

Colour, complexes and catalysis in the d-block

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Transition metals are d-block elements that form ions with a partially filled d subshell. They show variable oxidation states, form coloured complex ions with ligands, and act as catalysts. Colour arises when ligands split the d orbitals and electrons absorb light of energy ΔE to jump between them.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.2.5

What makes an element a transition metal?

The d-block elements from titanium to copper fill the 3d subshell after 4s. Their atoms and ions have properties that set them apart from group 1 and group 2 metals: several oxidation states, coloured compounds, catalytic activity and complex ion formation.

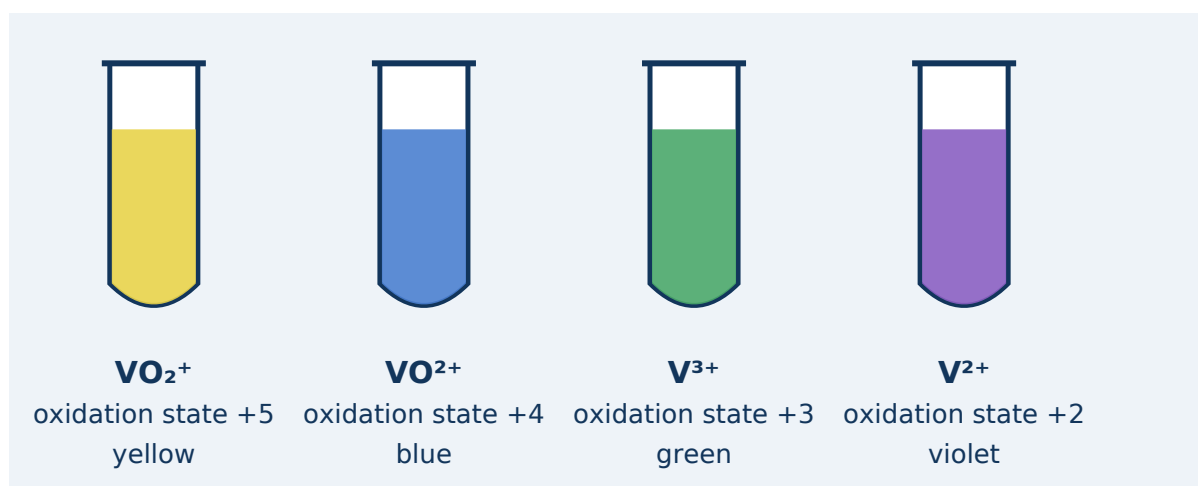
Definition

A **transition element** is a d-block element that forms at least one stable ion with a partially filled d subshell.

Scandium forms only Sc^{3+} ($3d^0$) and zinc only Zn^{2+} ($3d^{10}$), so neither is a transition element even though both are in the d-block. Iron is $[\text{Ar}] 3d^6 4s^2$, and when it ionises the 4s electrons leave first: Fe^{2+} is $[\text{Ar}] 3d^6$ and Fe^{3+} is $[\text{Ar}] 3d^5$. Chromium ($[\text{Ar}] 3d^5 4s^1$) and copper ($[\text{Ar}] 3d^{10} 4s^1$) are exceptions that gain stability from a half-full or full d subshell.

Why do transition metals have variable oxidation states?

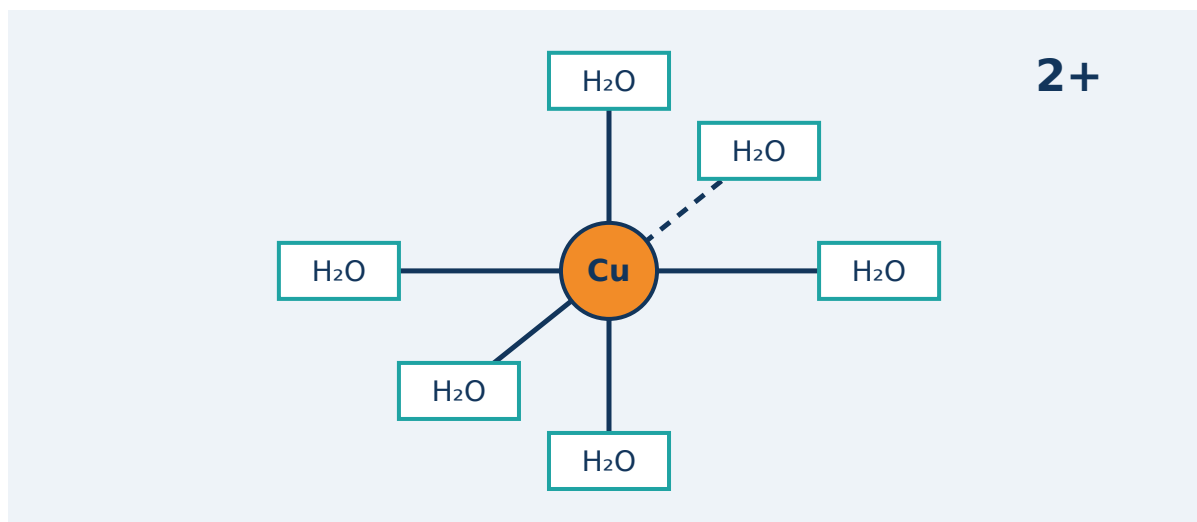
The 3d and 4s energies are very close, so a similar amount of energy removes different numbers of electrons. Vanadium shows +2, +3, +4 and +5, and each state has its own colour. Manganese ranges from +2 (pale pink Mn^{2+}) to +7 (purple MnO_4^-).



The same metal gives four colours as its oxidation state changes from +5 down to +2.

What is a complex ion?

A complex ion is a central metal ion bonded to ligands by dative covalent bonds. Each ligand donates a lone pair. The number of dative bonds is the coordination number.



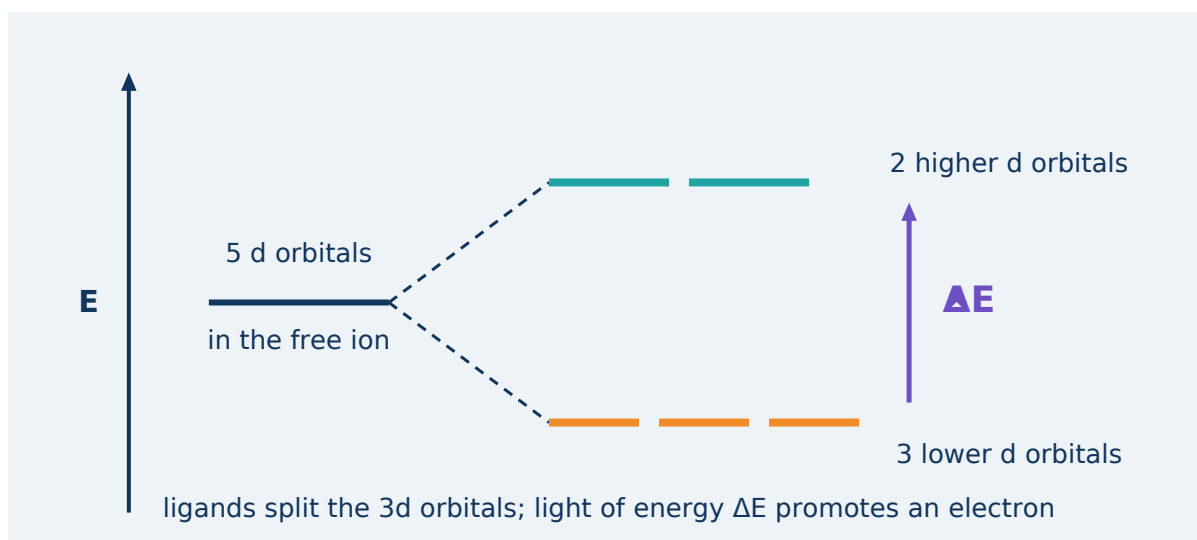
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ has six dative bonds from water molecules, so the coordination number is 6 and the shape is octahedral.

Ligand	Type	Bonds per ligand	Example
H_2O , NH_3 , Cl^- , CN^-	monodentate	1	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (en), $\text{C}_2\text{O}_4^{2-}$	bidentate	2	$[\text{Ni}(\text{en})_3]^{2+}$
EDTA^{4-}	hexadentate	6	$[\text{Fe}(\text{EDTA})]^-$

Six ligands usually give an octahedral shape, four give tetrahedral ($[\text{CuCl}_4]^{2-}$) or square planar (cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$), and two give linear ($[\text{Ag}(\text{NH}_3)_2]^+$). The charge on the complex is the sum of the metal ion and ligand charges: Cr^{3+} with four NH_3 and two Cl^- gives $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$.

Why are transition metal complexes coloured?

Ligands split the five 3d orbitals into two sets separated by an energy gap ΔE . An electron absorbs a photon of exactly this energy and jumps to the higher set. The remaining wavelengths are transmitted, so the solution shows the complementary colour.



In a complex ion the d orbitals split by ΔE . Light with energy ΔE is absorbed and the rest is seen as colour.

Formula

$\Delta E = hc \div \lambda$, with $h = 6.63 \times 10^{-34} \text{ J s}$, $c = 3.00 \times 10^8 \text{ m s}^{-1}$ and λ in metres. For one mole multiply by the Avogadro constant, $6.02 \times 10^{23} \text{ mol}^{-1}$.

Worked example

A complex absorbs light of wavelength 650 nm. Calculate ΔE in J per ion and in kJ mol^{-1} .

$\Delta E = (6.63 \times 10^{-34} \times 3.00 \times 10^8) \div (650 \times 10^{-9}) = \mathbf{3.06 \times 10^{-19} \text{ J}}$. Per mole: $3.06 \times 10^{-19} \times 6.02 \times 10^{23} = 1.84 \times 10^5 \text{ J mol}^{-1} = \mathbf{184 \text{ kJ mol}^{-1}}$. Red-orange is absorbed, so the solution looks blue-green.

Ion	Colour in solution	Ion	Colour in solution
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	pale blue	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	deep blue
$[\text{CuCl}_4]^{2-}$	yellow-green	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	pale green
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	yellow-brown	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	pink

Changing the ligand, the oxidation state or the coordination number changes ΔE , which changes the colour. This is called ligand substitution: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$.

How do transition metals act as catalysts?

Heterogeneous catalysts such as iron in the Haber process and vanadium(V) oxide in the contact process provide a surface where reactants adsorb and react; vanadium(V) oxide alternates between +5 and +4. Homogeneous catalysts such as Fe^{2+} or Fe^{3+} in the reaction of iodide with peroxodisulfate switch between oxidation states, avoiding the repulsion between two negative ions: $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$, then $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$.

Worked example

Chiamaka titrates 25.0 cm^3 of iron(II) solution with 22.40 cm^3 of $0.0200 \text{ mol dm}^{-3}$

potassium manganate(VII). $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$. Calculate the iron(II) concentration.

$n(\text{MnO}_4^-) = 0.02240 \times 0.0200 = 4.48 \times 10^{-4} \text{ mol}$; $n(\text{Fe}^{2+}) = 5 \times 4.48 \times 10^{-4} = 2.24 \times 10^{-3} \text{ mol}$; $c = 2.24 \times 10^{-3} \div 0.0250 = \mathbf{0.0896 \text{ mol dm}^{-3}}$.

Common mistake

Do not call every d-block element a transition element. Zinc and scandium do not form an ion with a partially filled d subshell, so they are not transition metals, and zinc compounds are white.

Lina's tip

For ions, remove the 4s electrons first, then 3d. Write the neutral atom, take electrons from 4s, and check that the subshell count equals the oxidation state.

Key points to remember

- Transition element: forms an ion with a partially filled d subshell (Sc and Zn are not)
- Fe is $[\text{Ar}] 3d^6 4s^2$; Cr is $[\text{Ar}] 3d^5 4s^1$; Cu is $[\text{Ar}] 3d^{10} 4s^1$
- Complex ion = metal ion + ligands joined by dative bonds; coordination number = number of bonds
- Colour: $\Delta E = hc \div \lambda$ for the light absorbed
- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$

Colour, complexes and catalysis in the d-block: frequently asked questions

Why is zinc not a transition metal?

Zinc forms only Zn^{2+} , which has a full $3d^{10}$ subshell. A transition element must have an ion with a partially filled d subshell, so zinc compounds are also colourless.

What is a ligand?

A ligand is a molecule or ion with a lone pair that forms a dative covalent bond to a central metal ion. Water, ammonia and chloride ions are common ligands.

Why do complexes have different colours?

The ligands split the d orbitals by an energy gap ΔE . The complex absorbs light of energy ΔE and transmits the other wavelengths, which we see as the complementary colour.

How do transition metals catalyse reactions?

They can change oxidation state, so they form intermediates and provide a lower-energy pathway. Solid catalysts also hold reactants on their surface.

Why does copper(II) solution change colour with ammonia?

Ammonia replaces water ligands to form $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. This changes the energy gap, so the colour changes from pale blue to deep blue.