Introduction to the Chemistry of Transition Elements (A2)

- **Definition:** (transition elements = transition metals)

  D-block elements forming one or more stable ions with partially filled (incomplete) d-orbitals

  (d block elements — the elements in the Periodic Table which correspond to the d levels filling.)

- The electronic configurations of the d block elements are shown as follow, ...

Element	Atomic no.	Electronic configuration							
			3d						4S
Scandium Sc	21	[Ar]	↑						↑↓
Titanium Ti	22	[Ar]	↑	↑					↑↓
Vanadium V	23	[Ar]	↑	↑	↑				↑↓
Chromium Cr	24	[Ar]	↑	↑	↑	↑	↑	*	↑
Manganese Mn	25	[Ar]	↑	↑	↑	↑	↑		↑↓
Iron Fe	26	[Ar]	↑↓	↑	↑	↑	↑		↑↓
Cobalt Co	27	[Ar]	↑↓	↑↓	↑	↑	↑		↑↓
Nickel Ni	28	[Ar]	↑↓	↑↓	↑↓	↑	↑		↑↓
Copper Cu	29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	*	↑
Zinc Zn	30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓

(Note: 3d orbitals filling).

- Chromium and copper do not follow the pattern of filling. (chromium – seperating the electrons minimises the repulsions betwen them. Cu – completely occupied bigger sub-shell 3d is more stable.)

Scandium and Zinc are not Transition Element.

- When Scandium forms ions, it always loses the 3 outer electrons and ends up with an argon electronic configuration. Sc^{3+} ([Ar] $3d^0$)
- The Sc^{3+} ion has no d electrons and so doesnt meet the definition.
- When Zinc forms ions, it always loses the 2 4s electrons to give a 2+ ion with the electronic configuration [Ar] $3d^{10}$.
- The Zn^{2+} ion has full d levels (3d orbitals completely occupied with electrons) and doesnt meet the definition either.

Copper as a transition element/metal

- Cu forms 2 ions. Cu^+ ion [Ar] $3d^{10}$
  Cu^{2+} ion [Ar] $3d^9$
- Cu is definitely a transition element because the Cu^{2+} ion has an incomplete d orbitals.

Metallic properties

- all transition elements are metals.
- strong metallic bonds due to small ionic size and close packing.
- higher melting, boiling points and densities than s-block metals.

	T_m / °C	density/gcm^{-3}
K	63	0.86
Ca	850	1.55
Sc	1400	3.0
Ti	1677	4.5
V	1917	6.1
Cr	1903	7.2
Mn	1244	7.4
Fe	1539	7.9
Co	1495	8.9
Ni	1453	8.9
Cu	1083	8.9

Characteristic properties of transition element and their compounds

- Variable oxidation state - due to close proximity in energy level of the 4S and 3d electrons, all ions formed are equally stable.
- Formation of coloured ions - due to electron transition between d-orbitals.
- Formation of complexes - due to availability of vacant orbitals which allow forming of dative bonds with ligands.
- Catalytic activity - either by homogeneous or heterogeneous catalysis.
- Paramagnetism - due to transition elements having unpaired electrons are attracted to a magnetic field.

Transition element ions

- When the Periodic Table is being built, the 4S orbital is filled before the 3d orbitals.
- This is because in the empty atom, 4S orbitals have a lower energy than 3d orbitals.
- Once the electrons are actually in their orbitals, the energy order changes, and in all the chemistry of the transition elements, the 4S orbital behaves as the outermost, highest energy orbital.
- Remember : When d-block elements form ions,
  the 4S electrons are lost first.

- Example 1: Cobalt.

Co	$[Ar]\,3d^7 4S^2$
Co^{2+}	$[Ar]\,3d^7$

The 2+ ion is formed by the loss of the 2 4S electrons

- Example 2: Vanadium

V	$[Ar]\,3d^3 4S^2$
V^{3+}	$[Ar]\,3d^2$

The 4S electrons are lost first followed by one of the 3d electrons.

Variable oxidation states in transition elements

- is due to the small energy difference between the 4s and 3d subshells.
- Example : Iron,

	Oxidation state	
Fe^{2+}	+2	common
Fe^{3+}	+3	
ferrate(VI) ion, FeO_4^{2-}	+6	less common

- Example : Manganese,

	Oxidation state
Mn^{2+}	+2
Mn_2O_3	+3
MnO_2	+4
MnO_4^{2-}	+6
MnO_4^{-}	+7

Explaining Iron has +2 & +3 oxidation states (Magnesium has only +2)

- The first 4 successive ionisation energies ($kJ\,mol^{-1}$) for iron and magnesium are as follows:

element	first	second	third	fourth
magnesium	736	1450	7740	10500
iron	762	1560	2960	5400

- When compounds are formed, energy must be supplied to remove electrons (the sum of the various ionisation energies) from the atoms of the elements,
- The energy for this ionisation is supplied by the energy given out when the new bonds are formed. This will be lattice energy for solid compounds (hydration enthalpies of the ions for solution)
- When Mg forms compounds, Mg^{2+} ions are easily formed.
- For example, the lattice energy liberated when the Mg^{2+} and O^{2-} ions come together is easily enough to supply the ionisation energy (736 + 1450 kJ mol^{-1}) to form Mg^{2+} ions,
- However, this reaction will not supply the much larger amount of energy (7740 kJ) needed to remove the 3rd electron, which is from an inner shell. Hence Mg only forms Mg^{2+} ions and not Mg^{3+} or Mg^{4+} etc.
- When iron forms compounds, Fe^{2+} ions are easily formed – like Mg^{2+} in magnesium.
- However there is no big increase in the amount of energy required to remove the 3rd electron (from the 3d subshell) because of the small energy difference between the 4s and 3d.

- As long as enough energy is liberated in the formation of an iron(III) compound, then the 3rd electron can be removed to form Fe^{3+} ions.
- The same applies to the loss of more electrons to form higher oxidation state compounds of transition metals. There is no big jump in ionisation energy, so more electrons can be lost provided enough energy is liberated in the formation of the compound.

Oxidation States in Transition Element Compounds

- Oxidation states of the transition elements in their compounds. (Sc and Zn have been included)

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

common oxidation states for each element - circled in red.

- The closeness of energy levels between 3d and 4s subshells means the electrons from orbitals of both subshells ~~can~~ can be easily lost, so they can form different ions with almost equal stability.
- The first 5 elements (Sc → Mn), the highest oxidation states same as the total number of 4s and 3d electrons for the element.
- The second 5 elements (Fe → Zn), the highest oxidation states same as total number of unpaired 3d electrons and 4s electrons
- Example: Nickel atom,

$$\text{Nickel atom } [Ar]\ \overset{3d}{\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{\text{unreactive electron pairs}}\underbrace{\boxed{\uparrow}\boxed{\uparrow}\quad\overset{4s}{\boxed{\uparrow\downarrow}}}_{\text{can be used for bonding (4 electrons)}}}$$

- Example of common oxidation states of Iron:

$$\text{Fe atom}\quad [Ar]\ \overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \overset{4s}{\boxed{\uparrow\downarrow}}$$

$$Fe^{2+}\text{ ion}\quad [Ar]\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad \boxed{}$$

- the loss of the two 4s electrons from the outer shell. These are less strongly held by the nucleus than 3d electrons

$$Fe^{3+}\text{ ion}\quad [Ar]\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad \boxed{}$$

- the loss of the two 4s electrons and one 3d electron. The 3d electron is one of an electron pair. There is considerable repulsion between between electrons in a pair and therefore one of the pair is relatively easily removed.

- Important note: when electrons are removed the come from the 4s orbital first.

- Example: Copper,

Cu	$[Ne]\,3s^2 3p^6 3d^{10} 4s^1$
Cu^+	$[Ne]\,3s^2 3p^6 3d^{10}$
Cu^{2+}	$[Ne]\,3s^2 3p^6 3d^9$

- Example: Titanium

Ti	$[Ne]\,3s^2 3p^6 3d^2 4s^2$
Ti^{2+}	$[Ne]\,3s^2 3p^6 3d^2$
Ti^{3+}	$[Ne]\,3s^2 3p^6 3d^1$
Ti^{4+}	$[Ne]\,3s^2 3p^6$

- The lower oxidation states are usually found in ionic compounds – Cr^{3+}, Mn^{2+}; Fe^{2+}, Fe^{3+}, Cu^{2+} etc)
- Higher oxidation states occur in complex ions egs

complex ions	oxidation no.
CrO_4^{2-}	+6
$Cr_2O_7^{2-}$	+6
MnO_4^-	+7

Transition Element Ions in Redox Reactions.

$Fe^{2+}_{(aq)}/Fe^{3+}_{(aq)}$

- Solutions of $Fe^{2+}_{(aq)}$ are readily oxidised to Fe^{3+} by many oxidising agents (eg. acidified $K_2Cr_2O_7$ and atmospheric oxygen)
- The reaction with oxygen in air is summarised as follow :

$$\begin{array}{ll} O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O & E^\ominus = +1.23V \\ Fe^{2+} \longrightarrow Fe^{3+} + e^- & E^\ominus = -0.77V \\ \hline O_2 + 4H^+ + 4\underset{\text{Green}}{Fe^{2+}} \longrightarrow 2H_2O + 4\underset{\text{Brown}}{Fe^{3+}} & E^\ominus_{cell} = +0.46V \end{array}$$

- Solutions of $Fe^{3+}_{(aq)}$ are readily reduced by many reducing agents (eg. potassium iodide)
- The reaction is summarised below:

$$\begin{array}{ll} Fe^{3+} + e^- \longrightarrow Fe^{2+} & E^\ominus = +0.77V \\ 2I^- \longrightarrow I_2 + 2e^- & E^\ominus = -0.54V \\ \hline 2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2 & E^\ominus_{cell} = +0.23V \end{array}$$

$Cr_2O_7{}^{2-}{}_{(aq)} / Cr^{3+}{}_{(aq)}$

- Solutions of dichromate (VI), $Cr_2O_7{}^{2-}$ are oxidising agents.
- A solution of potassium iodide is oxidised by acidified dichromate(VI) to iodine.
- The reaction is summarised below:

$$\begin{array}{ll} Cr_2O_7{}^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O & E^\circ = +1.33V \\ 2I^- \longrightarrow I_2 + 2e^- & E^\circ = -0.54V \\ \hline Cr_2O_7{}^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2 & E^\circ_{cell} = +0.79V \end{array}$$

orange green

$MnO_4{}^-{}_{(aq)} / Mn^{2+}{}_{(aq)}$

- Solutions of manganate(VII), $MnO_4{}^-$ are oxidising agents.
- A solution of iron(II) sulfate is oxidised to iron(III) by acidified manganate (VII) ions.
- The reaction is summarised below:

$$\begin{array}{ll} Fe^{2+} \longrightarrow Fe^{3+} + e^- & E^\circ = -0.77V \\ MnO_4{}^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O & E^\circ = +1.52V \\ \hline MnO_4{}^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O & E^\circ_{cell} = +0.75V \end{array}$$

purple light brown

- Exercise:

Both acidified $KMnO_{4(aq)}$ and acidified $K_2Cr_2O_{7(aq)}$ are commonly used oxidising agents in laboratory.

(use data booklet whenever relevant)

a) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad E^\ominus = +1.52\,V$

Predict whether MnO_4^- can convert:

(i) H_2O_2 to O_2

(ii) Conc. HCl to Cl_2

b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad E^\ominus = +1.33\,V$

Predict whter $Cr_2O_7^{2-}$ can convert:

(i) Fe^{2+} to Fe^{3+}

ii) H_2O_2 to O_2