

Pioneer Junior College H2 Chemistry (9647)

An Introduction To The Chemistry Of Transition Elements

References

- 1 Chemistry for advanced level – Peter Cann & Peter Hughes (pg 345 – 368)
- 2 Chemistry in Context 3rd Ed. – Graham C. Hill & John S. Holman (pg 292 – 307)
- 3 Chemguide (<http://www.chemguide.co.uk/inorganic/transitionmenu.html#top>;
<http://www.chemguide.co.uk/inorganic/complexmenu.html#top>)

Syllabus Content

- General physical and characteristic chemical properties of the first set of transition elements, titanium to copper
- Colour of complexes

Assessment Objectives

By the end of the lectures, you should be able to:

- (a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with incomplete d orbitals
- (b) state the electronic configuration of a first row transition element and of its ions
- (c) state that the atomic radii, ionic radii and first ionisation energies of the transition metals are relatively invariant
- (d) contrast, qualitatively the melting point; density; atomic radius; ionic radius; first ionisation energy and conductivity of transition elements with those of calcium as a typical s-block element
- (e) describe the tendency of transition elements to have variable oxidation states
- (f) predict from a given electronic configuration, the likely oxidation states of a transition element
- (g) describe and explain the use of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ as examples of redox systems
- (h)
 - (i) explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) ions with water and ammonia
 - (ii) describe the formation, and state the colour of, these complexes
- (i) predict, using E^θ values, the likelihood of redox reactions
- (j) explain qualitatively that ligand exchange may occur, including CO/O_2 in haemoglobin
- (k) explain how some transition metals and/or their compounds can act as catalyst
- (l) explain, in terms of d orbital splitting, why transition element complexes are usually coloured

Lecture Outline

- 1 Introduction
 - 1.1 What are transition elements?
 - 1.2 Electronic configuration of the first row transition elements and ions
- 2 Physical properties of transition elements
 - 2.1 Atomic (metallic) radius
 - 2.2 Ionic radius
 - 2.3 Ionisation energy
 - 2.4 Melting point
 - 2.5 Density
 - 2.6 Electrical conductivity
- 3 Chemical properties of transition elements
 - 3.1 Variable oxidation state
 - 3.2 Transition metal and their ions in redox systems
 - 3.3 Complex formation
 - 3.4 Reactions involving ions of d-block
 - 3.5 Formation of coloured compounds and ions
 - 3.6 Catalytic activity
- 4 Summary

1 Introduction

1.1 What are transition elements?

The Periodic Table of the Elements																						
Group																						
I		II												III	IV	V	VI	VII	0			
										1.0 H hydrogen 1												4.0 He helium 2
<div><div>Key</div><div>relative atomic mass atomic symbol name atomic number</div><div>First row d-block elements</div></div>																						
6.9 Li lithium 3	9.0 Be beryllium 4											10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10					
23.0 Na sodium 11	24.3 Mg magnesium 12											27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulphur 16	35.5 Cl chlorine 17	39.9 Ar argon 18					
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36					
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	98.9 Tc technetium 43	101 Ru ruthenium 44	101 Rh rhodium 45	106 Pd palladium 46	108 Ag silver 47	112 Cd cadmium 48	115 In indium 49	119 Sn tin 50	122 Sb antimony 51	128 Te tellurium 52	127 I iodine 53	131 Xe xenon 54					
133 Cs caesium 55	137 Ba barium 56	139 La lanthanum 57	178 Hf hafnium 72	181 Ta tantalum 73	184 W tungsten 74	186 Re rhenium 75	190 Os osmium 76	192 Ir iridium 77	195 Pt platinum 78	197 Au gold 79	201 Hg mercury 80	204 Tl thallium 81	207 Pb lead 82	209 Bi bismuth 83	— Po polonium 84	— At astatine 85	— Rn radon 86					
— Fr francium 87	— Ra radium 88	— Ac actinium 89	— Rf rutherfordium 104	— Db dubnium 105	— Sg seaborgium 106	— Bh bohrium 107	— Hs hassium 108	— Mt meitnerium 109	— Unn ununium 110	— Uuu ununium 111	— Uub unubium 112	— Uuq ununquadium 114	— Uuh ununhexium 116	— Uuo ununoctium 118								

Fig. 1 Periodic Table

A transition element is defined as a d-block element which forms at least one stable ion in which there is a partially filled d-subshell of electrons.

1.2 Electronic configuration of the first row transition elements and ions

1.2.1 Electronic configuration of first row d-block element

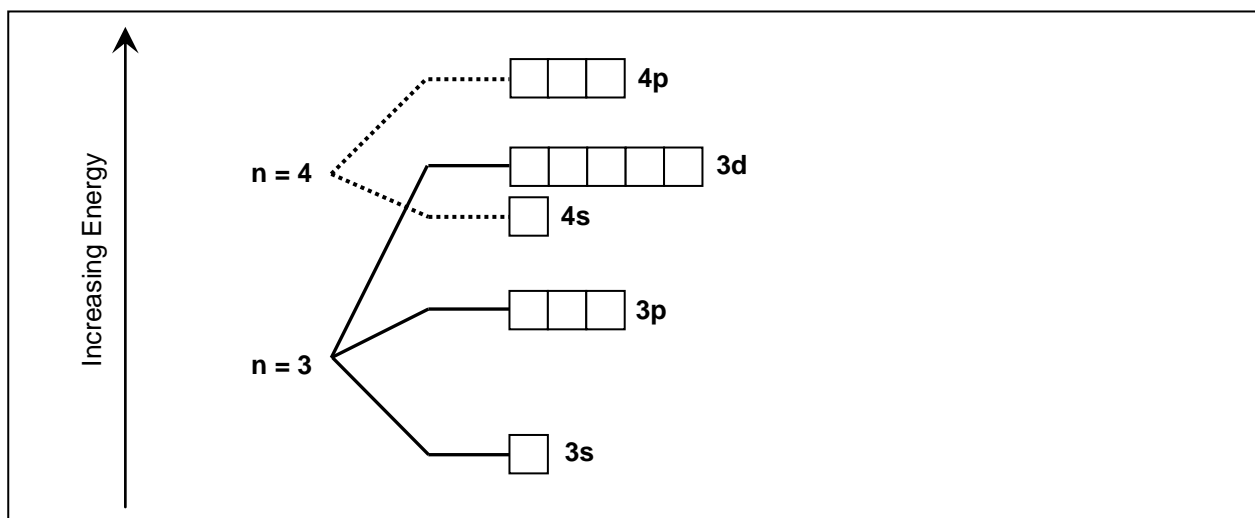
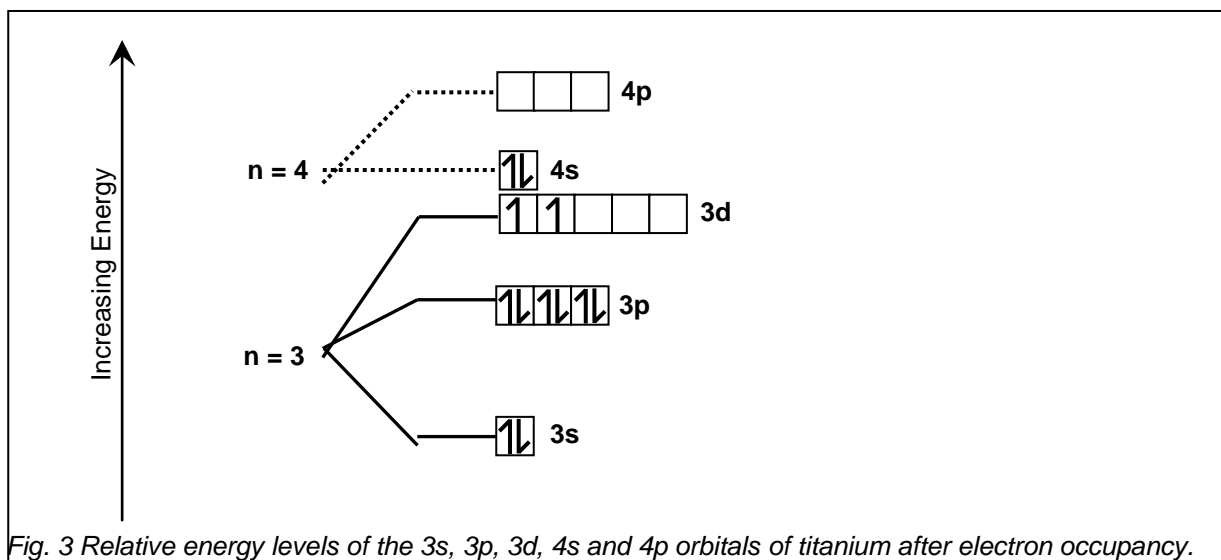


Fig. 2 Relative energy levels of the 3s, 3p, 3d, 4s and 4p orbitals before electron occupancy

- For period 4, the **vacant** 4s orbital is of lower energy than the **vacant** 3d orbital, thus the 4s subshell is filled **before** the 3d orbitals.
- After the 4s subshell is filled, the electrons are then placed in the 3d orbitals, according to Hund's rule.
- However, when a 3d orbital is filled with an electron, the electron in the 3d orbital (being closer to the nucleus) will repel electrons in the 4s orbitals further away from the nucleus and to a higher energy level.

- Because of this, 3d orbitals come before the 4s when writing electronic configuration even though the 4s orbital is filled up first.



Example

Complete the electron in box diagram for the following d-block elements.

Element		3d					4s
$_{21}\text{Sc}$	[Ar]	1					1↓
$_{22}\text{Ti}$	[Ar]	1	1				1↓
$_{23}\text{V}$	[Ar]	1	1	1			1↓
$_{24}\text{Cr}$	[Ar]	1	1	1	1	1	1
$_{25}\text{Mn}$	[Ar]	1	1	1	1	1	1↓
$_{26}\text{Fe}$	[Ar]	1↓	1	1	1	1	1↓
$_{27}\text{Co}$	[Ar]	1↓	1↓	1	1	1	1↓
$_{28}\text{Ni}$	[Ar]	1↓	1↓	1↓	1	1	1↓
$_{29}\text{Cu}$	[Ar]	1↓	1↓	1↓	1↓	1↓	1
$_{30}\text{Zn}$	[Ar]	1↓	1↓	1↓	1↓	1↓	1↓

Points to note:

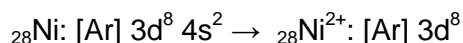
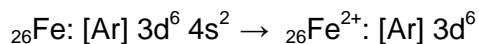
- Electronic configuration of Cr: $[\text{Ar}] 3d^5 4s^1$ and not $[\text{Ar}] 3d^4 4s^2$
- Electronic configuration of Cu: $[\text{Ar}] 3d^{10} 4s^1$ and not $[\text{Ar}] 3d^9 4s^2$

Reason: The $3d^5$ (half-filled d-subshell) and $3d^{10}$ (completely filled d-subshell) configurations have a **symmetrical** electron cloud that shields the nucleus more effectively than the other configurations, this confers greater stability to these two configurations.

1.2.2 Electronic configuration of ions of d-block elements

- Thus, when a transition metal takes part in a chemical reaction to form a cation, the valence 4s electrons are lost / removed first.

- Examples:



Points to note:

- Scandium and zinc are d-block elements which are not considered as transition elements. Why?
- Sc **only** forms Sc^{3+} in all its compounds.
 ${}_{21}\text{Sc}: [\text{Ar}] 3d^1 4s^2 \rightarrow {}_{21}\text{Sc}^{3+}: [\text{Ar}] 3d^0$
- Zn **only** forms Zn^{2+} in all its compounds.
 ${}_{30}\text{Zn}: [\text{Ar}] 3d^{10} 4s^2 \rightarrow {}_{30}\text{Zn}^{2+}: [\text{Ar}] 3d^{10}$
- As transition elements must be able to form at least one stable ion, with partially filled d-orbitals, scandium and zinc are not transition elements.
- As a result, the compounds of Sc and Zn have different properties from those of typical transition elements. For example,
 - (i) they have **only one oxidation state** in their compounds,
 - (ii) both show **little / no catalytic activity**,
 - (iii) the solutions of Zn and Sc compounds are **colourless**.

Quick Check 1

- For which transition metal does its ground-state atom have an unpaired electron in an s-orbital? [N1996/IV/17; J1991/I/22]
A chromium **B** cobalt **C** iron **D** manganese
- Which of the following ions contains five unpaired d-electrons? [J1997/3/16]
A Cr^{3+} **B** Fe^{3+} **C** Mn^{3+} **D** Ni^{2+}
- What is the order of increasing energy of the listed orbitals in the atom of titanium? [J2004/I/4]
A 3s, 3p, 3d, 4s **B** 3s, 4s, 3p, 3d
C 3s, 3p, 4s, 3d **D** 4s, 3s, 3p, 3d

2 Physical properties of d-block elements

- Generally, for elements in a period e.g. Na to Cl, there is a gradual change in properties.
- However, the transition elements are **remarkably similar** in their **physical properties** even as we move across a period.
 - ✓ They are all **metals**.
 - ✓ They are **hard** and have **high densities**.
 - ✓ They have **very high melting** and **boiling points**.
 - ✓ They are **good conductors** of heat and electricity.

Element	Density/ g cm ⁻³	m.p. / °C	b.p. / °C	Metallic radius / nm	Ionisation energies / kJ mol ⁻¹		
					1 st I.E	2 nd I.E	3 rd I.E
Sc	2.99	1541	2831	0.164	631	1235	2389
Ti	4.50	1660	3287	0.147	658	1310	2653
V	5.96	1890	3380	0.135	650	1414	2828
Cr	7.20	1857	2670	0.129	653	1592	2987
Mn	7.20	1244	1962	0.137	717	1509	3249
Fe	7.86	1535	2750	0.126	759	1561	2958
Co	8.90	1495	2870	0.125	758	1646	3232
Ni	8.90	1455	2730	0.125	737	1753	3394
Cu	8.92	1083	2567	0.128	746	1958	3554
Zn	7.14	420	907	0.137	906	1733	3833

Fig. 4 Physical properties of d-block elements

2.1 Atomic (metallic) radius

Atomic radii of transition elements are relatively constant (decreasing slightly). See Fig. 5.

Explanation:

- Across the period from Sc to Zn, there is an increase in number of protons, hence **nuclear charge increases**.
- However, electrons are added to the **penultimate shell** (inner 3d sub-shell), resulting in an **increase of shielding effect** too.
- These 3d orbital electrons shielded the outer 4s orbital electrons from the increased in nuclear charge. As a result, **the effective nuclear charge only increases very slightly**.

Comparison with s-block elements:

- Atomic radii of transition elements are smaller than those of the s-block elements because transition elements have higher nuclear charge and the 3d electrons shield the 4s electrons poorly. These result in a greater nuclear attraction for the valence electrons in transition elements than s-block elements.

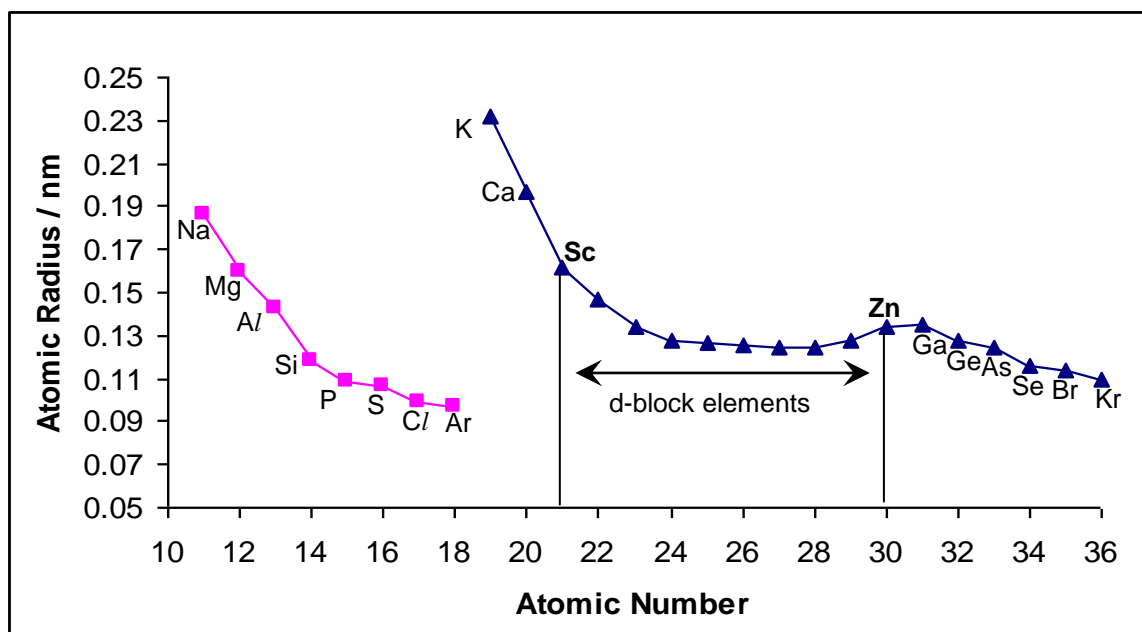


Fig. 5 Variation of atomic radius for Period 3 and Period 4 elements

2.2 Ionic radius

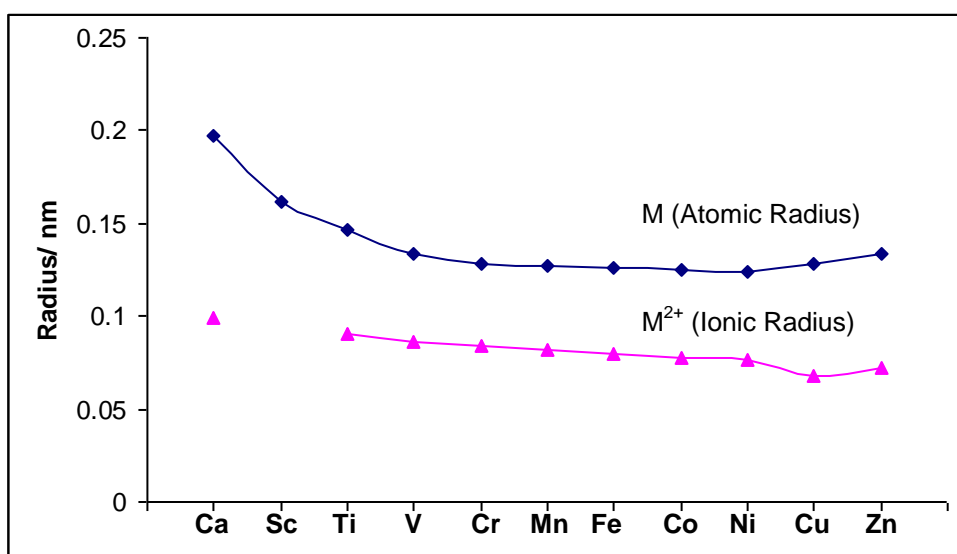


Fig. 6 Atomic radii and ionic radii of transition elements

- Ionic radii are relatively constant (decreases marginally) similar to the atomic radii of the transition elements (Fig. 6).
- Ionic radii < atomic radii because valence 4s electrons are lost when cations are formed.

Comparison of transition metal ions with s-block metal ions

- Ionic radii of transition elements are smaller than those of the s-block elements. Thus, the charge density of transition metal ions is higher than s-block metal ions with similar charge.

2.3 Ionisation energy

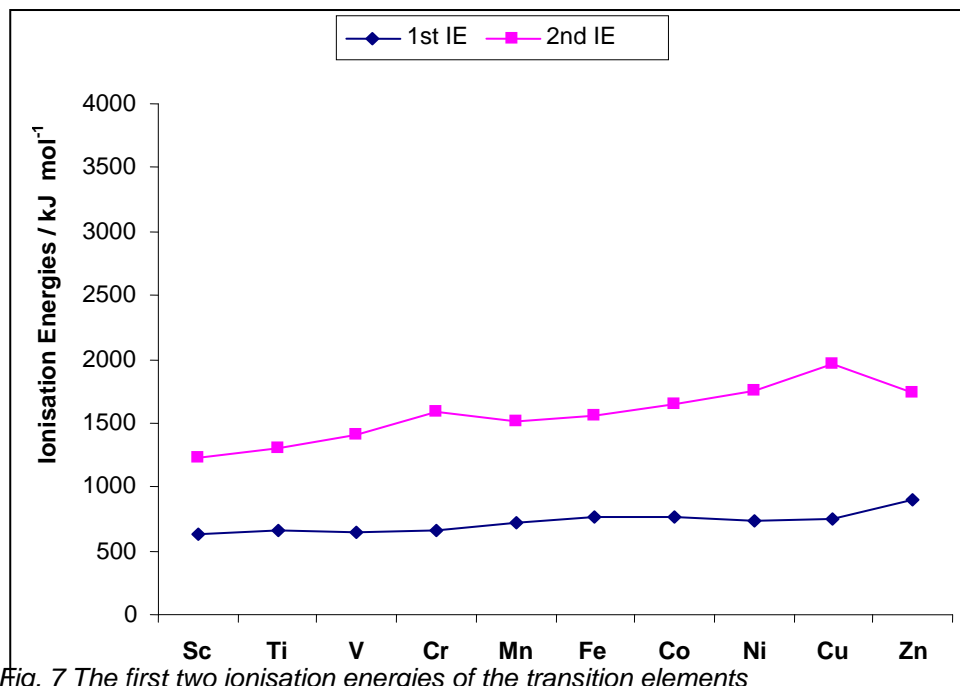


Fig. 7 The first two ionisation energies of the transition elements

1st and 2nd Ionisation Energies

Very gradual increase in 1st and 2nd I.E. from Sc to Zn

Explanation:

- For first row d-block elements, the 1st I.E. is the amount of energy required to remove the first electron from the valence 4s-orbital: $M(g) \rightarrow M^+(g) + e^-$.
- Going across the period from Sc to Zn, the effective nuclear charge attraction on the valence 4s electron increases only very gradually (because the 3d electrons provide shielding of the valence 4s electrons).
- Hence, only a small increase in amount of energy is required to remove the 4s e^- , accounting for the gradual increase in 1st I.E. of the transition metals. (631 kJ mol⁻¹ to 906 kJ mol⁻¹)
- Similar explanation for the gradual increase in 2nd I.E.

Comparison with s-block elements:

- Transition elements have higher 1st IE than s-block metals like Ca (see Fig. 8), due to their higher effective nuclear charge.

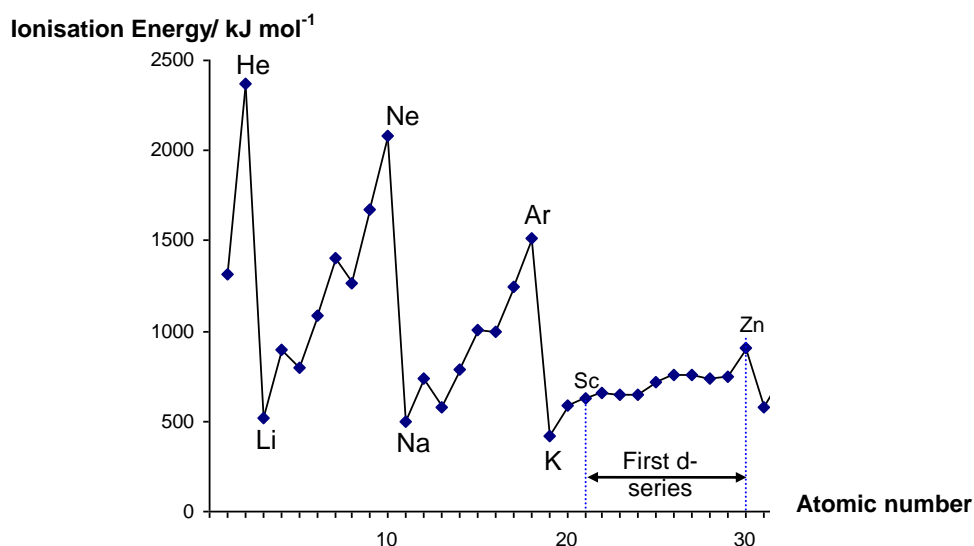


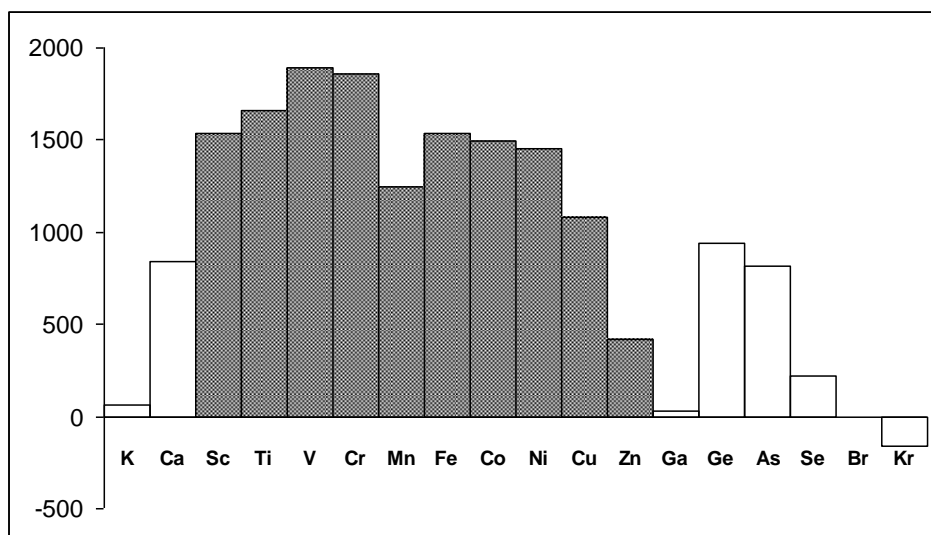
Fig. 8 The first ionisation energies of the elements

2.4 Melting points

All transition elements have very high melting points $> 1000\text{ }^{\circ}\text{C}$ due to the strong metallic bonds. The melting and boiling points are typically higher than that of s-block elements (See Fig. 9). Note that Mn has relatively low melting point because the half-filled subshell of 3d electrons is not readily available for metallic bonding.

Explanation:

- Metallic bonds exist between metal cations and the 'sea of delocalised electrons'. To bring about melting in transition metals, energy must be supplied to weaken the strong metallic bonds.
- Group I metals contribute one valence electron for metallic bonding and Group II metals only contribute two. For transition metals, both the 3d and 4s electrons are involved in metallic bonding (this is because the energy level difference between 3d and 4s orbitals is small).
- Furthermore, transition metal ions have higher charge density than those of s-block metals.
- With more valence electrons involved in metallic bonding and a higher charge density of the transition metal ions, metallic bond formed between the transition metal cations and the 'sea of delocalised electrons' is much stronger compared to that of the s-block metals.



2.5 Density

There is a gradual increase in density from Sc to Cu due to a considerable increase in relative atomic mass and slight decrease in atomic radii.

The transition elements are generally much denser than s-block elements in the same period.

Explanation:

- The transition metal atoms have greater mass than that of s-block elements in the same period.
- Their atoms have relatively smaller atomic radii.
- Thus, transition elements have more closely packed structures.
- This results in transition metals having higher density than s-block elements.

2.6 Electrical conductivity

The number of electrons contributed to the sea of delocalised electrons from the 3d and 4s orbitals of the transition element is higher (than s-block elements), hence transition elements are better conductors of electricity.

Quick Check 2

- 1 The following data refer to copper as a typical transition element and to calcium as an s-block element. For which property are the data under the correct element? [J1996/III/16]

	<i>property</i>	<i>Copper</i>	<i>Calcium</i>
A	density / g cm ⁻³	8.92	1.54
B	electrical conductivity / relative units	9.6	85
C	melting point / °C	810	1083
D	metallic radius / nm	0.197	0.117

3 Chemical properties of transition elements

Transition metals show similarity in their chemical properties. Some of these properties are as follows:

- they exhibit variable oxidation states,
- they have a strong tendency to form complexes,
- they form coloured compounds and ions,
- the elements and their compounds are good catalysts.

3.1 Variable oxidation states

- Transition metals have variable oxidation states due to the small energy difference between the 3d and 4s orbitals.
- This **close similarity** in energy means that both 3d and 4s electrons can behave as **valence** electrons and are available for bond formation.
- Thus, different number of 3d and 4s electrons may be lost to form stable ions or compounds of different oxidation states and of approximately equal stability.

Example:

Fe: Fe^{2+} , Fe^{3+}

Mn: Mn^{2+} , MnO_2 , MnO_4^-

- Unlike transition metals, the s-block elements are limited to oxidation states of +1 (Group I) or +2 (Group II).
 - This is because once the outermost electrons in the s orbital are removed; a stable noble gas configuration is obtained and subsequent removal of electrons involves the inner shell electrons, which are closer to the nucleus and more tightly held. Due to the large amount of energy required, ionisation is not favourable.
 - This can be illustrated by comparing the successive ionisation energies of calcium and vanadium.

Element	Electronic Configuration	1 st IE / kJ mol^{-1}	2 nd IE / kJ mol^{-1}	3 rd IE / kJ mol^{-1}	4 th IE / kJ mol^{-1}
Ca	$[\text{Ar}] 4s^2$	590	1150	4940	6480
V	$[\text{Ar}] 3d^3 4s^2$	648	1370	2870	4600

- The known oxidation numbers of the elements from Sc to Zn. Those highlighted represent the oxidation numbers considered to be of the greatest relevance for our study, although they are not necessarily common or stable.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+1	+1	+1	+1	+1	+1	+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

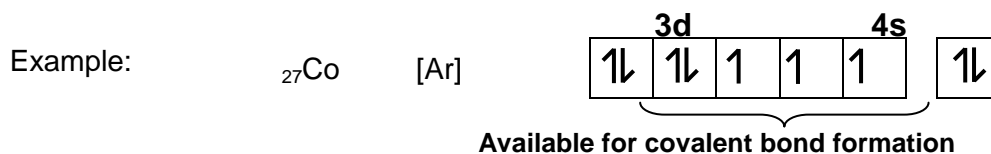
Fig. 10 Oxidation states of d-block elements

General trends in the oxidation states of transition elements

1. Sc only has one oxidation state of +3 in its compounds.
2. From Ti to Mn
 - There is an increase in number of oxidation states.
 - Maximum oxidation state increases, with Mn having the highest oxidation state of +7. Note that the **maximum** oxidation state corresponds to the sum of unpaired 3d and 4s electrons (all unpaired 3d and 4s electrons can be used in bonding to form stable ions or oxo-anions).

3. From Mn to Cu

- There is a decrease in number of oxidation states. Pairing of d electrons will occur in the element's configuration after manganese (Hund's rule) and the decrease in the number of oxidation states exhibited by elements with more than five d electrons reflects the decreased number of unpaired d electrons available for covalent bond formation.



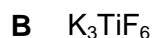
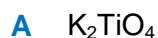
4. Zn only has one oxidation state of +2 in its compounds.
5. All except Sc show +2 oxidation state.
6. All except Zn show +3 oxidation state.
7. The lower oxidation states are usually found in predominantly ionic compounds.
8. Higher oxidation states are found in compounds which are predominantly covalent e.g. TiCl_4 , V_2O_5 , or those that contain covalently bonded ions (oxo-anions) e.g. CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- .

The hypothetical cation e.g. $\text{Cr}^{6+}(\text{aq})$ and $\text{Mn}^{7+}(\text{aq})$ ion do **NOT** exist but instead they exist as oxo-anions, $\text{CrO}_4^{2-}(\text{aq})$ and MnO_4^- . This is because:

- extremely high ionisation energies are required to form these cations
 - in aqueous solution, the extremely high charge density of the 'hypothetical cations' Cr^{6+} and Mn^{7+} would polarise the coordinated H_2O molecules extensively to give CrO_4^{2-} and MnO_4^- .
9. The oxides of transition elements with
 - low oxidation states are usually ionic and basic e.g. MnO ,
 - high oxidation states are usually covalent and acidic e.g. Mn_2O_7 ,
 - intermediate oxidation states are usually amphoteric e.g. Cr_2O_3 .

Quick Check 3

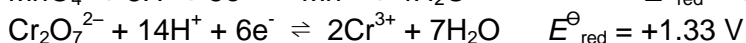
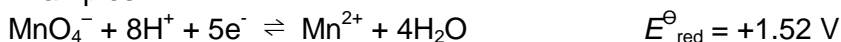
- 1 Titanium has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$. Which titanium compound is **unlikely** to exist? [N1992/IV/20]



3.2 Transition metal and their ions in redox systems

- Oxo-anions of transition elements with higher oxidation states tend to have oxidising properties (indicated by their highly positive E^\ominus_{red} values) and are used as **oxidising agents**, such as MnO_4^- .

Examples:

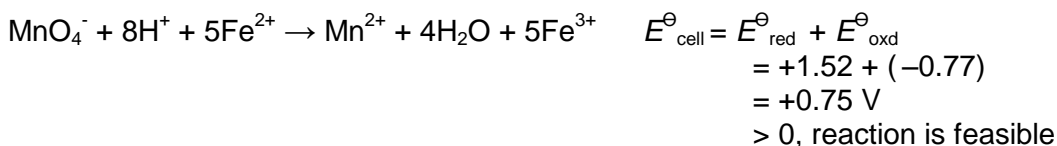


- The larger the E^\ominus_{red} value, the more likely the reduction is to take place.
- Transition metal elements tend to have reducing properties; i.e. they are likely to be reducing reagents as indicated by their negative E^\ominus_{red} values.

Examples:



- The more positive the E^\ominus_{ox} value, the more likely the transition metal will be oxidised, thus the transition metal will be a better reducing agent.
- The reducing ability of the metals tends to decrease across the first row transition elements as the increased nuclear charge makes it more difficult for the removal of valence electrons
- Example:
Oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ by acidified potassium manganate(VII)



In presence of strong oxidising agents, e.g. $MnO_4^-(aq)$, Fe^{2+} will be oxidised to Fe^{3+} .

3.3 Complex formation

3.3.1 Complex and ligands

- A **complex** consists of a central metal atom / ion dative bonded to surrounding anions or molecules called ligands.

Example: $\text{Fe}^{2+}(\text{aq})$ actually exists as a cationic complex, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

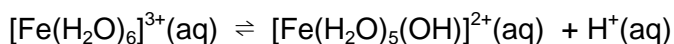
- A **ligand** is an anion or neutral molecule, which processes at least 1 lone pair of electrons. Examples of ligands: H_2O :, :NH_3 , :Cl^- , :CN^- . The ligands form co-ordinate (dative) bonds with the empty orbitals of the transition metal ions (or atom).
- Transition metal ions show a strong tendency for complex ion formation because the metal cations have incomplete d-subshell (can accept lone pair of electrons from ligands). As they are relatively small in size and highly charged; \therefore have high polarising power, they have high tendency towards covalent bond formation with ligands.

Points to note:

- In aqueous solution, most transition metal cations form complex ions of the type $[\text{M}(\text{H}_2\text{O})_6]^{n+}$, which is **octahedral** in shape.

Example:	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
Colour	Pale green	Yellow-brown	Green

- Due to the high charge density on some of the central metal cations, the aqua complexes can undergo hydrolysis, producing an acidic solution. Aqueous solutions of Fe^{3+} and Cr^{3+} are acidic.



3.3.2 Types of complex

- A complex may be classified as neutral, cationic or anionic depending on the net charge.
Net charge on the complex = sum of charges of the metal cation and ligands.
- The 'charge' on the central transition metal cation or atom is the oxidation number of the transition metal in the complex

Examples	Oxidation no of metal cation	Charge of ligand	Net Charge	Complex
$[\text{Ag}(\text{NH}_3)_2]^+$	Ag = +1	$\text{NH}_3 = 0$	$1 + 2(0) = 1+$	Cationic
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Cu = +2	$\text{H}_2\text{O} = 0$	$2 + 6(0) = 2+$	
$\text{Ni}(\text{CO})_4$	Ni = 0	$\text{CO} = 0$	$0 + 4(0) = 0$	Neutral
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe = +2	$\text{CN}^- = -1$	$2 + 6(-1) = 4-$	Anionic
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe = +3		$3 + 6(-1) = 3-$	
$[\text{CuCl}_4]^{2-}$	Cu = +2	$\text{Cl}^- = -1$	$2 + 4(-1) = 2-$	

Fig. 11 Type of complexes

3.3.3 Types of ligands

- The type of ligands can be classified by the number of lone pairs of electrons each ligand donates to form coordinate bonds with the central metal ion or atom.

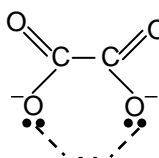
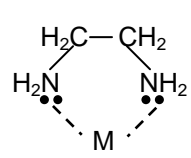
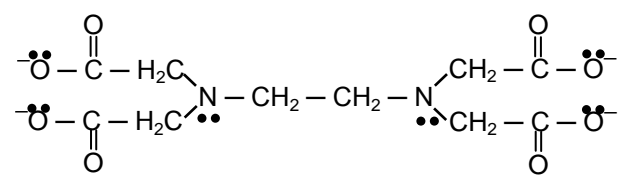
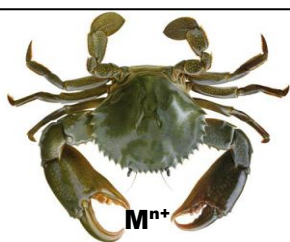
Type of Ligand	No of Co-ordinate Bonds	Examples
Monodentate	One	$\ddot{\text{N}}\text{H}_3$, $\ddot{\text{C}}\text{I}^-$, $\text{H}_2\ddot{\text{O}}$, $\ddot{\text{C}}\text{N}^-$
Bidentate	Two	  ethanedioate ethylenediamine (en)
Tridentate	Three	$\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ diethylenetriamine
Hexadentate	Six	 ethylenediaminetetraacetate (edta^{4-})

Fig. 12 Type of ligands

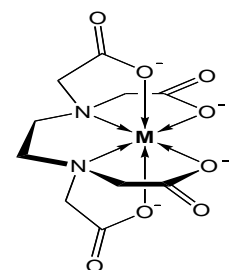
- Polydentate ligands are sometimes called **chelating agents** because of their ability to hold a metal ion like a claw. Chelating ligands form more stable complex ion with the central metal ion as the pincer-like grip of these polydentate ligands are able to hold or “grip” the cation more securely.



Chelation therapy

Chelation (from the Greek word, *chelè*, meaning a crab's claw) is the binding of a bi- or multidentate ligand.

In the field of medicine, chelating agents (e.g. EDTA) are administered as a treatment for toxic heavy metal poisoning (such as lead, mercury and cadmium) by converting them into a chemically inert form that can be excreted without further interaction with the body. This trapping of metal ions is called **sequestering**.



Metal-EDTA chelate

3.3.4 Co-ordination number and geometry of the complexes

- **Coordination number** refers to the total number of co-ordinate bonds from the ligands to the central transition metal atom or ion in the complex.

Note: Coordination number of a complex may not equal the number of ligands in the complex. E.g. $[\text{Cu}(\text{edta})]^{2-}$ only has 1 ligand but the coordination number is 6.

- Coordination numbers of 2, 4 and 6 are very commonly found in the complexes of the d-block elements.

Coordination number	2	4	4	6
Shape	Linear	Square Planar	Tetrahedral	Octahedral
Examples of Complex Ions	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{CuCl}_2]^-$ $[\text{Cu}(\text{CN})_2]^-$	$[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{2+}$	$\text{Ni}(\text{CO})_4$ $[\text{Zn}(\text{NH}_3)_4]^{2+}$ $[\text{Zn}(\text{CN})_4]^{2-}$ $[\text{CuCl}_4]^{2-}$ $[\text{CoCl}_4]^{2-}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$ $[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ $[\text{Cu}(\text{edta})]^{2-}$

Fig. 13 Examples of complexes with coordination numbers: 2, 4 and 6

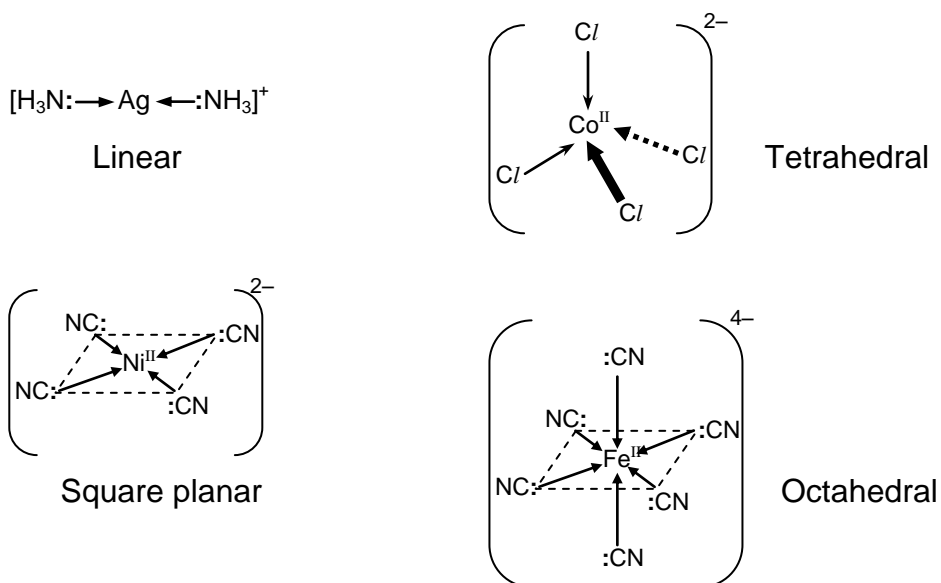


Fig. 14 Common geometries of complexes

3.3.5 Naming of metal complexes

The systematic name of a complex is obtained by following the sequence:

1. Name the ligand from anionic to neutral (if there is more than one type of ligands) followed by the name of central metal.
2. When more than one ligand of a particular kind is present, the Greek prefixes: di-, tri-, tetra-, penta- and hexa- are used to show the number of ligands present for a given type.
3. The name of anionic ligands ends with the letter o; whereas a neutral ligand is usually called by the name of the molecules with the exceptions of H_2O , CO and NH_3 .

Ligand	Type of Ligand	Name
H_2O	Neutral	aqua
CO		carbonyl
NH_3		ammine
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$		ethylenediamine (en)
CN^-	Anionic	cyano
Cl^-		chloro
OH^-		hydroxo
O^{2-}		oxo

4. The oxidation state of the metal is written in Roman numeral in parentheses following the name of the metal.
5. If the complex is **anionic** (net charge < 0), the suffix – **ate** follows the name of the metal, e.g. **zincate** and **chromate**. If the metal has a Latin name, then the Latin name of the metal is used, followed by the suffix – **ate**.

Element	Name in Anionic Complexes
Ti	titanate
V	vanadate
Cr	chromate
Mn	manganate
Fe	ferrate(II) or ferrate(III)
Co	cobaltate
Ni	nickelate
Cu	cuprate
Zn	zincate
Ag	argenate

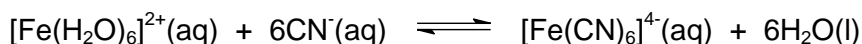
Example

Complete the following table using the rules above

Formula of Complex	No. of Ligands	Name of Ligands	Name of Metal Ion	Oxidation State	Co-ordination Number
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	hexa	aqua	chromium	(III)	6
$[\text{NiCl}_4]^{2-}$	tetra	chloro	nickelate	(II)	4
$[\text{Ni}(\text{CN})_4]^{2-}$	tetra	cyano	nickelate	(II)	4
$[\text{Ag}(\text{NH}_3)_2]^+$	di	ammine	silver	(I)	2
$[\text{Fe}(\text{CN})_6]^{4-}$	hexa	cyano	ferrate	(II)	6
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	tetraammine	di chloro	cobalt	(III)	6

3.3.6 Ligand exchange reactions

- In general, formation of ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ in aqueous solution involves the displacement of water molecules from the aqua complex, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, by the CN^- ligands.
- This is an example of a **ligand exchange reaction**, the substitution of one ligand by another:



- Sometimes, not all of the ligands undergo substitution, for example:



blue solution

dark blue solution

⇒ In general, a stronger ligand will replace a weaker ligand in a metal complex in solution.

⇒ Ligand strength refers to how strongly a ligand coordinates to the metal cation and resists replacement by another ligand.

⇒ For common ligands, an approximate order of **ligand strength** is as follows:



3.3.7 Ligand exchange in biological system

- Haemoglobin in blood contains iron in +2 oxidation state, Fe^{2+} , which is hexa-coordinated. (i.e. Fe^{2+} forms 6 coordinate bonds)
- The Fe^{2+} ion is part of a complex giant molecule called a haem group.
- The haem group contains 4 nitrogen atoms which act as ligands bonding to the four sites of Fe^{2+} .
- The fifth site is occupied by a nitrogen ligand from protein.
- In the lungs where O_2 concentration is high, O_2 molecules occupies the last site on Fe^{2+} to form oxyhaemoglobin.
- This O_2 molecule is **reversibly** bonded to Fe^{2+} .
- O_2 in the form of oxyhaemoglobin is transported to the tissues where O_2 is released to the tissue.
- Once released, the last site on Fe^{2+} is occupied by H_2O ligand.
- Hence, haemoglobin acts as an oxygen carrier.

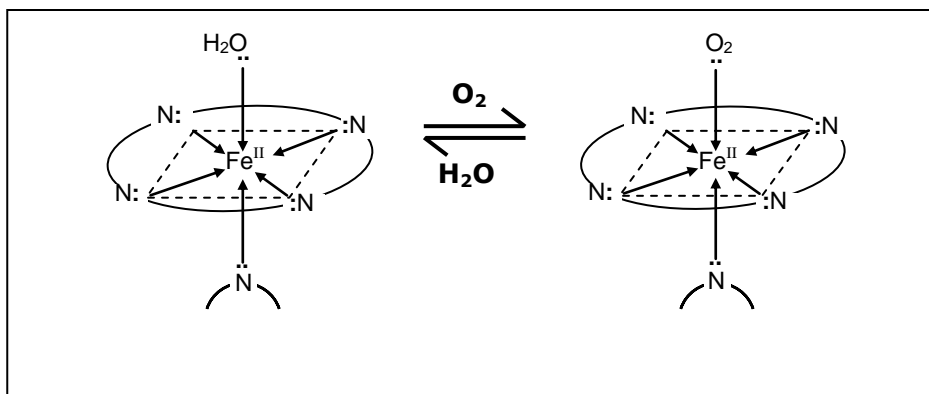


Fig. 15 Coordination of oxygen molecule to iron(II) of haemoglobin

▪ Toxicity of cyanide, CN^- and carbon monoxide

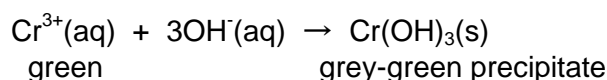
In the blood stream, CN^- and CO are strong ligands, i.e. they bind **strongly and irreversibly** to Fe^{2+} , forming very stable complexes. This prevents haemoglobin from taking up O_2 which explains the toxic nature of CN^- and CO.

3.4 Reactions involving ions of d-block elements

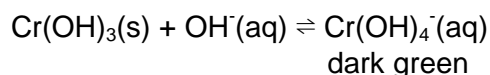
Reactions of $\text{Cr}^{3+}(\text{aq})$

▪ Reaction with $\text{NaOH}(\text{aq})$

Type of reaction: precipitation followed by complex ion formation



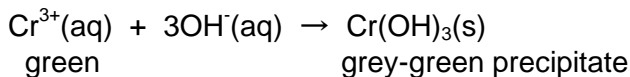
Grey-green precipitate is observed. Precipitate is soluble in excess $\text{NaOH}(\text{aq})$ to give a dark green solution due to the formation of $\text{Cr}(\text{OH})_4^-$ ion.



- **Reaction with $\text{NH}_3(\text{aq})$**

Aqueous ammonia, a weak base, is a source of hydroxide ions OH^- :
 $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

Type of reaction: precipitation

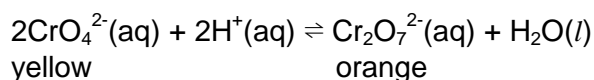


Grey-green precipitate is observed. Precipitate is insoluble in excess $\text{NH}_3(\text{aq})$.

Reactions of $\text{CrO}_4^{2-}(\text{aq})$

- **Reaction with acid (e.g. H_2SO_4) / alkali (e.g. NaOH)**

Type of reaction: acid-base / condensation



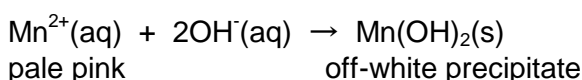
When an aqueous acid solution is added to the yellow solution of CrO_4^{2-} , the solution turns orange. This is because the increase in $[\text{H}^+]$ shifts equilibrium to the right, forming $\text{Cr}_2\text{O}_7^{2-}$.

The addition of alkali (e.g. NaOH) to an orange solution of $\text{Cr}_2\text{O}_7^{2-}$ will cause it to turn yellow as the OH^- reacts with the H^+ , causing the $[\text{H}^+]$ to decrease. This shifts the equilibrium to the left, forming CrO_4^{2-} .

Reactions of $\text{Mn}^{2+}(\text{aq})$

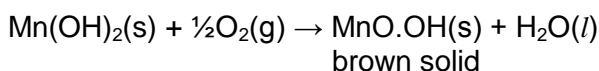
- **Reaction with $\text{NaOH}(\text{aq})$**

Type of reaction: precipitation



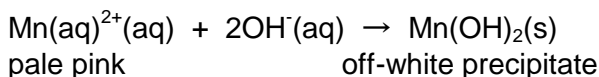
Off-white precipitate is observed. Precipitate is insoluble in excess $\text{NaOH}(\text{aq})$. Precipitate turns brown on standing in air due to the oxidation to form MnO.OH .

Type of reaction: redox



- **Reaction with $\text{NH}_3(\text{aq})$**

Type of reaction: precipitation

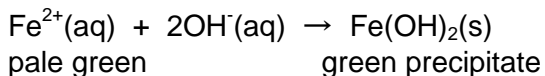


Green precipitate is observed. Precipitate is insoluble in excess $\text{NH}_3(\text{aq})$. Precipitate turns brown on standing in air due to the oxidation to form MnO.OH .

Reactions of Fe²⁺(aq)

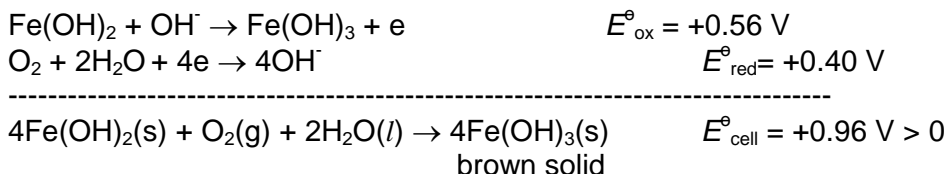
▪ Reaction with NaOH(aq)

Type of reaction: precipitation



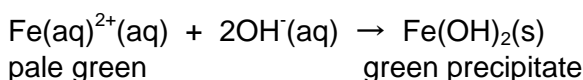
Green precipitate is observed. Precipitate is insoluble in excess NaOH(aq). Precipitate turns brown on standing in air due to the oxidation by air to form Fe(OH)₃.

Type of reaction: redox



▪ Reaction with NH₃(aq)

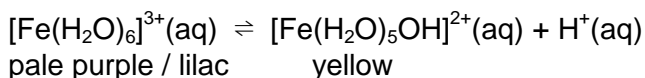
Type of reaction: precipitation



Green precipitate is observed. Precipitate is insoluble in excess NH₃(aq). Precipitate turns brown on standing in air due to the oxidation by air to form Fe(OH)₃.

Reactions of Fe³⁺(aq)

Due to the high charge density of Fe³⁺ (similar to Al³⁺), it is able to polarise the coordinated water molecules, weaken the O-H bond and cause H⁺ to be released. Therefore, an aqueous solution of Fe³⁺ is acidic.

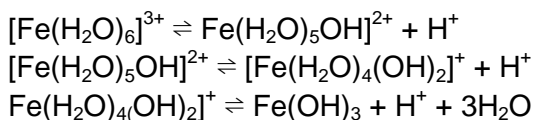


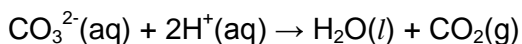
Due to the hydrolysis, an aqueous solution of Fe³⁺ is yellow in colour. When an aqueous solution of acid (e.g. HNO₃) is added, position of equilibrium shifts to the left and a pale purple solution is observed.

▪ Reaction with Na₂CO₃(aq)

Upon addition of Na₂CO₃(aq), effervescence (due to CO₂ evolved) is observed and a brown precipitate of Fe(OH)₃ is formed.

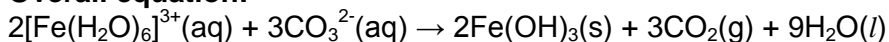
Type of reaction: acid-base and precipitation





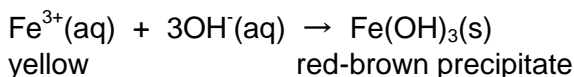
The H^+ from the hydrolysis reacts with CO_3^{2-} to form CO_2 and H_2O . This reduces the concentration of H^+ and promotes further hydrolysis to take place. Eventually, a red-brown precipitate of $\text{Fe}(\text{OH})_3$ is formed.

Overall equation:



▪ **Reaction with $\text{NaOH}(\text{aq})$**

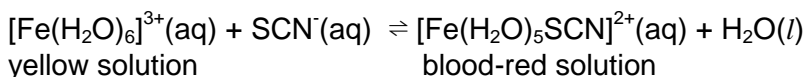
Type of reaction: precipitation



Red-brown precipitate is observed. Precipitate is insoluble in excess $\text{NaOH}(\text{aq})$.

▪ **Reaction with $\text{NH}_4\text{SCN}(\text{aq})$**

Type of reaction: ligand exchange

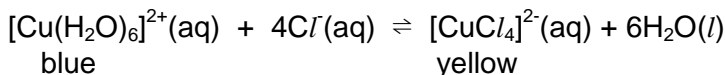


Yellow solution turns blood-red.

Reactions of $\text{Cu}^{2+}(\text{aq})$

▪ **Reaction with concentrated HCl**

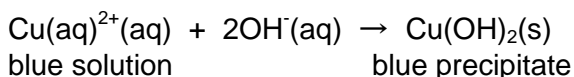
Type of reaction: ligand exchange



The blue solution turns green due to the presence of both $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and CuCl_4^{2-} .

▪ **Reaction with $\text{NaOH}(\text{aq})$**

Type of reaction: precipitation

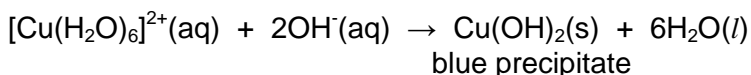


Blue precipitate is observed. Precipitate is insoluble in excess $\text{NaOH}(\text{aq})$.

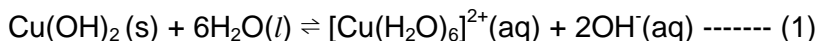
▪ **Reaction with $\text{NH}_3(\text{aq})$**

Type of reaction: precipitation followed by complex ion formation

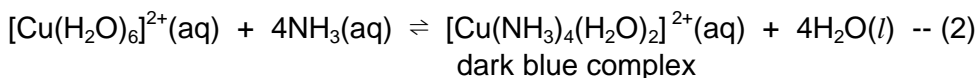
When $\text{NH}_3(\text{aq})$ is first added to the blue solution $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$, a blue precipitate of $\text{Cu}(\text{OH})_2$ forms at first:



The blue precipitate $\text{Cu}(\text{OH})_2$ dissolves slightly in water, to give $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and OH^- .



When **excess** $\text{NH}_3(\text{aq})$ is added to the blue precipitate $\text{Cu}(\text{OH})_2$, the ammonia ligands displace the H_2O ligands in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to form the deep blue complex $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

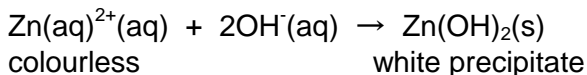


The formation of the stable $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex in (2) causes the concentration of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to decrease. By Le Chatelier's principle, equilibrium (1) will shift to the right to counteract the change. Thus, the blue precipitate of $\text{Cu}(\text{OH})_2$ dissolves.

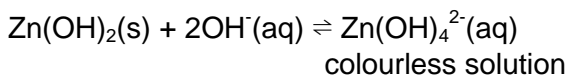
Reactions of $\text{Zn}^{2+}(\text{aq})$

▪ **Reaction with $\text{NaOH}(\text{aq})$**

Type of reaction: precipitation followed by complex ion formation

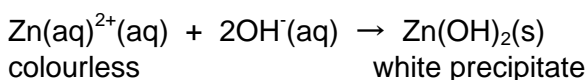


White precipitate is observed. Precipitate is soluble in excess $\text{NaOH}(\text{aq})$ to give a colourless solution due to the formation of $\text{Zn}(\text{OH})_4^{2-}(\text{aq})$.

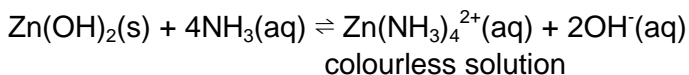


▪ **Reaction with $\text{NH}_3(\text{aq})$**

Type of reaction: precipitation followed by complex ion formation



White precipitate is observed. Precipitate is soluble in excess $\text{NH}_3(\text{aq})$ to give a colourless solution due to the formation of $\text{Zn}(\text{NH}_3)_4^{2+}(\text{aq})$.



3.5 Formation of coloured compounds and ions

- Transition metal compounds are usually coloured both in the solid and aqueous states.
- The colour of transition element compounds is due to the **selective absorption** of light in the visible region of the electromagnetic spectrum.

3.5.1 d-orbital splitting in an octahedral complex

- In an isolated gaseous transition metal ion M^{n+} , all the five d-orbitals of a gaseous transition metal ion are degenerate (having the same energy).
- In complexes, the five 3d orbitals are split into two sets of different energy levels as the electrons in the d-orbitals experience different extent of electrostatic repulsion by the electron pair of the coordinated ligands. This is known as **d-orbital splitting**.
- In **octahedral** complexes, the lone pairs of the six ligands will approach the central metal atom or ion along the three x, y, and z axes. The energy level of any electron in all the d-orbitals would be higher than that in a gaseous atom as a result of electrostatic repulsion by the electron pairs of the incoming ligands. However, the energy level of an electron in the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals will be raised by a greater extent since it experiences **stronger inter-electronic repulsion** arising as a result of the direct interaction with the ligand's lone pair of electrons.

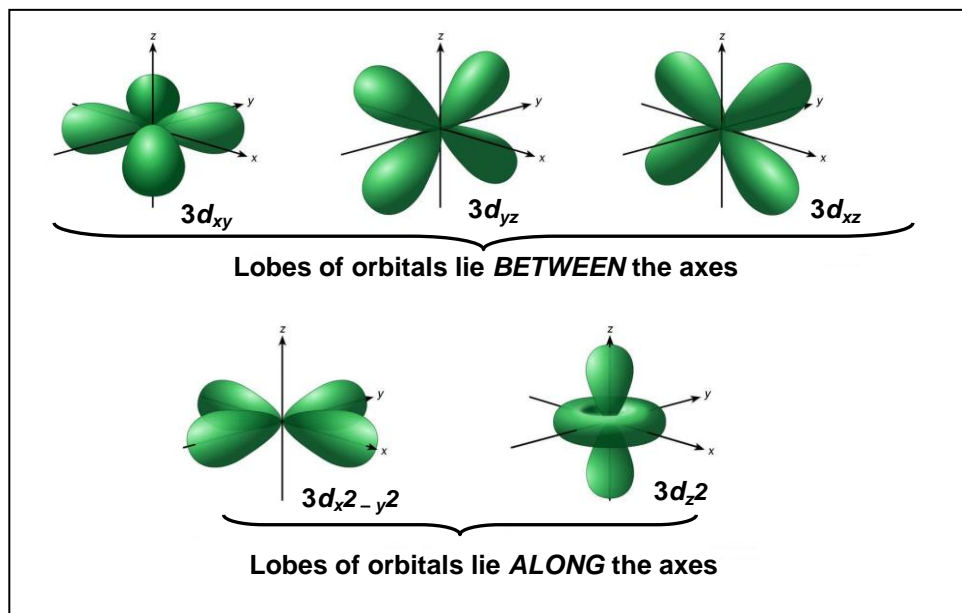


Fig. 16 Arrangement of the 3d-orbitals along the different axes

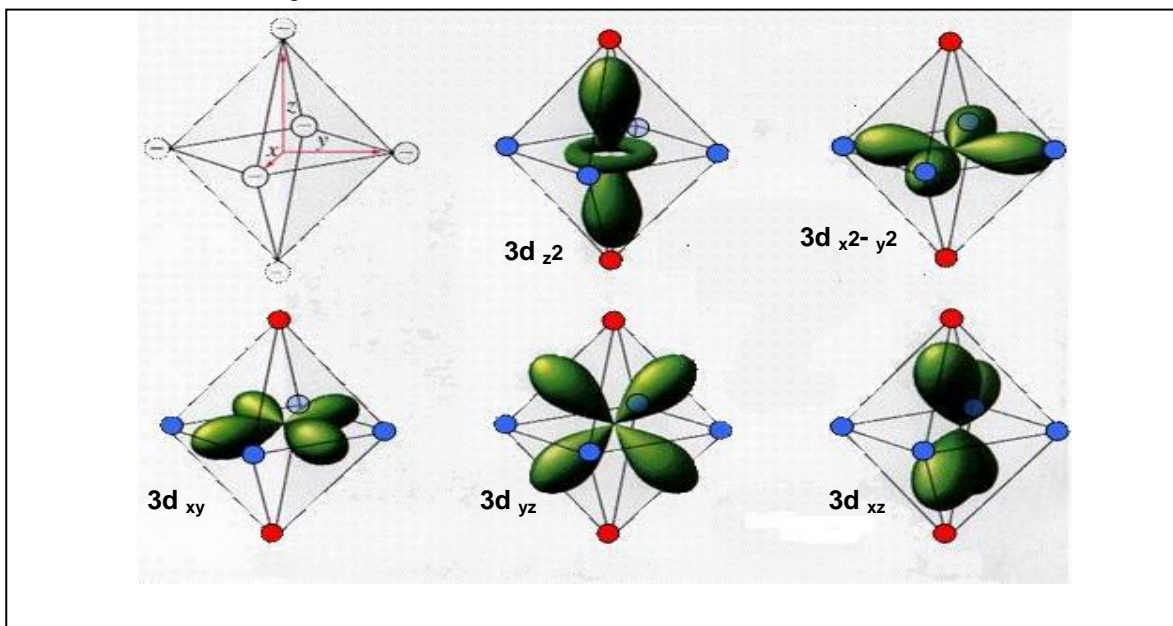


Fig. 17 Electronic repulsion in octahedral complexes

- Hence the five 3d-orbitals are split into two energy levels as shown below in Fig. 18. The difference in energy between the two energy levels, ΔE , is known as the crystal field splitting energy

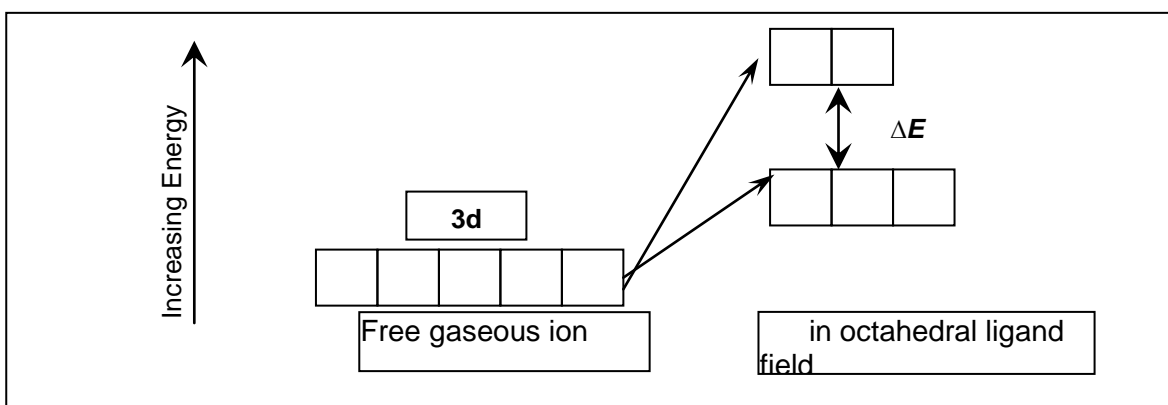


Fig. 18 d-splitting in octahedral complexes

3.5.2 d-orbital splitting in tetrahedral complex

- In tetrahedral complexes, the situation is reversed. The four ligands in these complexes will approach the central metal atom or ion in between the axes. Electrons in the $3d_{xy}$, $3d_{yz}$, and $3d_{xz}$ orbitals now experience greater electrostatic repulsion from the ligands' lone pairs. As a result, the $3d_{xy}$, $3d_{yz}$, and $3d_{xz}$ orbitals are of higher energy than the $3d_{x^2-y^2}$ and $3d_z^2$ orbitals.

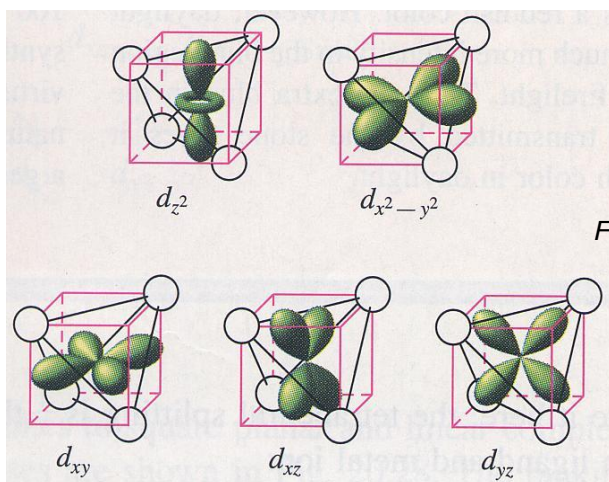
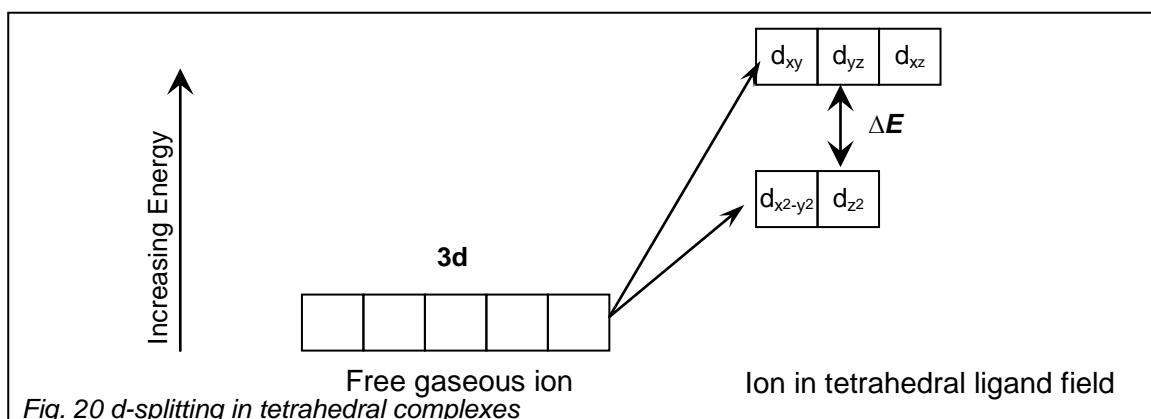


Fig. 19 Electronic repulsion in tetrahedral complexes



3.5.3 d-to-d electronic transition

- In sections 3.4.1 and 3.4.2, you have learnt how the five 3d orbitals are split into 2 sets having different energy for both octahedral and tetrahedral complexes.
- As the energy difference corresponds to the energy of the visible region of the electromagnetic spectrum, transition metal complexes can absorb the light, causing an electron to be promoted from the lower energy d-orbital to a vacant / half-filled higher energy d-orbital. Such transition is known as **d-to-d transitions**.
- As the energy from one part of the spectrum is absorbed, a colour which is the complement of the colours absorbed will be observed. E.g. A solution of Cu^{2+} appears blue because light energy is absorbed in the orange wavelengths while the blue is unabsorbed. \therefore It appears blue.

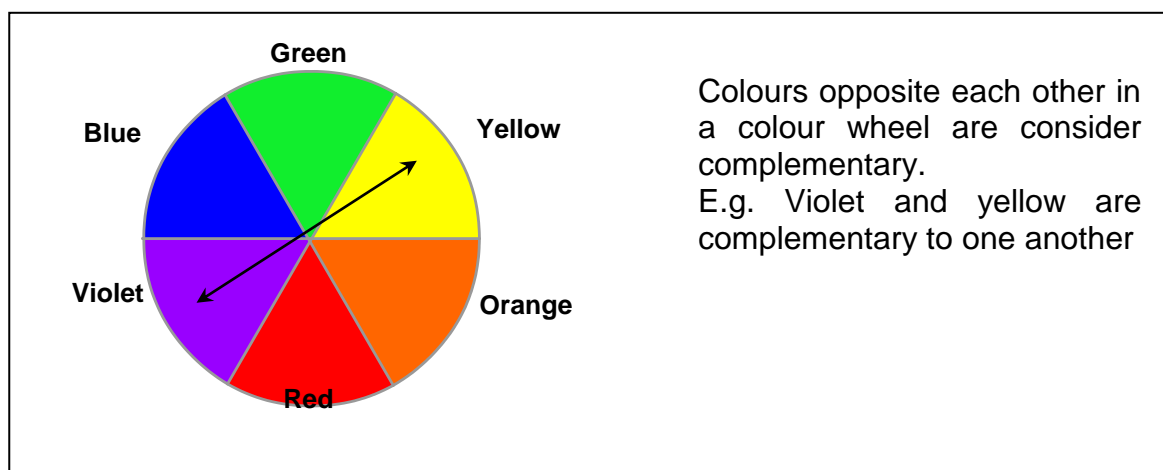


Fig. 21 Colour wheel

Quick Check 4

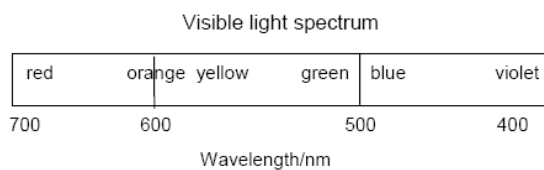
The complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ absorbs light primarily in the red region of the visible spectrum. What is the colour of the complex?

Answer: green

Quick Check 5

The complex ion $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ has an absorption band at about 630 nm. What is the colour of the complex?

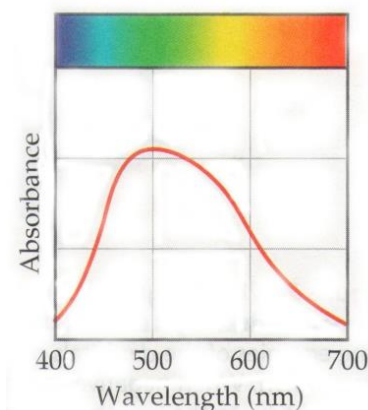
Answer: blue



Quick Check 6

Based on the absorption spectrum, what is the colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$?

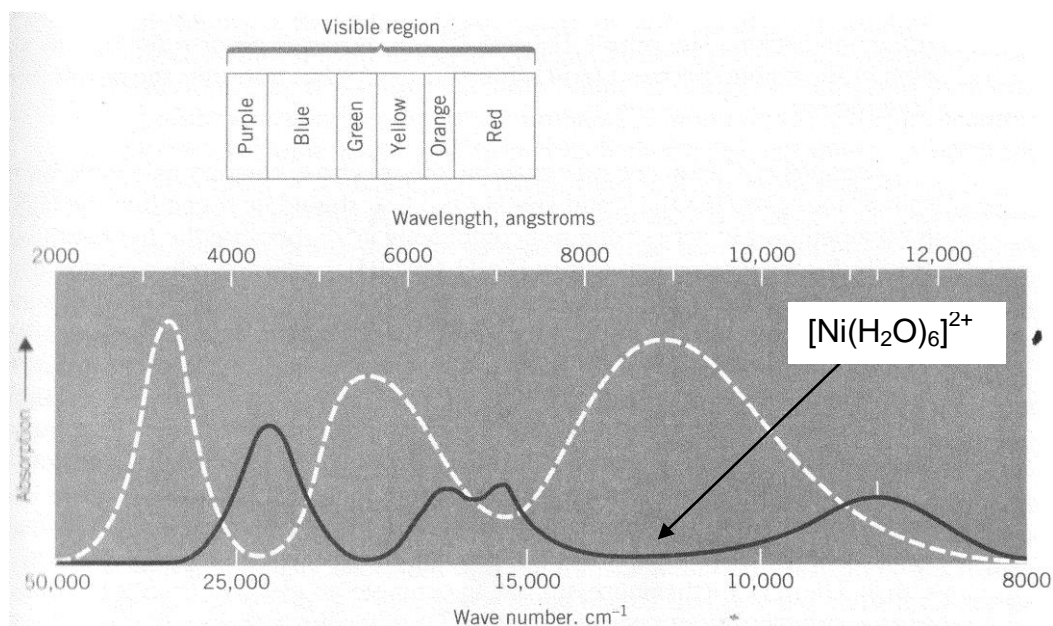
Answer: red-violet



Quick-check 7

Based on the absorption spectrum, what is $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$?

the colour of



Answer: green

3.5.4 Factors affecting colour of complexes

The colour of complexes depends on the energy difference, ΔE between the two sets of d-orbitals. This energy difference in turn is affected by:

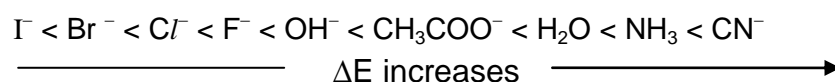
(a) Nature of ligand

Different ligands have different capacities of splitting the d-orbitals of a particular transition metal

E.g. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ vs $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq})$
blue yellow-orange

The larger the ΔE , the higher the frequency of light absorbed and the lower the wavelengths absorbed, the longer the wavelengths observed.

For a given transition metal cation, the **ligand field strength** is shown below.



Note: Do not confuse ligand strength (page 23) with ligand field strength.

(b) Oxidation state of the cation

Example: $\text{Cr}^{2+}(\text{aq})$ is blue while $\text{Cr}^{3+}(\text{aq})$ is violet.

Different number of electrons in the d-orbitals of the transition metal ion will result in different interactions with the electrons from the ligands. This gives rise to different energy gap, ΔE , thus wavelengths of light absorbed will be different.

Points to note:

- Apart from d-to-d transitions, colour of some transition metal ions / compounds can be explained in terms charge transfer (an electron from one of the atoms of the bond is excited to a higher energy level) e.g. intense purple colour of MnO_4^- .
- In order to absorb light in the first place, the metal ions has to contain at least one electron in the d-orbital and also a higher energy d-orbital that is not completely filled. The absence of colour (white or colourless) is due to the fact that they either have no d electrons e.g. $\text{Sc}(\text{III})$ or have a d^{10} arrangement e.g. $\text{Cu}(\text{I})$ and $\text{Zn}(\text{II})$. In either case, no d-d transition is possible.

3.6 Catalytic activity

- Transition elements and their compounds are effective and important catalysts.
- A catalyst increases the rate of reaction by providing an alternative pathway for the reaction with lower activation energy, E_a (without itself undergoing any permanent chemical change).
- There are two types of catalysts:
 - (a) Heterogeneous catalyst – the catalyst and reactants are in **different** physical states.
 - (b) Homogeneous catalyst – the catalyst and reactants are in **same** physical states.

3.6.1 Heterogeneous catalyst

- First row transition elements and their compounds are heterogeneous catalysts in many reactions because of the partially filled 3d orbitals, which allow reactant molecules to be readily adsorbed onto the surface of the catalyst.
- Adsorption involves formation of weak bonds between the reactants and atoms on the surface of the catalyst.
- The partially filled 3d-orbitals have 2 possible effects:
 - Availability of 3d electrons for donation to reactant molecules.
 - Availability of vacant orbitals which can accept electron pairs from reactant molecules
- In either case, the formation of weak bonds between the reactant particles and the catalyst surface (adsorption) increases the rate of reaction as shown in Fig 22.

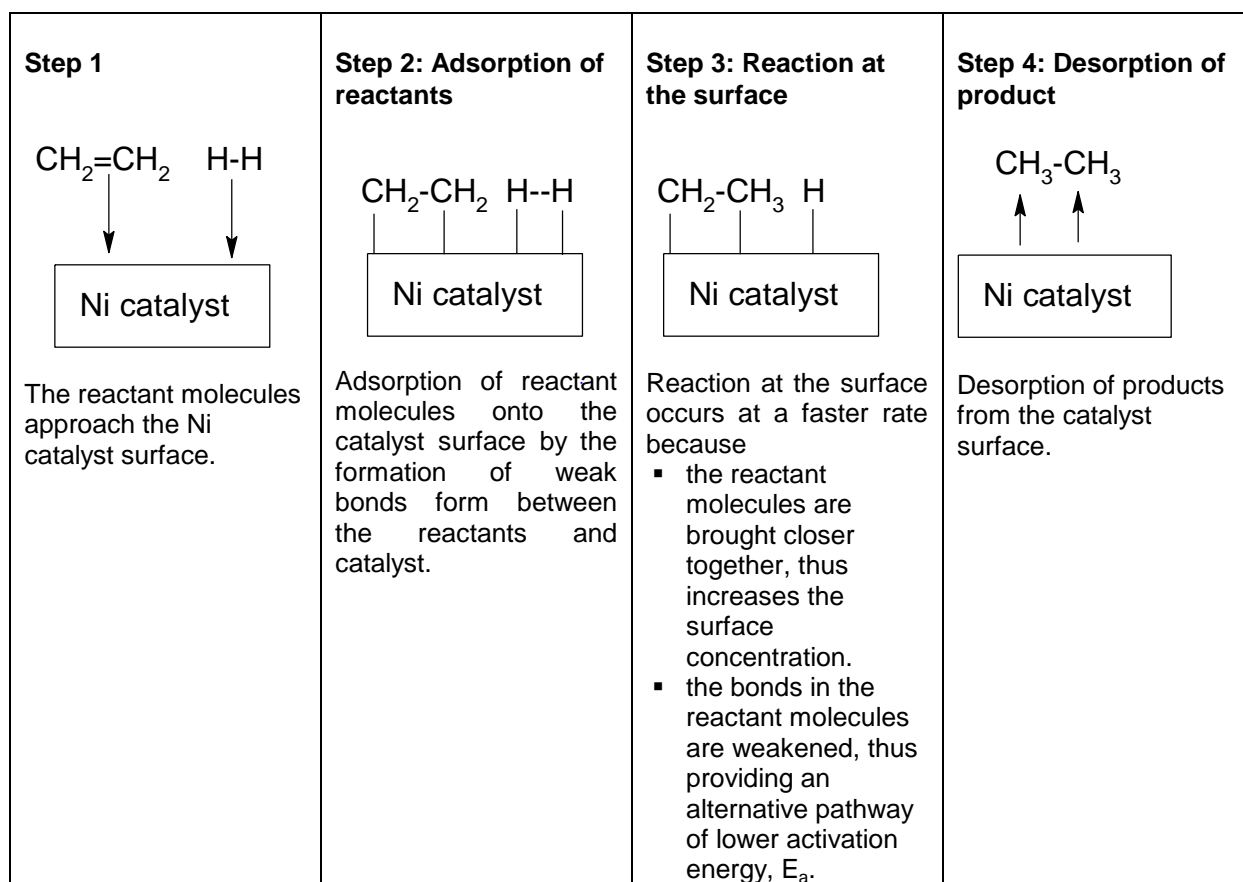
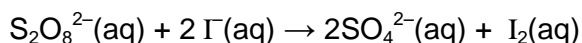


Fig. 22 Steps involved in heterogeneous catalysis

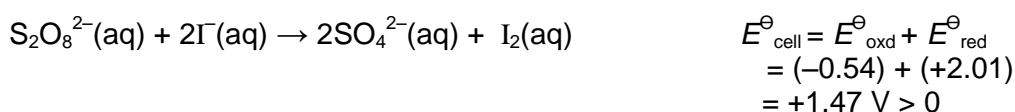
- Other examples of the heterogeneous catalysts:
 - Use of Fe in Haber process
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - Use of V_2O_5 in the Contact process
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

3.6.2 Homogeneous catalyst

- Transition elements also function well as homogeneous catalysts due to their ability to exhibit variable oxidation states.
- The ease of interconversion between the different oxidation states of the transition metal ions enables them to provide an alternative reaction pathway of lower activation energy.
- Consider the oxidation of iodide, I^- by peroxodisulfate, $\text{S}_2\text{O}_8^{2-}$



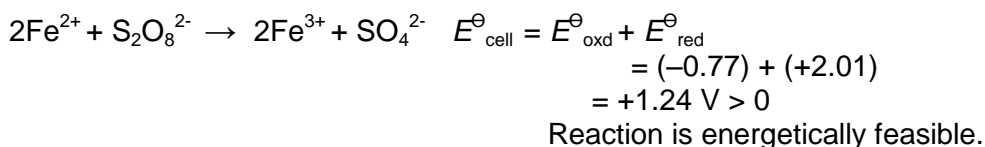
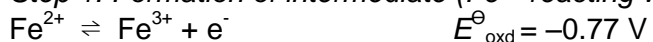
In the above reaction,



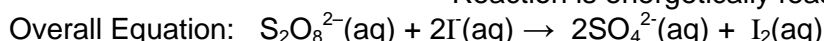
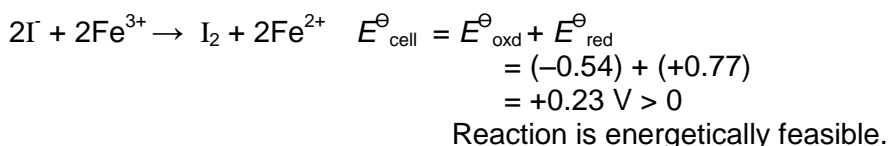
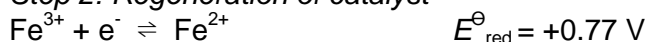
The reaction is found to have $E_{\text{cell}}^\ominus = +1.47 \text{ V}$, and is expected to take place readily. However, the rate of reaction is found to be very slow. This is due to high activation energy involving the reaction between two negatively charged ions.

- Fe^{2+} can catalyse this reaction. A possible catalysed pathway having lower activation energy with Fe^{2+} as the catalyst involves 2 steps.

Step 1: Formation of intermediate (Fe^{2+} reacting with $\text{S}_2\text{O}_8^{2-}$)



Step 2: Regeneration of catalyst



- This alternative two-step route offers a lower energy pathway as it enables the reaction between oppositely charged ions in both steps.
- Fe^{2+} can act as a catalyst as it can change its oxidation state to +3 and then revert to +2. If Fe^{3+} is used instead, the two steps above will take place in the reverse order and the overall effect will still be the same.
- Other couples involving transition metal cations could also act as catalyst for the reaction so long as their values are between +0.54 V and +2.01 V. E.g. $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$.

4 Summary

- A transition element is defined as a d-block element which forms at least one stable ion in which there is a partially filled d-subshell of electrons.
- With the exception of scandium and zinc, the elements from Ti to Cu show features of transition elements, i.e. variable oxidation states and coloured ions.
- Transition metals have high melting and boiling points (higher than that of the s-block metals) because of their stronger metallic bonds.
- The first and second ionisation energies increase only slightly from scandium to zinc because the 4s electrons that are being removed are shielded from the nuclear attraction by the inner 3d electrons.
- Most of the elements from scandium to zinc form M^{2+} ions by loss of the 4s electrons, and some form M^{3+} ions as well.
- Elements from scandium to manganese have a maximum oxidation number equal to the sum of the 3d and 4s electrons.
- A complex consists of a central metal atom / ion dative bonded to surrounding anions or molecules called ligands. Transition metals form stable complex ions because their ions have high charge density. They also have 3d orbitals of low energy that can accommodate electrons donated by the ligands.
- d-block ions with d^0 and d^{10} configurations are colourless. Other d-block ions are coloured because of d-orbital splitting and d-to-d transition.

In transition metal complexes, the presence of ligands cause the degenerate 3d orbitals of the metal atom / ion to split into 2 sets of different energy (d-orbital splitting). The energy gap corresponds to the energy of the visible region of the electromagnetic radiation. On absorbing energy from the visible light, an electron from a lower d-orbital gets promoted to a vacant / half-filled orbital of higher energy (d-to-d transition). The colour of the complex observed is complementary to the colour of the light absorbed.

- Many d-block ions act as homogeneous catalysts because of their ease of conversion from one oxidation state to the other.
- Many d-block metals / compounds act as heterogeneous catalysts because of the presence of partially filled d orbitals which allow reactant molecules to be readily adsorbed onto the surface of the catalyst. Besides increasing surface concentration, bonds in the reacting particles are also weakened. Thus, providing an alternative reaction pathway of lower activation energy.