, is acceptable.

## 7.2 From wavelength to frequency and energy

Use the equations from the data booklet: $\mathbf{c = \lambda f}$ and $\mathbf{E = hf}$, with $c = 3.00 \times 10^{8}$ m $s^{-1}$, $h = 6.63 \times 10^{-34}$ J s and $N_A = 6.02 \times 10^{23}$ $mol^{-1}$. Always convert nanometres to metres first: $1\ nm = 1 \times 10^{-9}$ m.

**Worked example — $[Ti(H_2O)_6]^{3+}$ absorbs most strongly at 510 nm. Calculate (a) the frequency of this light, (b) the energy gap ΔE for one ion, and (c) ΔE in kJ $mol^{-1}$. (d) Predict the colour of the complex.**

(a) $f = c / \lambda = (3.00 \times 10^{8}) / (510 \times 10^{-9}) = \mathbf{5.88 \times 10^{14}\ s^{-1}}$ (Hz)

(b) $\Delta E = hf = (6.63 \times 10^{-34}) \times (5.88 \times 10^{14}) = \mathbf{3.90 \times 10^{-19}\ J}$

(c) per mole: $(3.90 \times 10^{-19}) \times (6.02 \times 10^{23}) = 2.35 \times 10^{5}$ J $mol^{-1} = \mathbf{235\ kJ\ mol^{-1}}$

(d) 510 nm is in the green segment (491–575 nm), so the complex absorbs green light and appears **red-violet (purple)**, the complementary colour.

**Worked example — the reverse: a complex appears orange. Estimate the frequency of the light it absorbs.**

Orange is observed, so **blue** (424–491 nm) is absorbed. Take $\lambda = 450$ nm: $f = c / \lambda = (3.00 \times 10^{8}) / (450 \times 10^{-9}) = \mathbf{6.67 \times 10^{14}\ s^{-1}}$. (Any wavelength in the range gives a frequency between about 6.1 and $7.1 \times 10^{14}\ s^{-1}$.)

**Wavelength, frequency and energy move in opposite directions**

A **larger** splitting $\Delta E$ means a photon of **higher** energy and **higher** frequency is absorbed, which means a **shorter** wavelength. In Figure 12, ammonia increases $\Delta E$, so the copper complex absorbs at a shorter wavelength than the aqua complex.

## 7.3 Absorption spectra

A UV-visible spectrophotometer passes light of each wavelength through a solution and measures how much is absorbed. The wavelength of maximum absorbance is written $\lambda_{max}$. The colour wheel tells you which colour this corresponds to. The absorptions of complexes are **broad bands** rather than the sharp lines of atomic spectra, because in a complex the electronic transition is combined with changes in the vibrations of the bonds, so a range of slightly different energies is absorbed.

## 7.4 Colorimetry: finding a concentration (Tool 1, Inquiry 2)

**Key idea**

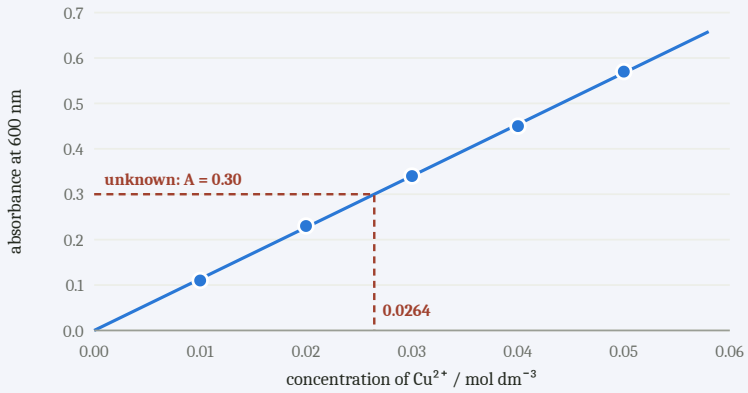
At a fixed wavelength, the **absorbance** of a solution is **directly proportional** to the concentration of the absorbing species (for the same path length through the solution).

1. Choose a wavelength (or a coloured filter) that the coloured species **absorbs strongly**, usually at or near $\lambda_{max}$: the complementary colour of the solution.
2. Make up at least five **standard solutions** of known concentration by diluting a stock solution, and measure the absorbance of each. Zero the instrument with a blank (the solvent).
3. Plot absorbance against concentration and draw the line of best fit: the **calibration curve**.
4. Measure the absorbance of the unknown at the same wavelength and read its concentration from the curve. The unknown must lie within the range of the standards.

### Worked example — copper(II) in an alloy sample

Excess ammonia was added to standard copper(II) solutions to form the deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion, which absorbs more strongly than the aqua ion, and the absorbance was measured at 600 nm.

| $[Cu^{2+}]$ / mol dm$^{-3}$ | Absorbance |
|---|---|
| 0.010 | 0.11 |
| 0.020 | 0.23 |
| 0.030 | 0.34 |
| 0.040 | 0.45 |
| 0.050 | 0.57 |
| sample | 0.30 |




The points lie on a straight line through the origin. Reading across from A = 0.30 to the line and down gives **$[Cu^{2+}] \approx 0.026$ mol dm$^{-3}$**. Adding a ligand that gives a more intensely coloured complex ($NH_3$ for $Cu^{2+}$, $SCN^-$ for $Fe^{3+}$) makes the method more sensitive for dilute solutions.

### Examiner traps in 3.1.10 (calculations and colorimetry)

- Convert **nm to m** ($\times 10^{-9}$) before using $c = \lambda f$. Forgetting this gives answers wrong by a factor of $10^9$.
- For kJ mol$^{-1}$, multiply the energy per photon by $N_A$ and divide by 1000.
- Use the wavelength of the light **absorbed**, not the colour seen, in the calculation.
- In colorimetry, select light of the **complementary** colour (the colour absorbed); a blue solution is measured with orange-red light.
- Read the unknown concentration from the calibration curve only within the range of the standards; do not extrapolate.

# 8 Key points to memorise

Everything below is either wording that examiners look for, or knowledge you must carry into the exam yourself.

### A Definitions — near-verbatim

- **Transition element:** an element whose atoms have an incomplete d sublevel, or which can give rise to cations with an incomplete d sublevel.
- **Ligand:** a species that uses a lone pair of electrons to form a coordination bond with a metal ion.
- **Coordination bond:** a covalent bond in which both electrons are donated by one atom.
- **Complex ion:** a central metal ion bonded to ligands by coordination bonds. **Coordination number:** the number of coordination bonds to the central ion.
- **Complementary colours:** colours opposite each other on the colour wheel; the colour seen is complementary to the colour absorbed.

### B Configurations and oxidation states

- Cr [Ar] $3d^5\ 4s^1$; Cu [Ar] $3d^{10}\ 4s^1$. Ions lose **4s electrons first**: $Fe^{2+}$ $3d^6$, $Fe^{3+}$ $3d^5$, $Cu^{2+}$ $3d^9$.
- Zinc is not a transition element: Zn and $Zn^{2+}$ both $3d^{10}$. Scandium is by the IB definition (atom $3d^1$), but $Sc^{3+}$ is $3d^0$.
- Variable oxidation states: 3d and 4s close in energy, so **successive ionization energies are close** and increase gradually.
- Almost all show +2; maximum rises to **+7 at Mn** (all 3d + 4s electrons), then falls. High states are covalent oxyanions and oxidizing agents.

### C Properties in one line each

- **High melting point, density, conductivity:** 3d and 4s electrons both delocalized, so strong metallic bonding.
- **Magnetic:** unpaired d electrons; more unpaired, stronger attraction (Cr atom 6; $Fe^{3+}$ 5, $Fe^{2+}$ 4; Zn 0).
- **Catalysts:** Fe (Haber), Ni (hydrogenation), Pt/Pd/Rh (catalytic converters), $V_2O_5$ (Contact), $MnO_2$ ($H_2O_2$). Adsorption on the surface; variable oxidation states.
- **Complex ions:** ligands donate lone pairs; octahedral (6) for $H_2O$, $NH_3$; tetrahedral (4) for $Cl^-$; linear (2) for $[Ag(NH_3)_2]^+$.

### D Colour

- Ligands split the d sublevel; an electron is promoted from lower to upper d level by absorbing visible light; the complementary colour is seen.
- $3d^0$ ($Sc^{3+}$, $Ti^{4+}$) and $3d^{10}$ ($Zn^{2+}$, $Cu^+$): colourless.
- ΔE depends on: metal (nuclear charge), oxidation state, ligand, coordination number/shape.
- $\Delta E = hf$; $c = \lambda f$; λ in metres; × $N_A$ for per mole. Larger ΔE → shorter λ absorbed.
- Colorimetry: absorbance ∝ concentration; calibration curve from standards at a fixed wavelength.

**E Command terms — what each one is actually asking for**

- **Recognize** (properties of transition elements) — identify them from data or a description.
- **Deduce** (the configuration of an ion) — work from the atom, removing 4s electrons first; show the result in full or condensed form.
- **Explain** (why a complex is coloured) — the three steps: splitting by ligands, promotion by absorbing visible light, complementary colour seen.
- **Estimate** (a wavelength absorbed) — use the colour wheel and give a value within the correct range, with units.
- **Calculate** (ΔE) — show the equations, the conversion of nm to m, and units in the answer.

## 9 Check yourself

Cover the answers on the next pages. Marks are shown in brackets where a question is written in exam style. All questions are Higher Level. Use h = $6.63 \times 10^{-34}$ J s, c = $3.00 \times 10^{8}$ m $s^{-1}$, $N_A = 6.02 \times 10^{23}$ $mol^{-1}$, and the colour wheel in Figure 13.

1. Which is the electron configuration of $Cr^{3+}$?

   A [Ar] $3d^3$  B [Ar] $3d^1\,4s^2$  C [Ar] $3d^2\,4s^1$  D [Ar] $3d^4$

2. Deduce the condensed electron configurations of: (a) $Mn^{2+}$ (b) $Co^{3+}$ (c) $Cu^{+}$ (d) $Ti^{4+}$. **[4]**

3. (a) State the full electron configurations of Zn and $Zn^{2+}$. (b) Explain why zinc is not classed as a transition element. **[3]**

4. Outline one argument for and one argument against classifying scandium as a transition element. **[2]**

5. Which property is **not** characteristic of transition elements?

   A formation of coloured compounds  B low melting points  C catalytic activity  D formation of complex ions

6. Which atom would be attracted most strongly into a magnetic field?

   A Ca  B Zn  C Cr  D Ni

7. Compare the magnetic properties of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ ions, with reference to their electron configurations. **[2]**

8. Explain why the transition metals have higher melting points than the s-block metals in the same period. **[2]**

9. Explain why the atomic radii of the first-row transition elements are very similar, and state one consequence of this. **[3]**

10. Identify the transition metal (or compound) used as a catalyst in: (a) the Haber process (b) the hydrogenation of vegetable oils (c) catalytic converters (d) the Contact process. **[4]**

11. Describe how a heterogeneous catalyst such as nickel increases the rate of a reaction between two gases. **[3]**

12. Define the terms *ligand* and *coordination number*. **[2]**

13. For each compound, identify the complex ion, the ligands, the coordination number and the oxidation state of the metal: (a) $K_3[Fe(CN)_6]$ (b) $[Cr(NH_3)_4Cl_2]Cl$ (c) $[Cu(H_2O)_6]SO_4$. **[6]**

14. Which statements about $[CuCl_4]^{2-}$ are correct? I. Cu is +2. II. The coordination number is 4. III. Chloride ions act as Lewis bases.

    A I and II only  B I and III only  C II and III only  D I, II and III

15. Explain, with reference to successive ionization energies, why calcium shows only the +2 oxidation state but vanadium shows +2, +3, +4 and +5. **[3]**

16. An element has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$. Which oxidation states could it show?

    A +2 only  B +2 and +3 only  C +2, +3 and +4  D +2, +3, +4 and +5

17. State the highest oxidation state of manganese and explain its value. Give a species in which it occurs. **[3]**

18. State the oxidation states shown by aluminium and by chromium in their compounds, and explain the difference. **[3]**

19. Explain why $[Fe(H_2O)_6]^{2+}$ is coloured. **[3]**

20. Which ion forms a colourless aqueous solution?

    A $Ti^{3+}$  B $Sc^{3+}$  C $Cu^{2+}$  D $Mn^{2+}$

21. Suggest why the colour of: (a) $[Cr(H_2O)_6]^{3+}$ differs from that of $[Fe(H_2O)_6]^{3+}$; (b) $[Fe(H_2O)_6]^{2+}$ differs from that of $[Fe(H_2O)_6]^{3+}$; (c) $[Fe(NH_3)_6]^{2+}$ differs from that of $[Fe(H_2O)_6]^{2+}$. **[3]**

22. When concentrated hydrochloric acid is added to aqueous copper(II) sulfate, the colour changes from blue to yellow-green. (a) Write an equation for the reaction. (b) Explain why the two complexes have different colours. **[3]**

23. Nickel(II) sulfate solution is green. Use the colour wheel to estimate a wavelength of light absorbed, and calculate the corresponding frequency. **[2]**

24. A complex absorbs light with $\lambda_{max} = 600$ nm. Calculate the energy difference between the split d levels in kJ $mol^{-1}$, and predict the colour of the complex. **[4]**

25. Ammonia produces a larger splitting of the d orbitals than water. State and explain how the wavelength of light absorbed changes when water ligands are replaced by ammonia. **[2]**

26. Outline how a calibration curve would be used to determine the concentration of iron(III) ions in a water sample by colorimetry. Suggest why thiocyanate ions are added. **[4]**

## 10 Answers

1. **A.** Cr is [Ar] $3d^5\ 4s^1$; remove the 4s electron, then two 3d electrons.
2. (a) [Ar] $3d^5$ (b) [Ar] $3d^6$ (c) [Ar] $3d^{10}$ (d) [Ar] ($3d^0$) **[1]** each.
3. (a) Zn $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$; $Zn^{2+}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ **[1]**. (b) The d sublevel is complete in both the atom and its only ion **[1]**, so it does not fit the definition and does not show the characteristic properties (only +2; colourless compounds) **[1]**.
4. For: the Sc atom has an incomplete d sublevel ($3d^1$), so it fits the IB/IUPAC definition **[1]**. Against: its only common ion, $Sc^{3+}$, has no d electrons, so it has one oxidation state and forms colourless compounds **[1]**.
5. **B.** Transition metals have high melting points.
6. **C.** Cr ($3d^5\ 4s^1$) has six unpaired electrons; Ni has two; Ca and Zn have none.
7. $Fe^{2+}$ is $3d^6$ with 4 unpaired electrons; $Fe^{3+}$ is $3d^5$ with 5 unpaired electrons **[1]**. Both are attracted by a magnetic field, but $Fe^{3+}$ more strongly, because it has more unpaired electrons **[1]**.
8. Both 3d and 4s electrons are close in energy and are delocalized, so there are more delocalized electrons per atom **[1]**; the cations are also smaller and more highly charged, so the electrostatic attraction (metallic bonding) is stronger **[1]**.
9. Each additional electron enters the inner 3d sublevel **[1]**, which shields the outer 4s electrons from the additional proton, so the effective nuclear charge on the 4s electrons increases only slightly **[1]**. Consequence: similar first ionization energies, or they readily form alloys because atoms can replace one another in a lattice **[1]**.
10. (a) Fe (b) Ni (c) Pt, Pd or Rh (d) $V_2O_5$ **[1]** each.
11. Reactant molecules are adsorbed onto the surface of the metal, forming weak bonds with it (using its d orbitals) **[1]**. This weakens bonds within the reactants, concentrates them and holds them in a favourable orientation, so the activation energy is lower **[1]**. The products then desorb, freeing the surface **[1]**.
12. Ligand: a species with a lone pair that forms a coordination bond to a metal ion **[1]**. Coordination number: the number of coordination bonds from ligands to the central metal ion **[1]**.
13. (a) $[Fe(CN)_6]^{3-}$; six $CN^-$; 6; +3 **[2]**. (b) $[Cr(NH_3)_4Cl_2]^+$; four $NH_3$ and two $Cl^-$; 6; +3 (the third $Cl^-$ is a counter ion) **[2]**. (c) $[Cu(H_2O)_6]^{2+}$; six $H_2O$; 6; +2 ($SO_4^{2-}$ is a counter ion) **[2]**.
14. **D.** Chloride ions donate lone pairs, so they act as Lewis bases.
15. Calcium: there is a large jump between the second and third ionization energies **[1]**, because the third electron would come from the inner 3p sublevel, so only +2 is energetically possible **[1]**. Vanadium: its 4s and 3d electrons are close in energy, so the first five successive ionization energies increase gradually, and two, three, four or five electrons can be lost or used in bonding **[1]**.
16. **C.** This is titanium ($3d^2\ 4s^2$): four electrons can be used, giving a maximum of +4.
17. +7 **[1]**. Manganese has seven 3d and 4s electrons ([Ar] $3d^5\ 4s^2$), all close in energy, which can all be involved in bonding **[1]**. Example: $MnO_4^-$ (manganate(VII)) or $KMnO_4$ **[1]**.
18. Al: +3 only; Cr: +2, +3, +6 (and others) **[1]**. In aluminium the fourth electron would come from the inner 2p sublevel, a very large jump in ionization energy **[1]**. In chromium the 3d and 4s electrons are close in energy, so successive ionization energies rise gradually **[1]**.
19. The six water ligands split the 3d orbitals into two levels of different energy **[1]**. $Fe^{2+}$ ($3d^6$) has an electron that can be promoted from the lower to the higher level by absorbing a photon of visible light whose energy matches the gap **[1]**. The re-

maining light is transmitted and the complementary colour (pale green) is seen **[1]**.

20. **B.** $Sc^{3+}$ is $3d^0$.

21. (a) different metal: different nuclear charge (and number of d electrons) **[1]**; (b) different oxidation state of iron (charge on the ion) **[1]**; (c) different ligand **[1]**. Each changes the splitting ΔE, so a different wavelength is absorbed.

22. (a) $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ **[1]**. (b) The ligand changes ($H_2O$ to $Cl^-$) and so does the coordination number and shape (6, octahedral to 4, tetrahedral) **[1]**; this changes the size of the d-orbital splitting, so a different wavelength is absorbed **[1]**.

23. Green is observed, so red is absorbed: λ in the range 647–700 nm, e.g. 670 nm **[1]**. $f = (3.00 \times 10^8) / (670 \times 10^{-9}) = 4.48 \times 10^{14}$ $s^{-1}$ (accept 4.3–4.6 × $10^{14}$ $s^{-1}$ consistent with the λ chosen) **[1]**.

24. $f = (3.00 \times 10^8) / (600 \times 10^{-9}) = 5.00 \times 10^{14}$ $s^{-1}$ **[1]**; $E = (6.63 \times 10^{-34})(5.00 \times 10^{14}) = 3.32 \times 10^{-19}$ J **[1]**; × 6.02 × $10^{23}$ = 2.00 × $10^5$ J $mol^{-1}$ = 200 kJ $mol^{-1}$ **[1]**. 600 nm is orange light, so the complex appears blue **[1]**.

25. The wavelength absorbed decreases (shifts towards blue) **[1]**, because a larger ΔE requires a photon of higher energy and higher frequency, and $E = hc/\lambda$, so λ is shorter **[1]**.

26. Prepare at least five standard solutions of known $Fe^{3+}$ concentration and measure their absorbance at a fixed wavelength that the complex absorbs strongly **[1]**. Plot absorbance against concentration to give a calibration curve **[1]**. Measure the absorbance of the sample under the same conditions and read its concentration from the curve **[1]**. $SCN^-$ forms an intensely blood-red complex with $Fe^{3+}$, which absorbs much more strongly, so low concentrations can be measured accurately **[1]**.

### Structure 3.1 is complete

- **Booklet 1** — 3.1.1 to 3.1.5: the table, configuration and position, periodicity, group trends and the oxides.
- **Booklet 2** — 3.1.6 oxidation states and HL 3.1.7 discontinuities in first ionization energy.
- **Booklet 3** (this booklet) — HL 3.1.8 to 3.1.10: transition elements, variable oxidation states and coloured complexes.
- Links forward: **Structure 3.2** (functional groups), **Reactivity 2.2** (catalysts), **Reactivity 3.2** (redox titrations with $MnO_4^-$ and $Cr_2O_7^{2-}$), **Reactivity 3.4** (Lewis acids and bases, complex ions).

**These notes are a free resource, shared for any IB student who finds them useful.**

If a particular idea here still isn't clicking, specialist one-to-one support in Physics, Chemistry and Maths from a past A Level examiner is available at iBLaurel — call or message **+44 7404 710097**, or use the contact form at **www.iBLaurel.com**.

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