

d and f block

The **d-block** consisting of **Groups 3-12** occupies the large middle section of the **periodic table**. In these elements the inner *d* orbitals are progressively filled. The **f-block** is placed **outside** at the **bottom** of the **periodic table** and in the elements of this block, **4f** and **5f** orbitals are progressively filled.

--All the transition elements exhibit typical metallic properties such as --high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character.

--Their melting and boiling points are high which are attributed to the involvement of $(n - 1)$ *d* electrons resulting into **strong interatomic bonding**

--**Successive ionisation enthalpies** do not increase as steeply as in the main group elements with increasing atomic number

--**Electronic Configurations of the d-Block Elements**

In general the electronic configuration of these elements is $(n-1)d^{1-10}ns^{1-2}$.

Variation in Atomic and Ionic Sizes of Transition Metals

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity

Ionisation Enthalpies Due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right. There is the generally expected increasing trend in the values as the effective nuclear charge increases. However, the value of Cr is lower because of the absence of any change in the configuration and the value for Zn higher because it represents an ionisation from the 4*s* level. The lowest common oxidation state of these metals is +2

Oxidation States One of the notable features of a transition element is the great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.

Magnetic Properties Many of the transition metal ions are paramagnetic. Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin only' formula, i.e., $\mu = n(n + 2)$ where *n* is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM)

. **Formation of Coloured Ions** When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed

. **Formation of Complex Compounds** The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation. A few examples are: $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{PtCl}_4]^{2-}$.

Catalytic Properties The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Their activity is ascribed to their ability to adopt multiple oxidation states and to form complexes

Formation of Interstitial Compounds Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of

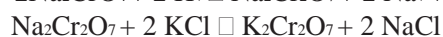
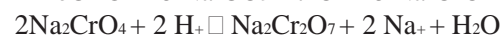
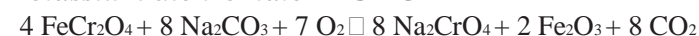
metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn₄N, Fe₃H, VH_{0.56} and TiH_{1.7}, etc

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert

Alloy Formation---alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance

Some Important Compounds of Transition Elements

Potassium dichromate $K_2Cr_2O_7$



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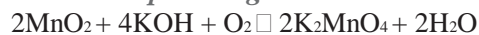
chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.



potassium dichromates as oxidising agent;----



Potassium permanganate $KMnO_4$



In acid solutions:

(a) Iodine is liberated from potassium iodide :



(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):



Oxalate ion or oxalic acid is oxidised at 333 K:



THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

lanthanoid contraction The overall decrease in atomic and ionic radii from lanthanum to lutetium is a unique feature & called **lanthanoid contraction**

Consequence of lanthanoid contraction

-Similar sizes of lanthanoid ions (M^{3+})

-Decrease in basic character from $La(OH)_3$ to $Lu(OH)_3$

-Similar size & properties of 4d & 5d series members e.g Zr-Hf, Nb-Ta, Mo-W

The Actinoids- The actinoids include the fourteen elements from Th to Lr

The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium ($Z=103$)

Electronic Configurations All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells

Ionic Sizes- There is a gradual decrease in the size of atoms or M^{3+} ions across the

series. This may be referred to as the *actinoid contraction* (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons

Oxidation States--- There is a greater range of oxidation states, which is in part attributed to the fact that the $5f$, $6d$ and $7s$ levels are of comparable energies. The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decrease in succeeding elements.

