

CH A P T E R: The d-Block Elements-transition elements

- IUPAC defines the transition metals as any element with an incomplete d subshell or that may form stable ions only with an incomplete d subshell. By this definition, zinc, cadmium, and mercury are excluded from the transition metals, as they have a d^{10} configuration. Only a few transient species of these elements that leave ions with a partly filled d subshell have been formed, and mercury(I) only occurs as Hg_2^{2+} , which does not strictly form a lone ion with a partly filled subshell, and hence these three elements are inconsistent with the latter definition. They do form ions with a 2+ oxidation state, but these retain the $4d^{10}$ configuration. Element 112 may also be excluded although its oxidation properties are unlikely to be observed due to its radioactive nature. This definition includes groups 3 to 11 on the periodic table.

The 40 transition metals

The transition metals are the forty chemical elements 21 to 30, 39 to 48, 71 to 80, and 103 to 112. The name *transition* comes from their position in the periodic table of elements. In each of the four periods in which they occur, these elements represent the successive addition of electrons to the d atomic orbital of the atoms. In this way, the **transition metals** represent the *transition* between group 2 elements and group 13 elements.

Electronic configuration

Elements with atomic numbers 1 through 20 have only electrons in s and p orbitals, with no filled d orbitals in their ground states.

In the fourth period, elements with atomic numbers 21 to 29 (**scandium to copper**) have a partially filled d subshell or ions with partly filled d subshell. **The outer ns orbitals in the d -block elements are of lower energy than the $(n-1)d$ orbitals.** As atoms occur in their lowest energy state, the transition metals tend to have their ns orbitals filled with electrons. Hence, these elements all have two electrons in their outer s orbital, with the exception of copper ($[\text{Ar}]4s^13d^{10}$) and chromium ($[\text{Ar}]4s^13d^5$). **These exceptions occur because half- and fully-filled subshells impart unusual stability to the atoms. Similar exceptions are more prevalent in the fifth, sixth and seventh period.**

There are four transition series :

1. The first transition series : Scandium (Sc) through Copper (Cu): $3d$ subshell is filling.

Irregularities are observed for Chromium, Cr, and Copper, Cu, because the listed electronic configurations are energetically favoured (i.e. $3d^54s^1$ is more stable than $3d^44s^2$, and $3d^{10}4s^1$ is more stable than $3d^94s^1$ respectively.).

2. The second transition series : Yttrium (Y) through Silver (Ag): $4d$ subshell is filling.

Irregularities are observed for Nb which skips from $4d^25s^2$ to $4d^45s^1$, and Pd, which goes from $4d^85s^2$ to $4d^{10}5s^1$.

3. The third transition series (inner): Lanthanum (La) to Hafnium (Hf) through Gold (Au): $5d$ subshell is filling.
4. The fourth transition series (inner) which is incomplete : Actinium (Ac) to element 104 through element 109: $6d$ subshell is filling , If elements 110 and 111 are found then this will complete this series..

Properties

Transition elements tend to have **high tensile strength, density and melting and boiling points**. As with many properties of transition metals, this is **due to *d* orbital electrons' ability to delocalise within the metal lattice**. In metallic substances, the more electrons shared between nuclei, the stronger the metal.

There are several common characteristic properties of transition elements:

- They often form coloured compounds.
- They can have a variety of different oxidation states.
- They are often good catalysts.
- They are silvery-blue at room temperature (except copper and gold).
- They are solids at room temperature (except mercury).
- They form complexes.

A **Coordination Complex** is a compound in which molecules or ions form coordinate bonds to a central metal atom or ion. The complex may contain positive ions, negative ions or neutral molecules. The formation of such coordination complexes is typical behaviour of transition metals.

- They are often paramagnetic.

Paramagnetism (i.e. attracted by a magnetic field) in the transition elements is caused by the presence of unpaired electrons in the *d* sub-orbital. **Diamagnetism** (i.e. not attracted by a magnetic field) is characteristic of compounds where all the electrons are paired in the *d* sub-orbitals.

The transition elements readily form alloys with themselves and with other elements (e.g. a copper-tin alloy is used for mirrors, brass is a copper-zinc alloy). Tungsten, is used to make tools and filaments in light bulbs.

Variable oxidation states

As opposed to group 1 and group 2 metals, ions of the transition elements may have **multiple, stable oxidation states, since they can lose *d* electrons without a high energetic penalty**. Manganese, for example has two *4s* electrons and five *3d* electrons, which can be removed. Loss of all of these electrons leads to a 7+ oxidation state. Certain patterns in oxidation state emerge across the period of transition elements:

- The number of oxidation states of each ion increases up to Mn, after which they decrease. Later transition metals have a stronger attraction between protons and electrons (since there are more of each present), which then would require more energy to remove the electrons.
- When the elements are in lower oxidation states, they can be found as simple ions. However elements in higher oxidation states are usually bonded covalently to electronegative compounds such as O or F, often as a polyatomic ion such as **chromate, vanadate and permanganate** ions.

Other properties with respect to the stability of oxidation states:

- Ions in higher oxidation states tend to make good oxidising agents, whereas elements in low oxidation states become reducing agents.
- The 2+ ions across the period start as strong reducing agents, and become more stable.
- The 3+ ions start stable and become more oxidizing across the period.

Catalytic activity

Transition metals form good homogeneous or heterogeneous catalysts, for example iron is the catalyst for the Haber process. Nickel or platinum is used in the hydrogenation of alkenes.

Colored compounds

We observe color as varying frequencies of electromagnetic radiation in the visible region of the electromagnetic spectrum. Different colors result from the changed composition of light after it has been reflected, transmitted or absorbed after hitting a substance. Because of their structure, transition metals form **many different colored ions and complexes**. Color even varies between the different ions of a single element - MnO_4^- (Mn in oxidation state 7+) is a purple compound, whereas Mn^{2+} is pale-pink.

Coordination by ligands can play a part in determining color in a transition compound, due to changes in energy of the d orbitals. Ligands remove degeneracy of the orbitals and split them into higher and lower energy groups. The energy gap between the lower and higher energy orbitals will determine the color of light that is absorbed, as electromagnetic radiation is only absorbed if it has energy corresponding to that gap. When a ligated ion absorbs light, some of the electrons are promoted to a higher energy orbital. Since, different frequency light is absorbed, different colors are observed.

The color of a complex depends on:

- the nature of the metal ion, specifically the number of electrons in the d orbitals
- the arrangement of the ligands around the metal ion (for example geometric isomers can display different colors)
- the nature of the ligands surrounding the metal ion. The stronger the ligands then the greater the energy difference between the split high and low $3d$ groups.

The complex formed by the d block element zinc (though not strictly a transition element) is colorless, because the 3d orbitals are full - no electrons are able to move up to the higher group.

Compound	Formula	Colour
Anhydrous Copper Sulphate	Cu(II)SO_4 ,	White
Hydrated Copper Sulphate	$\text{Cu(II)SO}_4 \cdot 5\text{H}_2\text{O}$	Light Blue
Ammoniacal Copper Sulphate	$[\text{Cu(II)(NH}_3)_4]\text{SO}_4$	Dark Blue
Potassium Permanganate	KMnO_4	Purple
Potassium Dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	Orange
Potassium Chromate	$\text{K}_2\text{Cr}_2\text{O}_4$	Green

$\text{V}(++++)$ is pale yellow,
 $\text{V}(++++)$ is blue,

F-block elements

The **f-block** (sometimes referred to as the *inner transition elements*) elements, in the atomic **ground state**, the highest-energy electrons occupy f-orbitals.

Unlike the other blocks, the conventional divisions of the f-block follow periods of similar atomic number rather than groups of similar electron configuration. Thus, the f-block is divided into the lanthanide series and the actinide series.

The name 'inner transition' is derived by analogy with the transition metals.

Like the s-block, the elements of the f-block are highly reactive metals. They catch fire in air very easily, and react with water to liberate hydrogen. Physically they are denser and have higher melting and boiling

points than the alkaline earth metals, but their reactivity makes them of very limited use structurally. Most of them are **extracted by electrolysis of molten chlorides**: the metals are much too reactive to be extractable from aqueous solutions.

The compounds of most f-block elements are **ionic** salts with M^{3+} ions, often hydrated in aqueous solutions. Cerium also forms a small series of strongly oxidising compounds with the +4, including ceric oxide (CeO_2). The *lighter* actinides (protactinium to americium) have f-electrons that can participate in bonding and form compounds in a variety of oxidation states from +2 to +6. Owing to the pulling of the inner f-electrons towards the nucleus, the *heavier* actinides (curium to lawrencium) tend not to use their inner f-electrons and resemble the lanthanides in forming salts with M^{3+} ions.

IRON, Fe

- **Cast iron** is used for man-hole covers because it is so hard wearing but it is brittle due to a high carbon content.
- When **alloyed with 1% carbon** iron forms **mild steel** which is not brittle, but is more malleable and corrosion resistant than cast iron. Mild steel is used for food cans, car bodies (but galvanising and several coats of paint help it to last!) and machinery etc.
- **Steel is an alloy based on iron mixed with carbon and usually other metals added too**. There are huge number of steel 'recipes' which can be made to suit particular purposes by changing the % carbon and adding other metals e.g. titanium steel for armour plating.
- **CHROMIUM, Cr**
 - Chromium steel (**stainless steel**, mixing and melting together **Fe + Cr** and maybe Ni too) with good anti-corrosion properties, used for cutlery and chemical plant reactors.



COPPER, Cu

- The alloy **BRASS is a mixture copper and zinc**. It is a much more hard wearing metal than copper (too soft) and zinc (too brittle) but is more malleable than bronze for 'stamping' or 'cutting' it into shape.
- **Copper is used in electrical wiring** because it is a good conductor of electricity but for safety it is insulated by using poorly electrical conductors like PVC plastic.
- **Copper is used in domestic hot water pipes** because it is relatively unreactive to water and therefore doesn't corrode easily.
- **Copper is used for cooking pans** because it is relatively unreactive to water and therefore doesn't corrode easily, readily beaten or pressed into shape but strong enough, it is high melting and a good conductor of heat.
- **Copper is also used as a roof covering** and weathers to a green colour as a surface coating of a basic carbonate is formed on corrosion.
- **The alloy BRONZE is a mixture of copper and tin** (Sn) and is stronger than copper and just as corrosion resistant, eg used for sculptures.
- **Iron and steel are used for boilers** because of their good heat conduction properties and high melting point.
- **Copper copper compounds are used in fungicides and pesticides** e.g. a traditional recipe is copper sulphate solution plus lime is used to kill greenfly.
- **Copper is alloyed with nickel to give 'cupro-nickel', an attractive hard wearing 'silvery' metal for coins**.
- **Steel, iron or copper are used for cooking pans** because they are malleable, good heat conductors and high melting.

- **NICKEL** is alloyed with copper to give 'cupro-nickel', an attractive hard wearing 'silvery' metal for coins.



ZINC

- **Zinc is used to galvanise (coat) iron or steel** to sacrificially protect them from corrosion. The zinc layer can be put on the iron/steel object by chemical or physically dipping it into a bath of molten zinc.
- **Zinc sulphate** solution can be used as the electrolyte for electroplating/galvanising objects with a zinc layer.
- **Zinc is used as a sacrificed electrode** in a zinc-carbon battery. It slowly reacts with a weakly acidic ammonium chloride paste, converting chemical energy into electrical energy.
- The alloy **BRASS is a mixture copper and zinc**. It is a much more hard wearing metal than copper (too soft) and zinc (too brittle) but is more malleable than bronze for 'stamping' or 'cutting' it into shape.

Transition metal compounds (often oxides) of copper, iron, chromium and cobalt are used to **pigments for artwork**, and give **bright colours to stained glass** and **ceramic/pottery glazes** e.g.



- **Paint pigments:** chromium oxide Cr_2O_3 **green**, iron oxide (haematite) Fe_2O_3 **red-brown**, manganese oxide MnO_2 **black**, copper hydroxide-carbonates (malachite-**green**, azurite-**blue**) and titanium dioxide TiO_2 **white**.
- **Stained glass:** cobalt oxide CoO **blue**, iron oxide/carbonate **green**, Cu metal **red**, CuO **turquoise**.
- **NICHROME is an alloy of chromium and nickel**. It has a high melting point and a high electrical resistance and so it is used for electrical heating element wires.
- **TUNGSTEN is used as the filament in light bulbs** because its melting point is so high.



Note on Aluminium

- **It is NOT a transition metal !**
 - eg **it does not form coloured compounds, it does not act as a catalyst** etc.
 - BUT it is high melting, of low density and one of the most used and useful non-transition metals.
 - It is rather weak BUT when **alloyed with copper**, manganese and **magnesium** and it forms a much stronger alloy called **duralumin**.
 - It does not readily corrode due to a permanent Al_2O_3 aluminium oxide layer on the surface which does not flake off and protects the aluminium from further oxidation.
 - Because of its alloyed strength, lightness and anti-corrosion properties it is used in aircraft construction, window frames, hifi chassis etc.
 - Its a good conductor of heat and can be used in radiators.
 - Its quite a good conductor of electricity, and also because its light, it is used in conjunction with copper (excellent electrical conductor) in overhead power lines (don't want them too heavy when iced up!). The cables however do have a steel core for strength!

- Poorly electrical conducting ceramic materials are used to insulate the wires from the pylons and the ground.

Other metals and their uses

- **A mixture of tin and lead is mixed to give the alloy SOLDER** which is a relatively low melting solid for electrical connections.
- **PEWTER is an alloy of mainly tin plus small amounts of copper, bismuth (Bi) and antimony (Sb)**, its stronger than tin but is easy to etch and engrave.
- **DENTAL AMALGAM ALLOY is a mixture of tin, mercury and silver**. When first prepared its soft and malleable before hardening to that undesired filling! It has good anti-corrosion properties and resists the attack of acidic products produced by bacteria in the mouth.