

## b) Variation in Atomic & Ionic sizes of Transition metals.

i) Atomic radius decrease in radius with increasing atomic number. Since new electron enters a d-orbital each time the nuclear charge increases by unity.

ii)  $3d < 4d < 5d$   
This phenomenon is associated with intervention of 4f orbitals which must be filled before 5d series of element. The filling of 4f before 5d orbital results in regular decrease in atomic radii called lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic no.

iii) ~~The decrease~~ The decrease in atomic radii in the beginning is due to the increase in effective nuclear charge, with increase in atomic no. However, with the increase in the no. of electrons in  $(n-1)d$ -subshell, the screening effect of these d-electrons on the outermost ns-electrons also increases so, increased screening effect neutralises increased effective nuclear charge. So atomic radii remain constant in the middle of the series.

iv) Increase in atomic radii towards the end is due to inter-electronic repulsions. The pairing-repulsive interactions between the paired electrons in the d-orbitals of penultimate shell become dominant towards the end of the series and cause the expansion of electron cloud, thereby increasing atomic no.

v) Increase in atomic no; the effective ~~charge~~ nuclear charge increases thereby decreasing the radius of ion.

$$\text{Radius} \propto \frac{1}{OS}$$

c) Ionisation Enthalpies - Increase in IE along each series of transition elements from left to right. [Table 8.2]

⇒ Due to increase in nuclear charge, smaller size, IE increases from left to right.

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3.$$

Table 8.2: Electronic Configurations and some other Properties of the First Series of Transition Elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration										
M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
$M^+$	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
$M^{2+}$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
$M^{3+}$	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	-	-
Enthalpy of atomisation, $\Delta_a H^\circ / \text{kJ mol}^{-1}$	326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy/ $\Delta_i H^\circ / \text{kJ mol}^{-1}$										
$\Delta_i H^\circ$ I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\circ$ II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\circ$ III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm										
M	164	147	135	129	137	126	125	125	128	137
$M^{2+}$	-	-	79	82	82	77	74	70	73	75
$M^{3+}$	73	67	64	62	65	65	61	60	-	-
Standard electrode potential $E^\circ / \text{V}$										
$M^{2+}/M$	-	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
$M^{3+}/M^{2+}$	-	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-
Density/ $\text{g cm}^{-3}$	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1