GENERAL PROPERTIES OF THE TRANSITION ELEMENTS

Physical Properties

Most transition elements exhibit characteristic metallic traits, including but not limited to high tensile strength, ductility, malleability, pronounced thermal and electrical conductivity, and a distinctive metallic sheen.

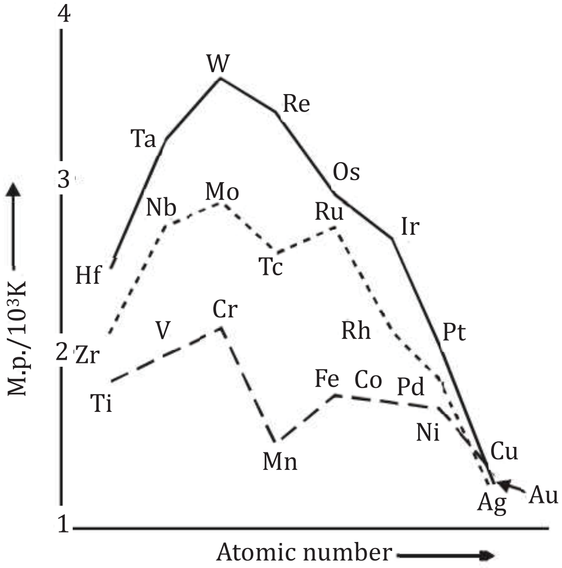
Lattice Structures of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (hcp)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp.bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = bcc body Centred cubic; hcp= hexagonal close packed; ccp cubic close packed, X = a typical metal structure)

With the notable exception of Zinc (Zn), Cadmium (Cd), and Mercury (Hg), transition metals tend to possess greater hardness and lower volatility. Moreover, they boast elevated melting and boiling points. The heightened melting points observed in these metals can be ascribed to the increased participation of electrons from the (n-1)d orbitals, in addition to the ns electrons, in the formation of interatomic metallic bonds.

In each row of transition metals, the melting points generally increase until reaching a peak at some point except for the anomalous behavior observed in Manganese (Mn) and Technetium (Tc). Subsequently, they tend to decrease consistently as the atomic number progresses. Additionally, these metals exhibit high enthalpies of atomization, as depicted in the accompanying figure.



Trends in melting points of transition elements

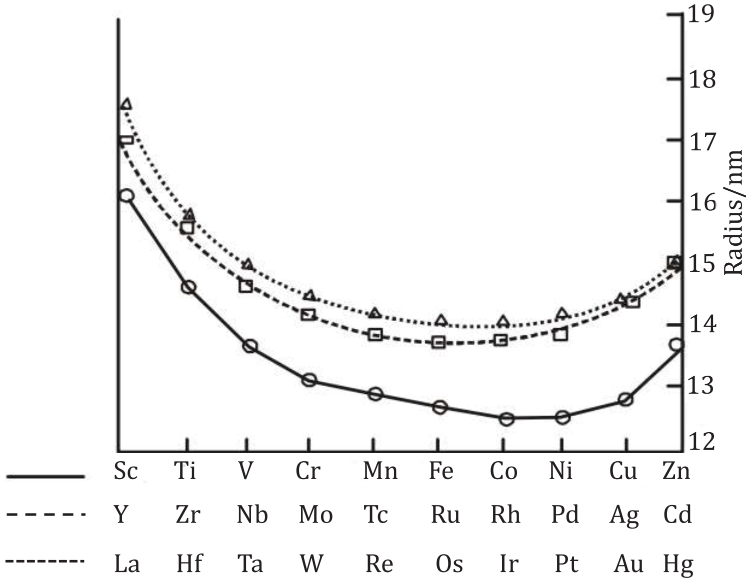
As a general rule, a greater number of valence electrons typically results in stronger bonding. This principle is significant because the enthalpy of atomization plays a crucial role in determining the standard electrode potential of a metal. Metals characterized by exceptionally high enthalpies of atomization, indicating very high boiling points, often exhibit noble behavior in their reactions.

Another generalization that can be made is that metals belonging to the 2nd and 3rd series tend to possess higher enthalpies of atomization compared to their counterparts in the 1st series. This observation is pivotal in understanding the prevalence of metal-metal bonding in compounds containing heavy transition metals.

Atomic and Ionic Size

Generally, ions within the same charge category in a given series exhibit a gradual reduction in radius as the atomic number increases. This phenomenon occurs because with each increment in atomic number, a new electron occupies a d orbital, while the nuclear charge simultaneously increases by one unit. However, the shielding effect provided by the d electrons is not sufficiently effective. Consequently, there is a net increase in the electrostatic attraction between the nuclear charge and the outermost electron, leading to a decrease in the ionic radius.

A similar pattern is observed in the atomic radii within a series, although the variations are relatively minor. Specifically, elements within the 4^d series tend to have larger sizes compared to those in the 3^d series. However, when comparing the sizes of elements in the 4^d and 5^d series within the same group, they are nearly identical. This phenomenon arises from the inadequate screening provided by the 4^f electrons.



Trends in atomic radii of transition elements

The orderly filling of the 4^f orbitals preceding the 5^d orbitals leads to a consistent reduction in atomic radii, a phenomenon known as the Lanthanoid contraction. This contraction essentially counteracts the anticipated expansion in atomic size that would typically occur with rising atomic number. Consequently, the net effect of the Lanthanoid contraction is that the 4^d and 5^d series display comparable radii and demonstrate markedly similar physical and chemical properties, far more than what would be expected based solely on their conventional family relationship.

Regarding density, the combination of a diminishing metallic radius alongside an increase in mass results in a general upsurge in the density of these elements. Notably, when progressing from Titanium (Ti) to Copper (Cu), a noticeable elevation in density can be observed.

Ionization Enthalpy

As the inner d orbitals are progressively filled, there is a concurrent increase in nuclear charge within each series of transition elements, leading to a rise in ionization enthalpy from left to right. Nonetheless, numerous minor fluctuations are observed within this trend.

The table on the preceding page presents the values for the first three ionization enthalpies of the first-row elements. These figures reveal that the successive enthalpies of these elements do not escalate as sharply as those of main group elements. While the first ionization enthalpy generally experiences an increase, the magnitude of the rise in the second and third ionization enthalpies for consecutive elements is notably greater.

The irregular pattern in the first ionization enthalpy of the 3^d metals, albeit of minor chemical significance, can be elucidated by considering that the removal of one electron affects the relative energies of the 4^s and 3^d orbitals. Consequently, the unipositive ions possess a d configuration devoid of 4^s electrons. Consequently, there is a reorganization energy accompanying ionization, along with some gains in exchange energy due to the increase in the number of electrons and the transfer of the s electron into the d orbital. Generally, an increasing trend in the values is expected as the effective nuclear charge rises. However, the value for Chromium (Cr) is lower due to the absence of any change in the d configuration, while the value for Zinc (Zn) is higher because it represents ionization from the 4^s level.

The most common oxidation state of these elements is +2 (excluding Scandium and Copper). To form the +2 ion from gaseous atoms, the sum of the first and second ionization energies is required, in addition to the enthalpy of atomization for each element.

Oxidation State

(a) They exhibit variable valency due to involvement of (ns) and (n-1) d-electrons. Due to less energy difference between these electrons.

(b) The oxidation states of all transition elements of '3d' series are as follows –

Element	Conf.	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	[↑][ ][ ][ ][ ] [⇅] 3d 4s	+3
Ti	$3d^2 4s^2$	[↑][↑][ ][ ][ ] [⇅]	+2 +3 +4
V	$3d^3 4s^2$	[↑][↑][↑][ ][ ] [⇅]	+2 +3 +4 +5
Cr	$3d^5 4s^1$	[↑][↑][↑][↑][↑] [↑]	+1 +2 +3 +4 +5 +6
Mn	$3d^5 4s^2$	[↑][↑][↑][↑][↑] [⇅]	+2 +3 +4 +5 +6 +7
Fe	$3d^6 4s^2$	[⇅][↑][↑][↑][↑] [⇅]	+2 +3 +4 +6
Co	$3d^7 4s^2$	[⇅][⇅][↑][↑][↑] [⇅]	+2 +3 +4
Ni	$3d^8 4s^2$	[⇅][⇅][⇅][↑][↑] [⇅]	+2 +3 +4
Cu	$3d^{10} 4s^1$	[⇅][⇅][⇅][⇅][⇅] [↑]	+1 +2

Zn	$3d^{10}4s^2$	⇅⇅⇅⇅⇅ ⇅	+2

(c) Highest oxidation state of transition elements can be calculated by n + 2 where (n = number of unpaired electrons) It is not applied for Cr and Cu.

(d) The transition metal ions having stable configuration like d^0 d^5 or d^{10} are more stable.

Ex. Sc^{+3}, Ti^{+4}, V^{+5}, Fe^{+3}, Mn^{+2}, Zn^{+2} etc.

(e) In aqueous medium Cr^{+3} is stable.

(f) Co^{+3} and Ni^{+2} is stable in complexes.

(g) In aqueous medium due to disproportionation Cu^{+1} is less stable than Cu^{+2} while its configuration is $3d^{10}$

(h) Most common oxidation state among the transition elements is +2.

(i) Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).

(j) The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.

(k) In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.

(l) They also show zero oxidation state in their carbonyl compounds like $Ni(CO)_4$.

(m) Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.

Ex. Sc^{+2}, Ti^{+2}, V^{+2}, Fe^{+2}, Co^{+2} etc are reducing agents

Cr^{+6}, Mn^{+7}, Mn^{+6}, Mn^{+5}, Mn^{+4} etc are oxidising agents.

Standard Electrode Potentials

The ionization enthalpy magnitude indicates the energy needed to remove electrons and create a specific oxidation state of the metal in a compound. Consequently, ionization enthalpy values provide insights into the thermodynamic stability of transition metal compounds in various oxidation states. A lower ionization enthalpy for the metal implies greater stability for its compound

For example, the first four ionisation enthalpies of nickel and platinum are given below:

Ionisation enthalpies	Ni	Pt
$IE^1 + IE^2$	2.49×10^3 Kj mol $^{-1}$	2.66×10^3 Kj mol $^{-1}$
$IE^3 + IE^4$	8.8×10^3 Kj mol $^{-1}$	6.70×10^3 Kj mol $^{-1}$
Total	11.29×10^3 Kj mol $^{-1}$	9.36×10^3 Kj mol $^{-1}$

It is clear from the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.

$$Ni \rightarrow Ni^{2+} + 2e^- \qquad I.E. = 2.49 \times 10^3 \text{ kJ mol}^{-1}$$

$$Pt \rightarrow Pt^{2+} + 2e^- \qquad I.E. = 2.66 \times 10^3 \text{ kJ mol}^{-1}$$

Consequently, the ionization of nickel to Ni^{2+} is more energetically advantageous in comparison to platinum. This establishes that nickel (II) compounds exhibit greater thermodynamic stability than platinum (II) compounds. Conversely, the total of the first four ionization enthalpies is lower for platinum than for nickel, as demonstrated by:

$Ni \rightarrow Ni^{4+} + 2e^-$ I.E. $= 11.29 \times 10^3$ kJ mol^{-1}

$Pt \rightarrow Pt^{4+} + 2e^-$ I.E. $= 9.36 \times 10^3$ kJ mol^{-1}

Hence, platinum (IV) compounds exhibit comparatively higher stability than nickel (IV) compounds. Consequently, K_2PtCl_6, which features Pt (IV), is a recognized compound, while the corresponding nickel compound remains unknown. However, in solutions, the stability of these compounds is contingent upon electrode potentials.

Electrode Potentials

In addition to ionization enthalpy, factors like enthalpy of sublimation, hydration enthalpy, and ionization enthalpy collectively contribute to the stability of a specific oxidation state in a solution. This can be elucidated based on their electrode potential values. The oxidation potential of a metal encompasses the following process:

$$M(s) \rightarrow M^+(aq) + e^-$$

This process actually takes place in the following three steps as given in following flowchart:

$$\begin{tikzcd}
M\ (S) \arrow[r, "\triangle H"] \arrow[d, "(i)"'] & M^+\ (aq) \\
M\ (g) \arrow[r, "I.E."', "(ii)"'] & M^+\ (g) \arrow[u, "(iii)"']
\end{tikzcd}$$

(i) In the first step, the atoms get isolated from one another and become independent in the gaseous state. This converts solid metal to the gaseous state. The energy needed for this step is known as enthalpy of sublimation.

$M(s) \rightarrow M^+(g)$ Enthalpy of sublimation, $\Delta_{sub}H^{\ominus}$

(ii) In the second step, the outer electron is removed from the isolated atom. The energy required for this change is ionisation enthalpy.

$M(s) \rightarrow M^+(g) + e^-$ Ionisation enthalpy, IE

(iii) In the third step the gaseous ion gets hydrated. In this process, energy known as hydration enthalpy, is liberated.

$M^+(g) + nH_2O \rightarrow M^+(aq)$ Enthalpy of hydration, $\Delta_{hyd}H$

The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is

$$\Delta H = \Delta_{sub}H^{\ominus} + IE + \Delta_{hyd}H$$

Hence, ΔH represents the enthalpy change necessary to transform the solid metal, M, into the monovalent ion in an aqueous medium, M+ (aq). A similar cycle can be constructed for the formation of an anion in a solution, with the ionization enthalpy potentially replaced by electron gain enthalpy as the gaseous atom transforms into a gaseous anion. ΔH aids in predicting the stability of a specific oxidation state.

The smaller the values of total energy change for a given oxidation state in an aqueous solution, the greater the stability of that oxidation state. Electrode potentials serve as a measure of total energy change. Qualitatively, the stability of transition metal ions in various oxidation states can be assessed based on electrode potential data. The lower the electrode potential, or the more negative the standard reduction potential of the electrode, the more stable the oxidation state of the transition metal in the aqueous solution.

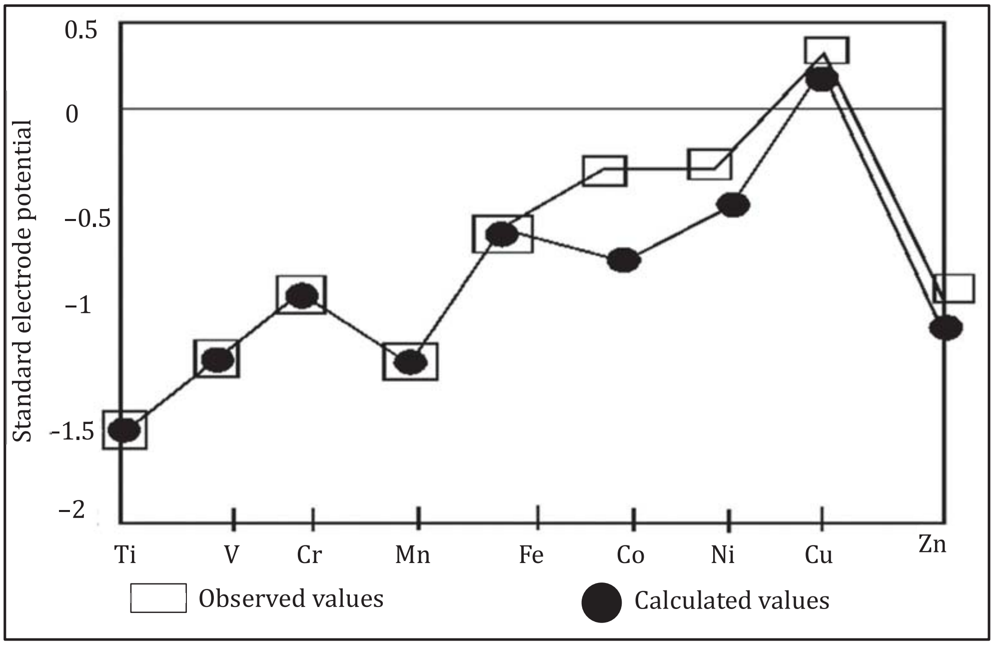
The electrode potentials of different metals can also be measured by forming the cell with standard hydrogen electrode. For the measurement of electrode potential of M^{2+} | 1M, the e.m.f. of the cell in which the following reaction occurs is measured:

$$2H^+(aq) + M(s) \rightleftharpoons M^{2+}(aq) + H_2(g)$$

Knowing the potential of $2H^+(aq)$ | $H_2(g)$, it is possible to determine the potential of M^{2+} (aq) | M.

For the first transition series, the $E^\ominus$ values of $M^{2+}(aq)$ | M are given below:

The observed values of $E^\ominus$ and those calculated using the data are compared in the following figure.



Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of MII to M

Element (M)	$\Delta_a H_q$ **(M)**	$\Delta_f H_1^\theta$	$\Delta_f H_2^\theta$	$\Delta_{hyd} H^\theta (M^{2+})$	E^θ / V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

The results lead to the following conclusions:

(i) There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies ($IE_1 + IE_2$) and the sublimation energies in the period.

(ii) It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = –2.87 V). Compared to group 2 elements, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomization. These reduce their electrode potentials though their hydration enthalpies are large.

(iii) Zinc has low enthalpy of atomization and fairly large hydration energy. But it has also low electrode potential (–0.76 V) because of its very high ionisation enthalpy ($IE_1 + IE_2$).

(iv) It is clear from above table and figure that copper has positive reduction potential, $E^{\ominus}$ (0.34 V) and this shows that copper is least reactive metal out of the first transition series. This unique behavior (+ve) E value of copper) also accounts for its inability to liberate H_2 from acids. It has been observed that only oxidizing acids (such as nitric acid and hot concentrated sulphuric acid) react with copper in which the acids are reduced. The high energy required to convert Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

(v) In general, the value becomes, less negative across the series. This is related to the general increase in the sum of first and second ionisation enthalpies. It is interesting to note that the values of E^{o} of Mn, Ni and Zn are more negative than expected from the general trend. The relatively more negative values of $E^{\ominus}$ for Mn and Zn are due to stability of half-filled d-sub-shell in Mn^{2+} ($3d^5$) and the completely filled ($3d^{10}$) configuration in Zn^{2+}. The exceptionally high $E^{\ominus}$ value of Ni from regular trend is related to the highest negative enthalpy of hydration of Ni^{2+} ion.

Trends in the M^{3+} | M^{2+} Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form M^{3+} ions in aqueous solutions. The standard reduction potentials for M^{3+} | M^{2+} redox couple are given below:

	Ti	V	Cr	Mn	Fe	Co
$E^{\ominus}$ (M^{3+}(aq) | M^{2+} (aq) (in Volt)	−0.37	−0.26	−0.41	+1.57	+0.77	+1.97

These values reveal the following facts:

(i) The low value of scandium reflects the stability of Sc^{3+} which has a noble gas configuration.

(ii) The comparatively high value for Mn shows that Mn^{2+} (d^5 configuration) is particularly stable. On the other hand, comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5 configuration).

(iii) The comparatively low value of V is related to the stability of V^{2+} (due to half-filled $t_{2g}{}^3$ energy level of 3d orbitals in octahedral crystal field spitting).

(iv) The $E^{\ominus}$ value for Mn^{3+}/Mn^{2+} couple much more positive than for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}. This is because of the much larger IIIrd ionisation energy of Mn (removal of electron from d^5 configuration).

Trends in Stability of Higher Oxidation States

Data on standard electrode potentials offer valuable insights into the stability of various oxidation states exhibited by an element. The highest oxidation states are typically observed in halides and oxides.

1. In Metal Halides

The transition elements undergo reactions with halogens at elevated temperatures, resulting in the formation of transition metal halides. These reactions exhibit substantial heat of reaction. However, once the reaction initiates, the generated heat is adequate to sustain the reaction. The halogens engage in the reaction in the following descending order

$$F_2 > Cl_2 > Br_2 > I_2$$

Halides of first transition series

Oxidation Number	Sc	Ti	V	Cr	Min	Fe	Co	Ni	Cu	Zn
+6				CrF_6						
+5			VF_5	CrF_5						
+4		TiX_4	VX_4^a	CrF_4	MnF_4					
+3	ScX_3	TiX_3	VX_3	CrF_3	MnF_3	FeX^a_3	CoF_3			
+2		TiX_2	VX_2^c	CrF_2	MnX_2	FeX_2	CoF_2	NiX_2	CuX_2^b	ZnX_2
+1									CuX^c	
	where X = F, Cl, Br, I, X^a = F, Cl, Br, X^b = F, Cl, X^c = Cl, Br, I									

Among the transition groups 3-12, variations in the stability of different oxidation states exist. Typically, the second and third transition series elements demonstrate higher coordination numbers, making their higher oxidation states more stable compared to the corresponding elements in the first transition series.

The following trends are observed from table regarding transition metal halides:

(i) In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.

(ii) Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, X = F, Cl, Br and I), VF_5 and CrF_6.

(iii) The +7-oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.

(iv) After Mn, the tendency to show higher oxidation states with halogens are uncommon. Iron and cobalt form trihalides FeX_3 (X = F, Cl or Br) and CoF_3.

(v) The tendency of fluorine to stabilize the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6.

(vi) V(V) is shown by VF_5 only. However, the other halides undergo hydrolysis to form oxyhalides, VOX_3.

(vii) Fluorides are relatively unstable in their low oxidation states.
For example, vanadium form only VX_2 (X = Cl, Br or I) and copper can form CuX (X = Cl, I). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidizes I^- to I_2.

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :

$$2Cu^{+} \rightarrow Cu^{2+} + Cu$$

Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{hyd}H^{\Theta}$) of Cu^{2+} (aq) than Cu^{+}, which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

2. In Metal Oxides and Oxo Cations.

Oxidation Number	Sc	Ti	V	Cr	Min	Fe	Co	Ni	Cu	Zn
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2	Fe_2O_3				
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_3O_4	Co_3O_4			
+2		TiO	VO	(CrO)	Mn_3O_4	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	
Mixed oxides					Mn_3O_4	Fe_3O_4	Co_3O_4			

Oxygen's capacity to stabilize the highest oxidation state is evident in its oxides. The highest oxidation states in these oxides correspond to the group number.

For instance, scandium in group 3 exhibits a highest oxidation state of +3 in its oxides, Sc_2O_3, while manganese in group 7 shows +7 in Mn_2O_7. However, beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Although higher oxidation states, such as +6, are seen in ferrates like $FeO4_2^-$ in alkaline medium, they readily decompose to Fe_2O_3 and O_2. In addition to oxides, the oxidation of metals also stabilizes higher oxidation states, as seen in V^{V} as VO_2^{+}, V^{IV} as VO^{2+}, and Ti^{IV} as TiO^{2+}. Notably, oxygen's ability to stabilize these high oxidation states surpasses that of fluorine.

For instance, manganese forms its highest fluoride as MnF_4, while its highest oxide is Mn_2O_7. This is attributed to oxygen's superior ability to form multiple bonds to metals. In covalent oxides like Mn_2O_7, each Mn is tetrahedrally surrounded by oxygen atoms, forming Mn–O–Mn bridges. Tetrahedral $[MO_4]^{n-}$ ions are also known for vanadium (V), chromium (VI), manganese (VI), and manganese (VII).

Transition elements in the +2 and +3 oxidation states predominantly form ionic bonds, while with higher oxidation states, the bonds become essentially covalent. For instance, in MnO_4^-, all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decreases. Mn_2O_7,

for example, is a covalent green oil. In these higher oxides, the acidic character is predominant. Thus, CrO_3 yields H_2CrO_4 and $H_2Cr_2O_7$, and Mn_2O_7 yields $HMnO_4$. V_2O_5 is amphoteric, mainly acidic, and reacts with alkalis to give VO_4^{3-} and with acids to produce VO_2^{+}.

The relative stability of various oxidation states

(a) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of $3d^{\circ}$,$3d^{5}$ & $3\,d^{10}$ configuration to some extent.

Ex. Stability of Ti^{4+} $(3d^{0}) > Ti^{3+}$ $(3d^{1})$ Mn^{2+} $(3d^{5}) > Mn^{3+}$ $(3d^{4})$

(b) The higher oxidation state of 4d and 5d series element are generally more stable than the elements of 3d series.

Ex.

(i) (oxidation state of Mo is +6), (4d series) & (5d series) are more stable due to their maximum oxidation state.

(ii) (3d-series) are strong oxidizing agents.

(c) Strongly reducing states probably do not form fluorides or oxides, but may well form the heavier halides Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and lodide.

Ex.

(i) V (Vanadium) react with halogens to form VF_5 VCl_5, VBr_3, but doesn' t form VBr_5 or VI_5 because in + 5 oxidation state Vanadium is strong oxidizing agent thus convert Br^- & I^- to Br_2 & I_2 respectively, So VBr_3 &VI_3 are formed but not VBr_5 & VI_5.

(ii) On the other hand, VF_5 is formed because V^{5+} ion unable to oxidize highly electronegative & small anion F^-

(iii) Similarly, highly electronegative and small O^{2-} ion formed oxides

Ex. $VO_4{}^{3-}$, $CrO_4{}^{2-}$ & $MnO_4{}^-$ etc.

Different oxidation state of chloride & oxides compound

+2	+3	+4	+5	+6	+7
$TiCl_2$	$TiCl_3$	$TiCl_4$			
VCl_2	VCl_3	VCl_4	$VOCl_3$		
(Ionic, basic)	Less ionic (Amphoteric)	Covalent and Acidic (Strong lewis acid)			

+2	+3	+4	+5	+6	+7
TiO	Ti_2O_3	TiO_2			
VO	V_2O_3		V_2O_5		
CrO	Cr_2O_3			CrO_3	
MnO	Mn_2O_3	MnO_2		MnO_3	Mn_2O_7
Ionic, basic	Less Ionic (Amphoteric)			Acidic, covalent	

(d) Such compounds are expected to be unstable except in case where vacant d-orbitals are used for accepting lone-pair from π-bonding ligand.

Ex. $[Ni(CO)_4]$, $[Ag(CN)_2]^-$,$[Ag)(NH_3)_2]^+$

Magnetic Properties

(a) Typically, transition elements display magnetic properties. Para magnetism refers to the attraction of a substance to a magnetic field, primarily attributed to the existence of unpaired electrons in atoms, ions, or molecules. This property varies inversely with temperature.

(b) Diamagnetic substances are slightly repelled by a magnetic field, and this characteristic is temperature-independent.

(c) As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature.

Ex. Ti^{+2} $[Ar]3d^2$, Ti^{+3} $[Ar]3d^1$. $V^{+2}[Ar]3d^3$, $Cr^{+3}[Ar]3d^3$

(d) Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature.

(e) The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.

(f) The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

$$\mu = \sqrt{n(n+2)}$$

Where - 'n' is the number of unpaired electrons in the metal ion.

μ = Magnetic moment in Bohr Magnetons (B.M.)

(g) The magnetic moment of diamagnetic substances will be zero.

(h) Transition metal ions with a d^5 configuration will exhibit maximum paramagnetic behavior due to the presence of the highest number of unpaired electrons.

Formation of Colored ions

Colour Property

(a) Most of the transition metal ions exhibit colour property.

(b) This is due to d-d transition of unpaired electrons in their t_{2g} and e_g sets of 'd' orbitals.

(c) They require less amount of energy to undergo excitation of electrons. Hence, they absorb visible region of light exhibiting colour.

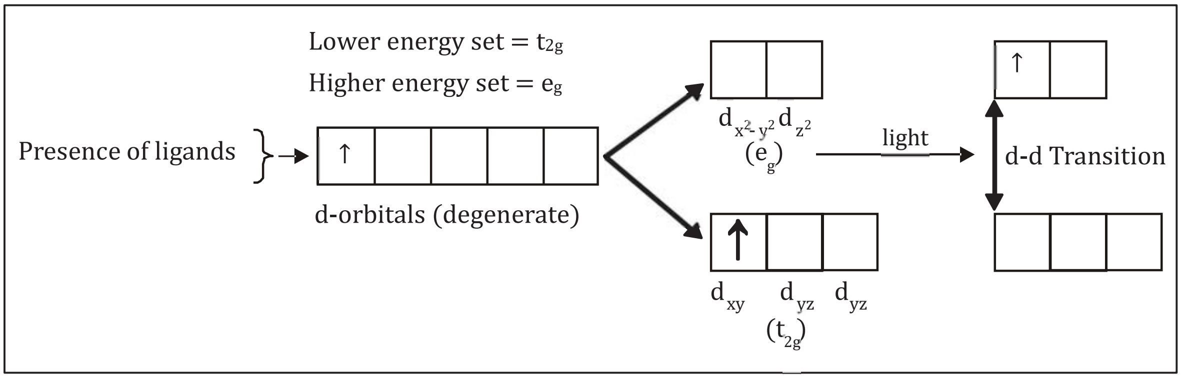
Ex. Sc^{+2} : $[Ar]3d^1$, Ti^{+2} : $[Ar]3d^2$, V^{+2} : $[Ar]3d^3$

(d) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.

Ex. Sc^{+3} : $[Ar]3d^0$, Cu^{+1} : $[Ar]3d^{10}$, Ti^{+4} : $[Ar]3d^0$ etc are colourless ions.

(e) A transition metal ion selectively absorbs a portion of the visible light spectrum and releases the remaining colors, resulting in the emitted light's overall hue. The color of the metal ion corresponds to the emitted light's color.

(f) In transition metal ion the 'd' orbitals split into lower energy set t_{2g} orbitals and higher energy set e_g orbitals. The electrons from t_{2g} set get excited to higher energy set $e_{.g.,}$ set. This excitation of electrons is called as 'd-d' transition. Due to this 'd -d' transition the transition metal ions exhibit colour property.



Factors affecting the colour of complex

The colour of a transition metal complex depends on-

(a) The magnitude of energy difference between the two d-levels (Δ_0),

(b) An increase in the magnitude of Δ_0 decreases the wave length (λ) of the light absorbed by the complexes.

$$\Delta_\circ \propto \frac{1}{\lambda(\text{wavelength of light absord})}$$

(c) Thus, with a decrease in the λ the colour of complex changes from Red to Violet.

Ex.

Complex ions	$[Co(H_2O)_6]^{3+}$		$[Co(NH_3)_6]^{3+}$		$[Co(CN)_6]^{3-}$
Ligand field strength	H_2O	$<$	NH_3	$<$	CN^-
Magnitude of Δ_0	$\Delta_0(H_2O)$	$<$	$\Delta_0(NH_3)$	$<$	$\Delta_0(CN^-)$
Magnitude of λ	$\lambda(H_2O)$	$<$	$\lambda(NH_3)$	$<$	$\lambda(CN^-)$
Colour of the transmitted	orange		Green-blue		violet
Colour of absorbed light (i.e., colour of the complex	Green-blue		Orange		Yellow-greenlight

(d) $KMnO_4$ (dark pink), $K_2Cr_2O_7$ (orange) having d° configuration but they are coloured due to charge transfer spectrum and charge is transferred from anion to cation.

Example of Some coloured metal ions:

Ti^{+3}	Purple	Mn^{+2}	Light pink
Fe^{+3}	Yellow	Ni^{+2}	Green
Sc^{3+}	Colourless	Ti^{3+}	Purple
V^{3+}	Green	Cr^{2+}	Blue
Mn^{3+}	Violet	Fe^{2+}	Green(light)
Co^{2+}	Pink	Zn^{2+}	Colourless
Cr^{+3}	Green	Fe^{+2}	Green
Co^{+3}	Pink	Cu^{+2}	Blue
Ti^{4+}	Colourless	V^{4+}	Blue
V^{2+}	Violet	Cr^{3+}	Green
Mn^{2+}	Pink	Fe^{3+}	Yellow
Ni^{2+}	Blue		

Ex. Explain the blue colour of $CuSO_4.5H_2O$.

Sol. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Formation of Complex Compound

The compact size of metal ions, coupled with their high ionic charges and the accessibility of d orbitals for bond formation, contribute to the propensity of transition elements to create numerous complex compounds.

Examples of such complex compounds or ions include:

$$[Fe(CN)_6]^{3-}, [Cu(NH_3)_4]^{2+}, [Mn(H_2O)_4]^{2+}, [CuCl_4]^{2-}$$

Catalytic Properties

(a) Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.

(b) When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.

(c) Transition metals and their compounds exhibiting catalytic properties in various processes are-

Catalyst	Uses
$TiCl_3$	Used as the Ziegler-Natta catalyst in the production of polythene.
MnO_2	Used as a catalyst to decompose $KClO_3$ to give O_2
Fe	Promoted iron is used in the Haber-Bosch process for making NH_3
$FeCl_3$	Used in the production of CCl_4 from CS and Cl_2
$FeSO_4$ and H_2O_2	Used as Fenton's reagent for oxidizing alcohols to aldehydes.
$PdCl_2$	Wacker process for converting $C_2H_4+H_2O+PdCl_2$ to $CH_3CHO+2HCl+Pb$.
Pd	Used for hydrogenation (e.g., phenol to cyclohexanone).
Pt/ptO	Adams catalyst, used for reductions.
Pt	Formerly used for $SO_2 \rightarrow SO_3$in the contact process for making H_2SO_4
Pt/Rh	Formerly used in the Ostwald process for making HNO_3 to NO
Cu	Is used in the direct process for manufacture of $(CH_3)2SiCl_2$ used to make silicones.
Cu/V	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylone-66
CuCl	Decon process of making Cl from HCl
Ni	Raney nickel, numerous reduction processes (e.g., manufacture of hexamethylenediamine, production of H_2 from NH_3 reducing anthraquinone to anthraquinol in the production of H_2O_2)

Biological Advantage of d-block Elements

Certain metals play crucial roles as components of enzymes or proteins essential for living organisms. In the following discourse, we will delve into specific metals, their respective enzymes, and elucidate their functions within biological systems.

Metal	Enzyme	Biological Function
Mo	Xanthine oxidase	Metabolisation of purine
Mn^{II}	Arginase	Urea formation

Fe^{ll} or Fe^{ll}	Ferredoxin	Photosynthesis
Fe^{ll}	Haemoglobin	Transport of O_2
Cu^{l} or Cu^{ll}	Tyrosinase	Skin Pigmentation

Formation of Interstitial Compounds

(a) Transition elements can create interstitial compounds with smaller nonmetal elements such as hydrogen, carbon, boron, nitrogen, and others.

(b) Smaller atoms become trapped within the interstitial spaces of the metal lattices, resulting in non-stoichiometric interstitial compounds that lack a specific formula.

(c) Weak Vander Waals forces of attraction hold the smaller elements in the interstitial spaces of transition elements.

(d) Interstitial compounds share the same chemical properties as their parent metals but exhibit differences in physical properties, including density and hardness. The absorption of excess hydrogen atoms by transition metals like Pd and Pt is termed occlusion.

Non-Stoichiometry

(a) Transition elements may exhibit variable valency, leading to the formation of nonstoichiometric compounds.

(b) These compounds possess an indefinite structure and proportion.

(c) For example, lron (II) Oxide FeO should be written as a bar over the formula $\mathrm{F\bar{e}O}$ to indicate the ratio of Fe & O atom is not exactly 1:1 (Fe_{0} $_{.94}$ O & $Fe_{0.84}$ O), $\mathrm{V\bar{S}e}$ ($VSe_{0.98}VSe_{1.2}$),

(d) Non stoichiometry is shown particularly among transition metal compounds of the group 16 elements (O, S, Se, Te).

(e) Sometimes nonstoichiometric is caused by defect in the solid structure.

Potassium Dichromate ($K_2Cr_2O_7$)

Preparation

It is derived from Chromite ore, Ferrochrome, or Chrome iron ($FeO.Cr_2O_3$ or $FeCr_2O_4$). The process encompasses several steps.

(a) Preparation of Sodium Chromate (Na_2CrO_4)

The chromite ore powder is fused with sodium hydroxide or sodium carbonate in the presence of air within a reverberatory furnace.

$$4FeCr_2O_4 + 16NaOH + 7^{\text{o}}{}_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

or

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Following the reaction, the roasted substance is extracted with water, causing complete dissolution of sodium chromate, while ferric oxide remains as a residue.

(b) Formation of Sodium Dichromate ($Na_2Cr_2O_7$) from Sodium Chromate (Na_2CrO_4)

The solution of sodium chromate is filtered and acidified with dil./con. H_2SO_4 acid giving its dichromate.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

On cooling, sodium sulphate being less soluble crystallizes out as $Na_2SO_4.10H_2O$ and is removed. The resulting solution contains sodium dichromate ($Na_2Cr_2O_7$).

(c) Formation of Potassium Dichromate from Sodium Dichromate

The hot concentrate solution of sodium dichromate is heated with calculated amount of KCl.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

The hot solution undergoes filtration to separate the least soluble compound, sodium chloride, which precipitates. Upon cooling, the remaining liquid yields orange-red crystals of potassium dichromate through crystallization.

Properties

(A) **Colour and Melting Point: -** Orange red crystals. 670 K

(B) **Solubility: -** Moderately soluble is cold water but readily soluble in hot water.

(C) **Action of Heat: -** It decompose on heating to give potassium chromate, chromic oxide and oxygen.

$$4K_2Cr_2O_7 \xrightarrow{\text{Heat}} \underset{\substack{\text{Potassium}\\\text{chromate}}}{4K_2CrO_4} + \underset{\substack{\text{Chromic}\\\text{oxide}}}{2Cr_2O_3} + 3O_2$$

(D) **Action of Alkalies: -** Upon exposure to alkalies, the dichromate solution undergoes a color transformation from orange to yellow, attributed to the creation of chromate ions.

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

or $$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

This chromate on acidifying reconverts into dichromate.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

or $$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

The interconversion is explained by the fact that dichromate ion and chromate ion exist in equilibrium at a pH of about 4.

$$Cr_2O_7^{2-} + H_2O \xrightleftharpoons{HCrO_4^{2-}} 2CrO_4^{2-} + 2H^+$$

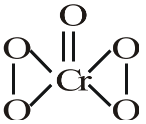
When alkali added, H^+ consumed so forward direction. When acid added, H^+ increases so backward direction.

(E) **Chromyl chloride Test: -** When potassium dichromate is heated with conc. H_2SO_4 acid and a soluble metal chloride (ex. NaCl) orange red vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

(F) **Reaction with H_2O_2: -** Acidified solution of dichromate ions give deep blue colour solution with H_2O_2 due to the formation of $[CrO(O_2)_2]$ or CrO_5. The blue colour fades away gradually due to the decomposition of CrO_5 into Cr^{+3} ions and oxygen.

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ \rightarrow 2CrO_5 + 5H_2O$$



(Butterfly structure)

(G) **Action with HCl: -** Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(H) Action of con. H_2SO_4

(i) In cold, red crystals of chromic anhydride are formed.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(ii) On heating the mixture oxygen is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(I) Oxidising properties

The dichromats act as powerful oxidising agent in acidic medium. In presence of dill H_2SO_4, $K_2Cr_2O_7$ liberates Nascent oxygen and therefore acts as an oxidising agent.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

From an electronic perspective, the ion acquires electrons in an acidic medium, thereby functioning as an oxidizing agent.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(i) It oxidizes iodides to iodine

$$+ 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

$$[2I^- \rightarrow I_2 + 2e^-] \times 3$$

$$+ 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 3I_2 + 7H_2O$$

Or $\quad K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

(ii) Acidified ferrous sulphate to ferric sulphate

$$+ 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

$$Fe^{+2} \rightarrow Fe^{3+} + e^-] \times 6$$

$$+ 14H^+ + 6Fe^{+2} \rightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

or $\quad K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + K_2SO_4$

(iii) Oxidises H_2S to sulphur

$$+ 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

$$H_2S \rightarrow S + 2H^+ + 2e^-] \times 3$$

$$+ 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 3S + 7H_2O$$

or $\quad K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S + 7H_2O + K_2SO_4$

Similarly, it oxidizes sulphites to sulphates, chlorides to chlorine, nitrites to nitrates, thiosulphates to sulphates and sulphur and stannous (Sn^{+2}) salts to stannic (Sn^{+4}) salts.

$$3SO_3^{-2} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

$$3NO_2^- + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3NO_3^- + 2Cr^{3+} + 4H_2O$$

$$3S_2O_3^{2-} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 3S + 2Cr^{3+} + 4H_2O$$

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$

$$3Sn^{+2} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Sn^{+4} + 2Cr^{3+} + 7H_2O$$

It oxidizes SO_2 to sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

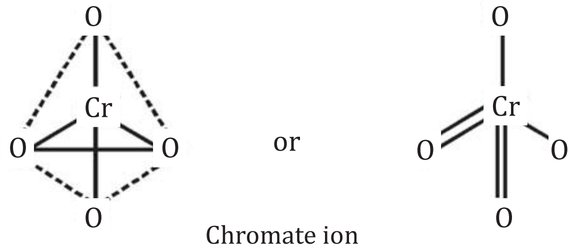
$$SO_2 + O + H_2O \longrightarrow H_2SO_4$$

Uses

(a) Employed for volumetric determination of ferrous salts, iodides, and sulphites.
(b) Utilized in the synthesis of various chromium compounds, such as chrome alum (K_2SO_4, $Cr_2(SO_4)_3.24H_2O$), chrome yellow ($PbCrO_4$), and chrome red ($PbCrO_4.PbO$).
(c) Found in photography for the toughening of gelatin film.
(d) Applied in the leather industry for chrome tanning.
(e) The chromic acid mixture, comprising $K_2Cr_2O_7$ and concentrated H_2SO_4, is utilized for cleaning glassware.
(f) In organic chemistry, it serves as an oxidizing agent.
(g) Employed in dyeing and calico printing.

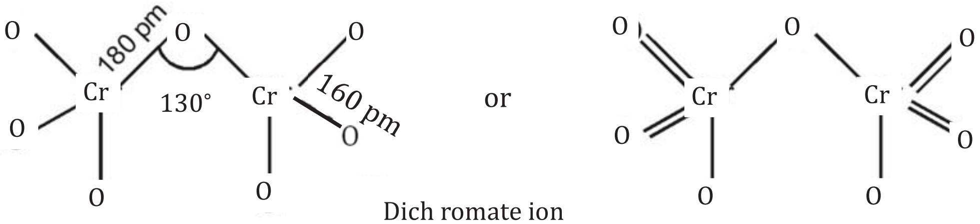
Structure

The chromate ion exhibits a tetrahedral structure, with four atoms surrounding the chromium atom arranged in a tetrahedral configuration.



Chromate ion

The dichromate ion's structure comprises two tetrahedra that share an oxygen atom at their common corner.



Dich romate ion

Alloy Formation

(a) Alloys are most likely to be formed by transition elements.
(b) Transition elements exhibit low reactivity and nearly identical sizes, allowing easy replacement of one transition metal atom by another in the lattice. This accounts for their high tendency to form alloys.
(c) The ratio of component metals in alloys remains constant.
(d) Alloys characterized by extreme hardness and a high melting point.

Some Important Alloy

(a)	Bronze	Cu (75 - 90 %) +Sn (10 - 25 %)
(b)	Brass	Cu (60 - 80 %) +Zn (20 - 40 %)
(c)	Gun metal	(Cu + Zn + Sn) (87:3:10)
(d)	German Silver	Cu + Zn + Ni (2:1:1)
(e)	Bell metal	Cu (80 %) + Sn (20 %)
(f)	Nichrome	(Ni + Cr + Fe)

(g)	Alnico	(Al, Ni, Co)
(h)	Type Metal	Pb + Sn + Sb
(i)	Alloys of steel	
	l Vanadium steel	V (0.2 - 1 %)
	l Chromium steel	Cr (2 - 4 %)
	l Nickel steel	Ni (3 -5 %)
	l Manganese steel	Mn (10 - 18 %)
	l Stainless steel	Cr (12 - 14 %) & Ni (2 - 4 %)
	l Tungsten steel	W (10 - 20 %)
	l Invar	Ni (36 %)
(j)	14 Carat Gold	54 % Au + Ag (14 to 30 %) + Cu (12 - 28 %)
(k)	24 Carat Gold	100 % Au
(l)	Solder	Pb + Sn
(m)	Magnalium	Mg (10%) + Al (90%)
(n)	Duralumin	(Al + Mn + Cu)
(o)	Artificial Gold	Cu (90 %) + Al (10%)
(p)	Constantan	Cu (60%) + Ni (40%)

% of Carbon in Different Type of Iron

	Name	**% of C**
(a)	Wrought Iron	0.1 to 0.25
(b)	Steel	0.25 to 2.0
(c)	Cast Iron	2.6 to 4.3
(d)	Pig Iron	2.3 to 4.6