9701 CHEMISTRY · TOPIC 26 · A LEVEL

Transition Elements — Properties

01 · DEFINITION

A **transition element** is a d-block element that forms one or more stable ions with a **partially filled d sub-shell**.

Sc and Zn are in the d block but are **not** transition elements: Sc^{3+} is $3d^0$ and Zn^{2+} is $3d^{10}$. Their compounds are white and they show only one oxidation state.

02 · ELECTRON CONFIGURATIONS

4s fills before 3d, so Fe is [Ar] $3d^6\ 4s^2$. **Exceptions:** Cr = [Ar] $3d^5\ 4s^1$ and Cu = [Ar] $3d^{10}\ 4s^1$ — a half-filled or full d sub-shell is more stable.

When ions form, the **4s electrons leave first**: Fe^{2+} = $3d^6$, Fe^{3+} = $3d^5$, Cu^{2+} = $3d^9$.

03 · THE FOUR CHARACTERISTIC PROPERTIES

1 · Variable oxidation states — 4s and 3d are close in energy, so different numbers of electrons can be lost.

2 · Coloured compounds — from d–d transitions in a split d sub-shell.

3 · Catalytic activity — variable oxidation states allow electron transfer, and surfaces adsorb reactants.

4 · Complex formation — small, highly charged ions with vacant orbitals accept lone pairs.

04 · COMMON OXIDATION STATES

Species	O.N.	Colour
MnO_4^-	+7	purple
$Cr_2O_7^{2-}$	+6	orange
Cr^{3+}	+3	green
Fe^{3+}	+3	yellow-brown
Fe^{2+}	+2	pale green
Mn^{2+}	+2	very pale pink
Cu^{2+}	+2	blue

05 · WHY THE COMPOUNDS ARE COLOURED

Ligands split the five d orbitals into two energy levels. An electron absorbs a photon of visible light and is promoted across the gap — a **d–d transition**.

The colour seen is the **complement** of the light absorbed. The size of the gap, and therefore the colour, depends on the metal, its oxidation state, the ligand and the shape of the complex.

No colour when the d sub-shell is empty (Sc^{3+}) or full (Zn^{2+}, Cu^+): there is no vacancy to be promoted into.

06 · COMPLEXES AND LIGANDS

A **ligand** is a species with a lone pair that forms a **dative covalent** bond to the central metal ion. **Coordination number** = number of such bonds.

Type	Examples
monodentate	H_2O, NH_3, Cl^-, CN^-, OH^-
bidentate	ethanedioate, 1,2-diaminoethane
polydentate	$EDTA^{4-}$ (six bonds)

07 · SHAPES OF COMPLEXES

C.N.	Shape	Example
6	octahedral, 90°	$[Fe(H_2O)_6]^{2+}$
4	tetrahedral, 109.5°	$[CuCl_4]^{2-}$
4	square planar	cisplatin
2	linear, 180°	$[Ag(NH_3)_2]^+$

Large ligands such as Cl^- favour a coordination number of 4; small ones such as H_2O and NH_3 give 6.

08 · NAMING AND CHARGE

Overall charge = metal charge + sum of ligand charges.

$[Cu(H_2O)_6]^{2+}$ — Cu is +2, water neutral
$[CuCl_4]^{2-}$ — $+2 + 4(-1) = -2$
$[Fe(CN)_6]^{3-}$ — $+3 + 6(-1) = -3$

Write the formula in square brackets with the charge outside.

09 · STEREOISOMERISM IN COMPLEXES

Cis–trans in square planar and octahedral complexes: cisplatin is the cis isomer of $[Pt(NH_3)_2Cl_2]$ and is the anticancer drug; the trans isomer is inactive.

Optical isomerism when an octahedral complex holds three bidentate ligands — the two forms are non-superimposable mirror images.

10 · PHYSICAL PROPERTIES

Transition metals are hard, dense and have high melting points: both 4s and 3d electrons are delocalised, giving strong metallic bonding.

Across the series the atomic radius changes very little — the added 3d electrons shield the extra nuclear charge almost completely.

11 · WORKED EXAMPLE — CONFIGURATION AND COLOUR

Explain why Zn^{2+} compounds are white but Cu^{2+} compounds are blue.

Zn^{2+} = [Ar] $3d^{10}$ — the d sub-shell is **full**, so no d–d transition is possible and no visible light is absorbed.

Cu^{2+} = [Ar] $3d^9$ — a vacancy exists, so an electron is promoted across the split d orbitals, absorbing red light and leaving the solution blue.

12 · WHY THE PROPERTIES ARISE

The 3d and 4s sub-shells are very close in energy. That single fact explains variable oxidation states, since removing one more electron costs little extra.

The ions are also small with a high charge density and empty low-energy orbitals, which is why they attract lone pairs and form complexes so readily — and why those complexes, having a partly filled d sub-shell, are coloured.

DEFINITIONS TO QUOTE

Transition element — a d-block element that forms at least one stable ion with a partially filled d sub-shell.

Ligand — a molecule or ion with a lone pair that forms a dative covalent bond to a central metal ion.

Complex — a central metal ion surrounded by ligands bonded datively.

MARKS LOST HERE

— Calling Sc and Zn transition elements.

— Writing Fe^{3+} as $3d^34s^2$; the 4s electrons go first.

— Saying a complex is coloured "because it is a transition metal" instead of explaining d–d transitions and the split d sub-shell.

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Ligand Exchange, Redox and Stability

13 · LIGAND EXCHANGE

One ligand replaces another. The colour usually changes because the new ligand splits the d orbitals by a different amount; the shape may change too if the new ligand is larger.

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$
pale blue → yellow, octahedral → tetrahedral

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
pale blue → deep blue, shape unchanged

14 · STABILITY CONSTANTS

$$K_{stab} = [complex] \div ([M^{n+}][ligand]^x)$$

The equilibrium constant for forming a complex from the aqueous ion. A **larger K_{stab}** means a more stable complex, so that ligand displaces one with a smaller value.

Order of stability for most ions: $CN^- > NH_3 > H_2O > Cl^-$. Polydentate ligands such as EDTA give very large values.

15 · WORKED EXAMPLE — K_{STAB}

Which is displaced when NH_3 is added to $[Cu(H_2O)_6]^{2+}$?
$K_{stab}[Cu(NH_3)_4(H_2O)_2]^{2+} = 1.2 \times 10^{13}$
$K_{stab}[CuCl_4]^{2-} = 4.2 \times 10^5$

The ammonia complex has the far larger K_{stab}, so **ammonia displaces both water and chloride** and the deep blue colour appears.

16 · REACTIONS WITH NAOH AND NH_3

Ion	With OH^-	In excess NH_3
Cu^{2+}	pale blue ppt	deep blue solution
Fe^{2+}	green ppt, browns in air	insoluble
Fe^{3+}	red-brown ppt	insoluble
Cr^{3+}	green ppt, soluble in excess	violet solution

The precipitate is the neutral hydroxide, e.g. $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$.

17 · REDOX CHEMISTRY OF MANGANESE

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E° = +1.52$ V
purple → colourless in acid

In alkali the reduction stops at MnO_2 (brown solid), so acid conditions matter. Use dilute sulfuric acid, never HCl or HNO_3.

18 · REDOX CHEMISTRY OF IRON AND COPPER

Fe^{2+} is readily oxidised to Fe^{3+} ($E° = +0.77$ V) — by MnO_4^-, $Cr_2O_7^{2-}$, Cl_2 or Br_2, and slowly by air.

$Cu^{2+} + I^-$: $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$. The iodine is then titrated with thiosulfate, $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$, using starch near the end point.

19 · WORKED EXAMPLE — IRON TITRATION

A 1.20 g iron tablet is dissolved in dilute H_2SO_4 and made up to 250 cm^3. A 25.0 cm^3 portion needs 18.6 cm^3 of 0.0100 mol dm^{-3} $KMnO_4$.

$n(MnO_4^-) = 1.86 \times 10^{-4}$ mol
$n(Fe^{2+})$ in 25 $cm^3 = 5 \times 1.86 \times 10^{-4} = 9.30 \times 10^{-4}$
in 250 $cm^3 = 9.30 \times 10^{-3}$ mol
$m(Fe) = 9.30 \times 10^{-3} \times 55.8 = 0.519$ g
% Fe $= 0.519 \div 1.20 \times 100 =$ **43.2 %**

20 · EFFECT OF LIGAND ON E°

Changing the ligand changes the stability of the two oxidation states, and so changes E°.

$[Fe(H_2O)_6]^{3+/2+}$ is +0.77 V, but with cyanide $[Fe(CN)_6]^{3-/4-}$ is only +0.36 V: CN^- stabilises the +3 state, making it harder to reduce. Adding a ligand that stabilises the higher state always lowers E°.

21 · CATALYSIS BY TRANSITION METALS

Heterogeneous: Fe in the Haber process, V_2O_5 in the Contact process, Ni in hydrogenation, Pt/Rh in catalytic converters. Reactants adsorb onto active sites, weakening their bonds.

Homogeneous: Fe^{3+} or Fe^{2+} catalysing $S_2O_8^{2-} + 2I^-$; Mn^{2+} autocatalysing the manganate(VII)–ethanedioate reaction. Both work by cycling between oxidation states.

22 · COMPLEXES IN LIFE AND MEDICINE

Haemoglobin — Fe^{2+} held in a porphyrin ring; oxygen binds reversibly at the sixth site. Carbon monoxide binds far more strongly and irreversibly, which is why it is toxic.

Cisplatin — square planar Pt(II) complex that binds DNA and prevents replication.

23 · CHROMIUM CHEMISTRY

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E° = +1.33$ V
orange → green in acid

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
orange in acid ⇌ yellow in alkali — an acid–base equilibrium, **not** a redox change: chromium stays at +6.

Zinc in acid reduces Cr^{3+} further to blue Cr^{2+}.

24 · WORKED EXAMPLE — THIOSULFATE TITRATION

25.0 cm^3 of Cu^{2+} solution is treated with excess KI. The iodine released needs 22.4 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$.

$n(S_2O_3^{2-}) = 2.24 \times 10^{-3}$ mol
$I_2 : S_2O_3^{2-} = 1 : 2 \rightarrow n(I_2) = 1.12 \times 10^{-3}$ mol
$Cu^{2+} : I_2 = 2 : 1 \rightarrow n(Cu^{2+}) = 2.24 \times 10^{-3}$ mol
$c(Cu^{2+}) =$ **0.0896 mol dm^{-3}**

Add starch only near the end point, when the solution is straw-coloured.

COLOURS WORTH MEMORISING

$Cu^{2+}(aq)$ pale blue · $Cu(OH)_2$ pale blue ppt · $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue · $[CuCl_4]^{2-}$ yellow

Fe^{2+} pale green · $Fe(OH)_2$ green ppt · Fe^{3+} yellow-brown · $Fe(OH)_3$ red-brown ppt

MnO_4^- purple · Mn^{2+} almost colourless · $Cr_2O_7^{2-}$ orange · Cr^{3+} green

MARKS LOST HERE

— Describing a ligand exchange without naming both the colour change and any change of shape.
— Using HCl to acidify a manganate(VII) titration.
— Forgetting the 5 : 1 ratio of Fe^{2+} to MnO_4^-.
— Treating K_{stab} as a rate: it measures stability, not speed.