

TRANSITION METALS

Introduction:

The transition elements may be strictly defined as the elements that have partially filled d or f subshells in its ground state or excited state. We adopt a broader definition and also include elements that have partly filled d or f subshells in their compounds. This means that we treat the coinage metals Cu, Ag and Au as transition metals. Since Cu(II) has a $3d^9$ configuration, Ag(II) has a $4d^9$ configuration and Au(III) has a $5d^3$ configuration. Appropriately we also consider these elements as transition elements. Because their chemical behavior is quite similar to that of other transition element.

Properties of transition metal:

(i) Common properties of transition metal:

- (1) They are metals
- (2) They are practically hard, strong, high melting, high-boiling metal that conduct heat and electricity.
- (3) They form alloy with one another and other metallic elements.
- (4) Many of them are sufficiently electropositive to dissolve in mineral acid, although a few are 'noble' that is, they have such low electrode potentials that they are unaffected by simple acids
- (5) With very few exceptions, they exhibit variable valency. Their ions and compounds are coloured in one if not all in oxidation states.
- (6) Because of partially filled shells they form at least some paramagnetic compounds

This large number of transition elements is subdivided into three main groups

(i) The main transition elements or *d*-block elements.

(ii) The lanthanide elements.

(iii) The actinide elements.

General Electronic Configuration of transition elements is $(n-1)d^{1-10} ns^{0-2}$.

The main transition group or *d*-block include those elements that have partially filled *d*-shells only.

Group	3	4	5	6	7	8	9	10	11	12
3d-series or 1 st transition series	Sc(21) $3d^1 4s^2$	Ti(22) $3d^2 4s^2$	V(23) $3d^3 4s^2$	Cr(24) $3d^5 4s^1$	Mn(25) $3d^5 4s^2$	Fe(26) $3d^6 4s^2$	Co(27) $3d^7 4s^2$	Ni(28) $3d^8 4s^2$	Cu(29) $3d^{10} 4s^1$	Zn(30) $3d^{10} 4s^2$
4d-series or 2 nd transition series	Y(39) $4d^1 5s^2$	Zr(40) $4d^2 5s^2$	Nb(41) $4d^2 5s^2$	Mo(42) $4d^5 5s^1$	Tc(43) $4d^5 5s^2$	Ru(44) $4d^7 5s^1$	Rh(45) $4d^8 5s^1$	Pd(46) $4d^{10} 5s^0$	Ag(47) $4d^{10} 5s^1$	Cd(48) $4d^{10} 5s^2$
5d-series or 3 rd transition series	La(71) $5d^1 6s^2$	Hf(72) $4f^{14} 5d^2 6s^2$	Ta(73) $5d^3 6s^2$	W(74) $5d^4 6s^2$	Re(75) $5d^5 6s^2$	Os(76) $5d^6 6s^2$	Ir(77) $5d^7 6s^2$	Pt(78) $5d^9 6s^1$	Au(79) $5d^{10} 6s^1$	Hg(80) $5d^{10} 6s^2$
6d-series or 4 th transition series	Ac(89) $6d^1 7s^2$	Rf(104) $5f^{14} 6s^2 7s^2$	Db(105) $6d^3 7s^2$	Sg(106) $6d^4 7s^2$	Bh(107) $6d^5 7s^2$	Hs(108) $6d^6 7s^2$	Mt(109) $6d^7 7s^2$	Ds(110)	Ag(111)	

(ii) Atomic and Ionic Radii:

The atomic and ionic radii decrease from Sc to Cu but the variation is small. The outermost electron configuration is $(n-1)d^x ns^2$. The screening power of d orbitals is small and electrons are being added in inner orbitals $(n-1)d$ orbitals. Therefore, change in atomic and ionic radii both are small.

Atomic Radii:

Variation in atomic radii can be tabulated as:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$r(\text{\AA})$	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25

Ionic Radii:

Variation in ionic radii can be tabulated as:

	Ti^{+2}	V^{+2}	Cr^{+2}	Mn^{+2}	Fe^{+2}	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}
$r(\text{\AA})$	0.80	0.73	0.80	0.90	0.85	0.80	0.69	0.76	0.74

In a group the atomic and ionic radii increases with increase in atomic number (because new orbitals are added in the configuration). It is followed in the first and the second transition series. But the radii of the third transition series elements are almost equal to the second transition series elements. The reason for this equality in radii is the lanthanide contraction. Atomic radii of transition elements are as shown below:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$r(\text{\AA})$	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.16	1.17	1.25
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$r(\text{\AA})$	1.62	1.45	1.34	1.29	-	1.25	1.28	1.28	1.34	1.41
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$r(\text{\AA})$	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

(iii) Bonding in Transition metal and its effect on properties:

All transition elements are metals. They have high melting, high boiling and have high heat of atomization and high densities. All these properties show that the atom in transition element are held together by strong metallic bonds. The strength of metallic bond mainly depends upon number of valence electrons. Larger the number of valence electrons stronger is the metallic bond.

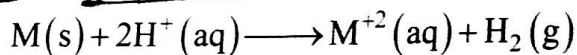
(iv) Melting point of Transition metal:

5d metals have highest m.p. as melting point increases with increase in number of unpaired electron in d-orbitals and then decreases, when number of unpaired electrons in d-orbitals decrease.

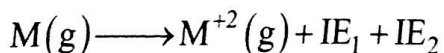
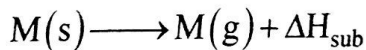
Mn and Tc show anomalous behaviour due to same e/r ratio as they belongs to same period.

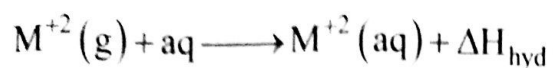
(v) Electrode Potential:

The stability of an oxidation state in aqueous medium depends very much on E^0 value.



The reaction can also be represented as





Therefore, $E = \Delta H_{\text{sub}} + (IE_1 + IE_2) + \Delta H_{\text{hyd}}$ ✓

As variation of these properties is not regular variation of E^0 is also not regular for +2 oxidation state (acid medium).

$M^{+2} + 2e^- \rightarrow M$	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Volts	-1.6	-1.18	-0.91	-1.18	-0.44	-0.28	-0.24	+0.34

(vi) Oxidation State:

All transition metals exhibit variable oxidation state. It arises due to removal of electrons from inner orbital.

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

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