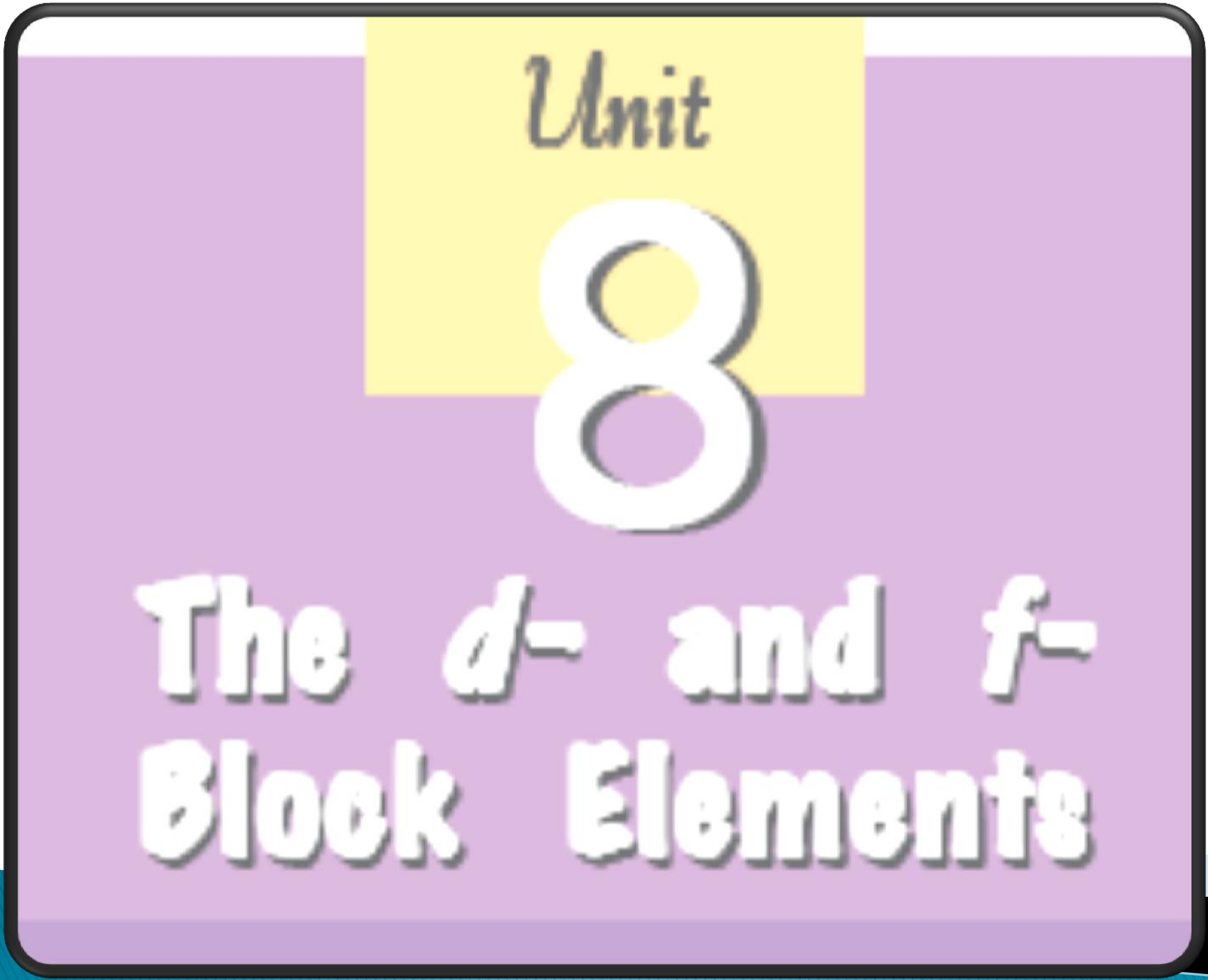

Unit

8

The *d*- and *f*- Block Elements

Unit VIII: d and f Block Elements

Syllabus

- General introduction, electronic configuration, occurrence and characteristics of transition metals,
- general trends in properties of the first row transition metals – metallic character, ionization
- enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial
- compounds, alloy formation. Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.
- *Lanthanoids: electronic configuration, oxidation states, chemical reactivity and lanthanoid* contraction.
- *Actinoids: Electronic configuration, oxidation states.*

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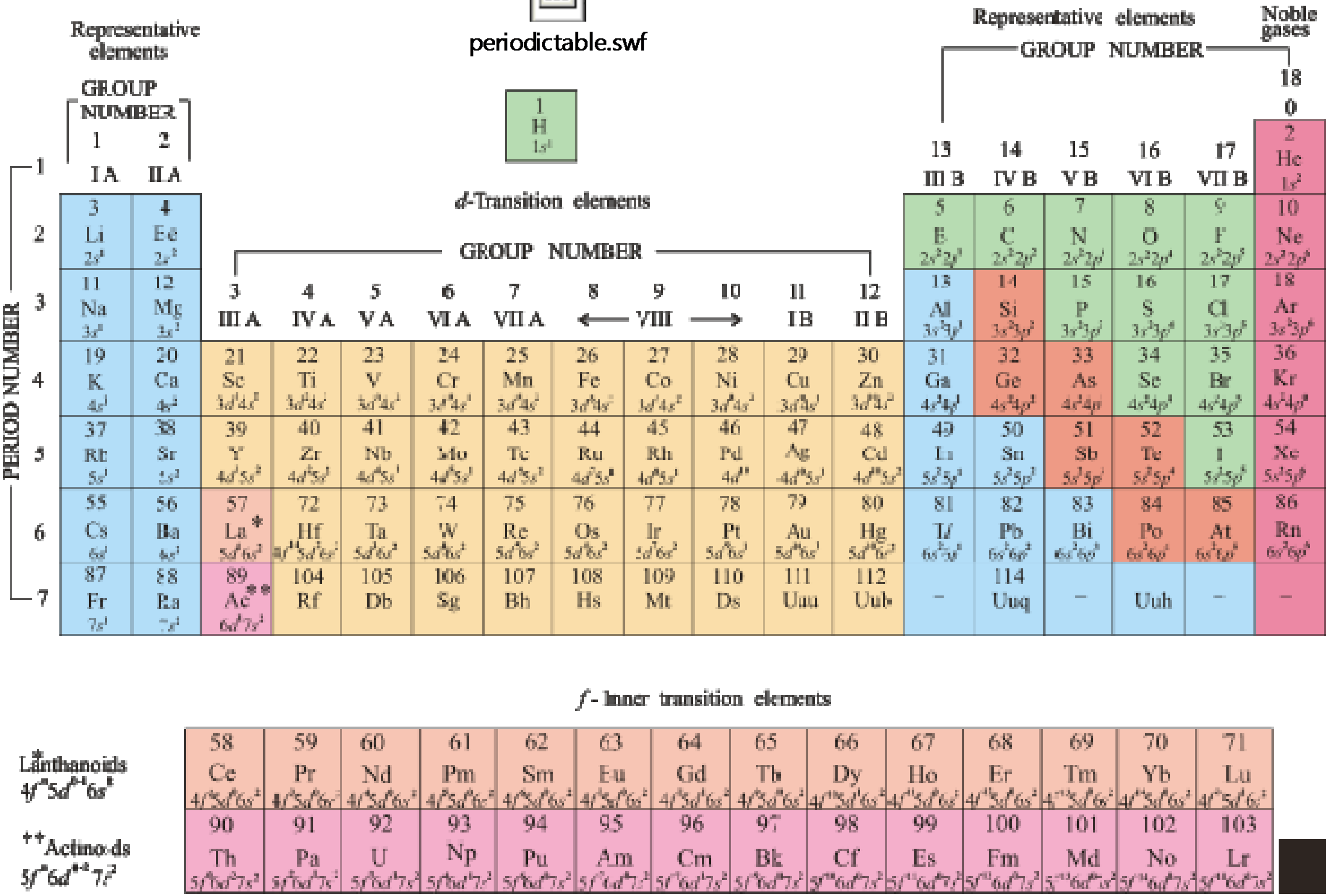
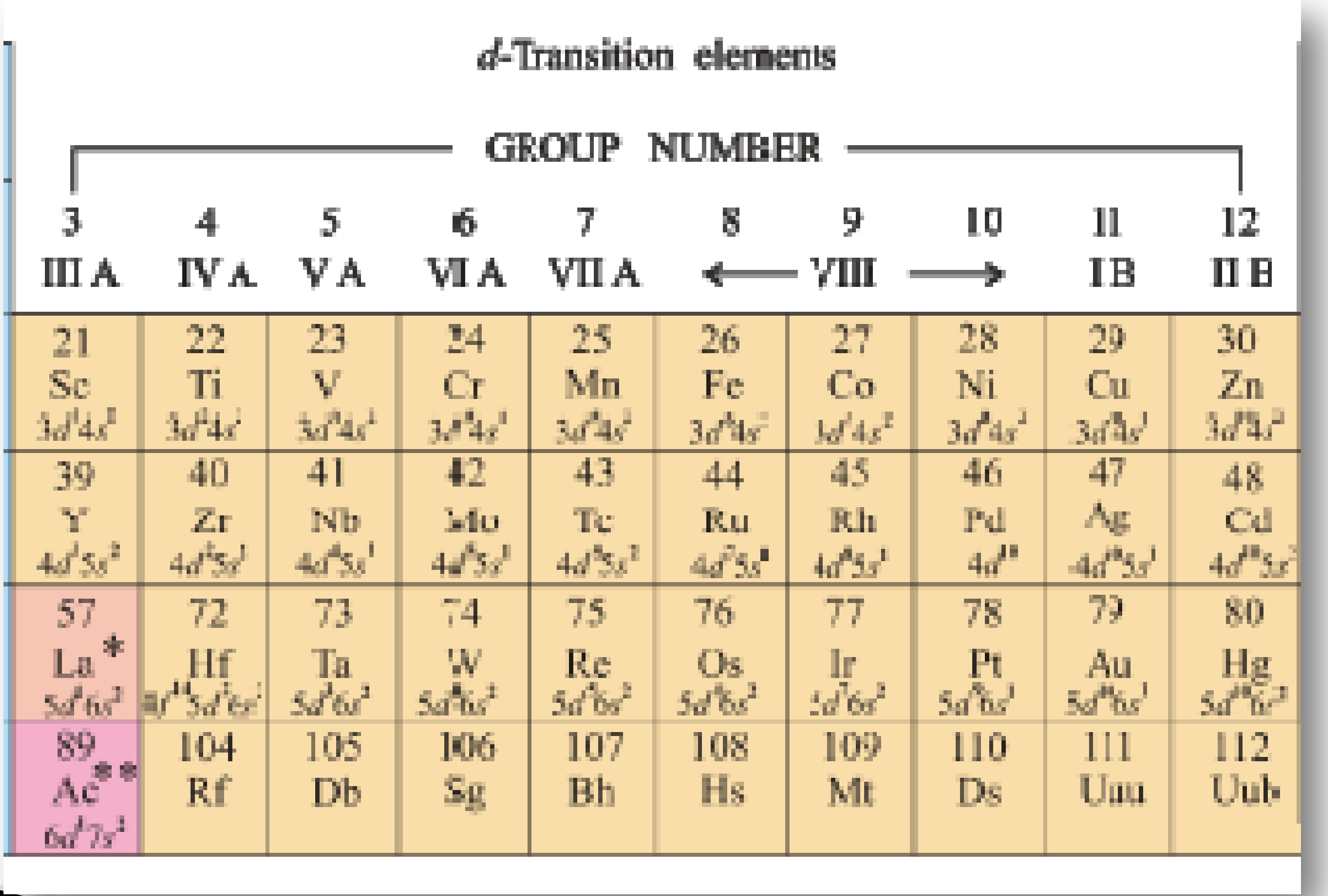


PERIOD NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	←	VIII	→	IB	IIB	III B	IV B	V B	VI B	VII B	0
	Representative elements		*d*-Transition elements										Representative elements					Noble gases
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	–	114 Uuq	–	Uuh	–	–

f - Inner transition elements

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^15d^16s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

d Block Elements



d-Transition elements

GROUP NUMBER

3	4	5	6	7	8	9	10	11	12
III A	IV A	V A	VI A	VII A	←	VIII	→	I B	II B
21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$
39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$
57 La * $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$
89 Ac ** $6d^1 7s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub

- The names *transition metals and inner transition* metals are often used to refer to the elements of *d-and f-blocks respectively.*
- There are mainly three series of the transition metals,
- **3d series (Sc to Zn),**
- **4d series (Y to Cd) and**
- **5d series (La to Hg, omitting Ce to Lu).**
- The fourth 6*d* series which begins with Ac is still incomplete.
- The two series of the inner transition metals, (4*f and 5f) are* known as ***lanthanoids*** *and* ***actinoids*** *respectively.*

- Transition element is defined as the one which has incompletely filled *d orbitals in its* ground state or in any one of its oxidation states.
- **Zinc, cadmium** and **mercury** of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.
- Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium form part of the transition metals.

Electronic Configurations of the d-Block Elements

- general the electronic configuration of these elements is
  - $(n\text{-}1)d^{1-10}ns^{1-2}$
- *The (n–1) stands for the inner d orbitals which may have* one to ten electrons and the outermost ns *orbital may have one or two* electrons.
- However, this generalisation has several exceptions because of very little energy difference between (n-1)*d and ns orbitals.*
- Furthermore, half and completely filled sets of orbitals are relatively more stable.

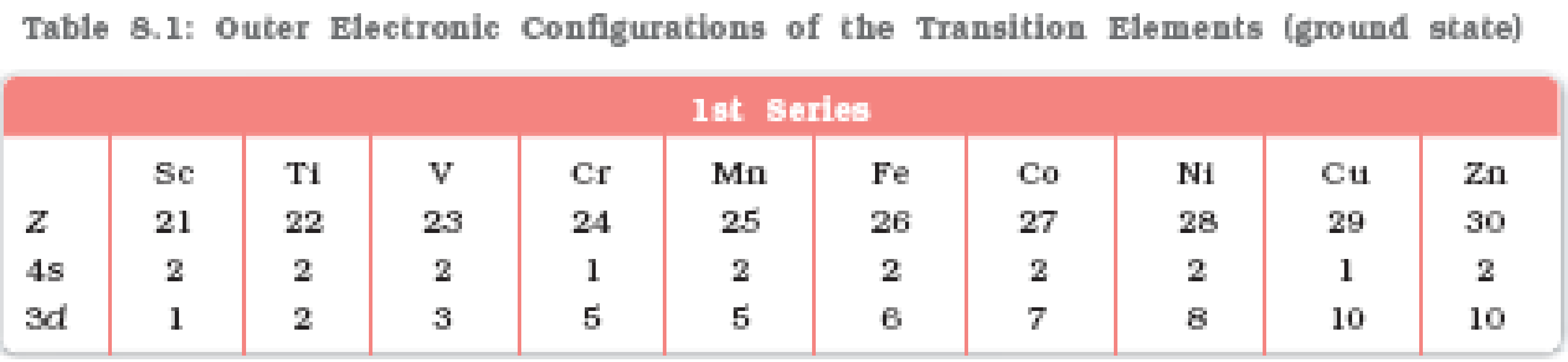
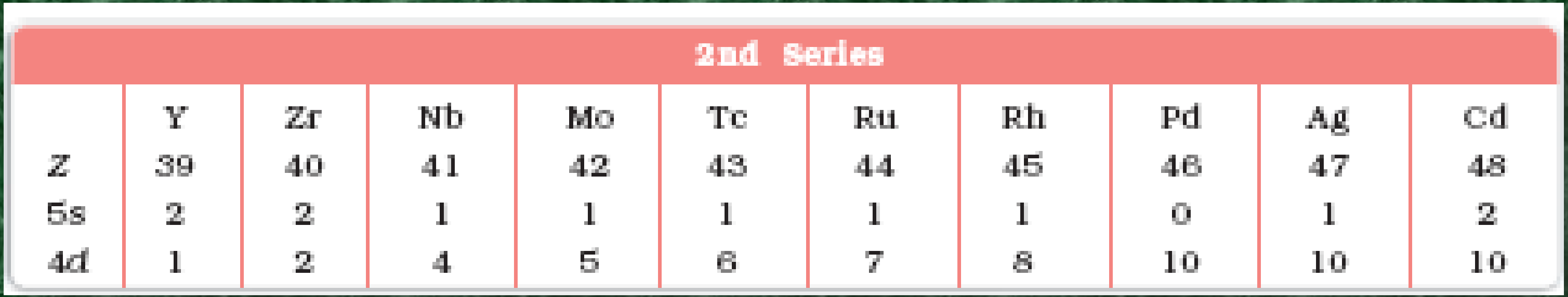
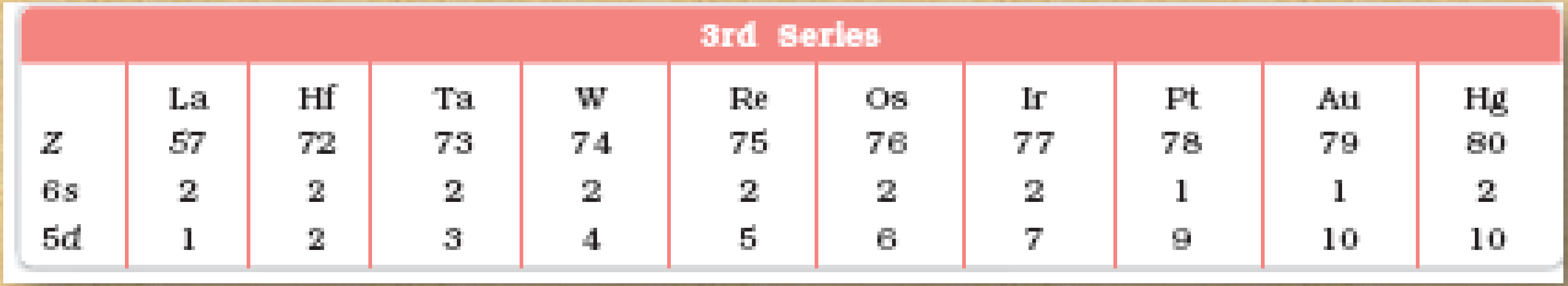


Table 8.1: Outer Electronic Configurations of the Transition Elements (ground state)

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

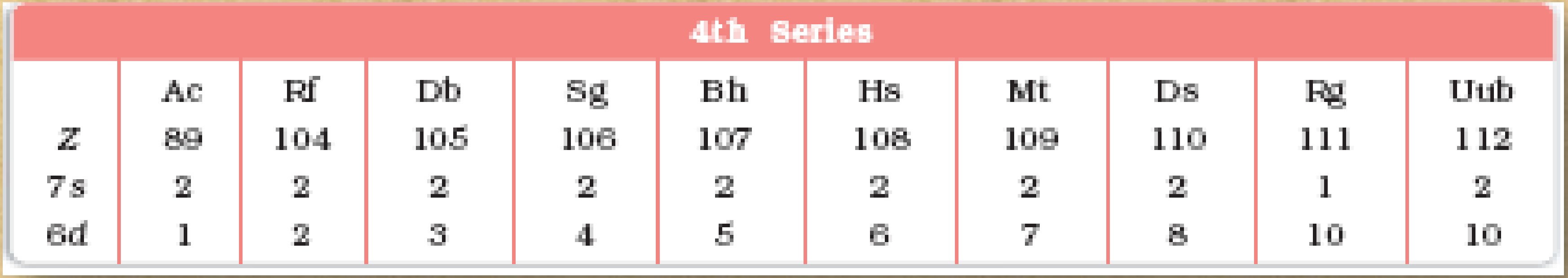


2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10



3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10



4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

Q. Why Zn, Cd and Hg are not regarded as transition elements?

Ans. The electronic configurations of Zn, Cd and Hg are represented by the general formula

$$(n-1)d^{10}ns^{2}.$$

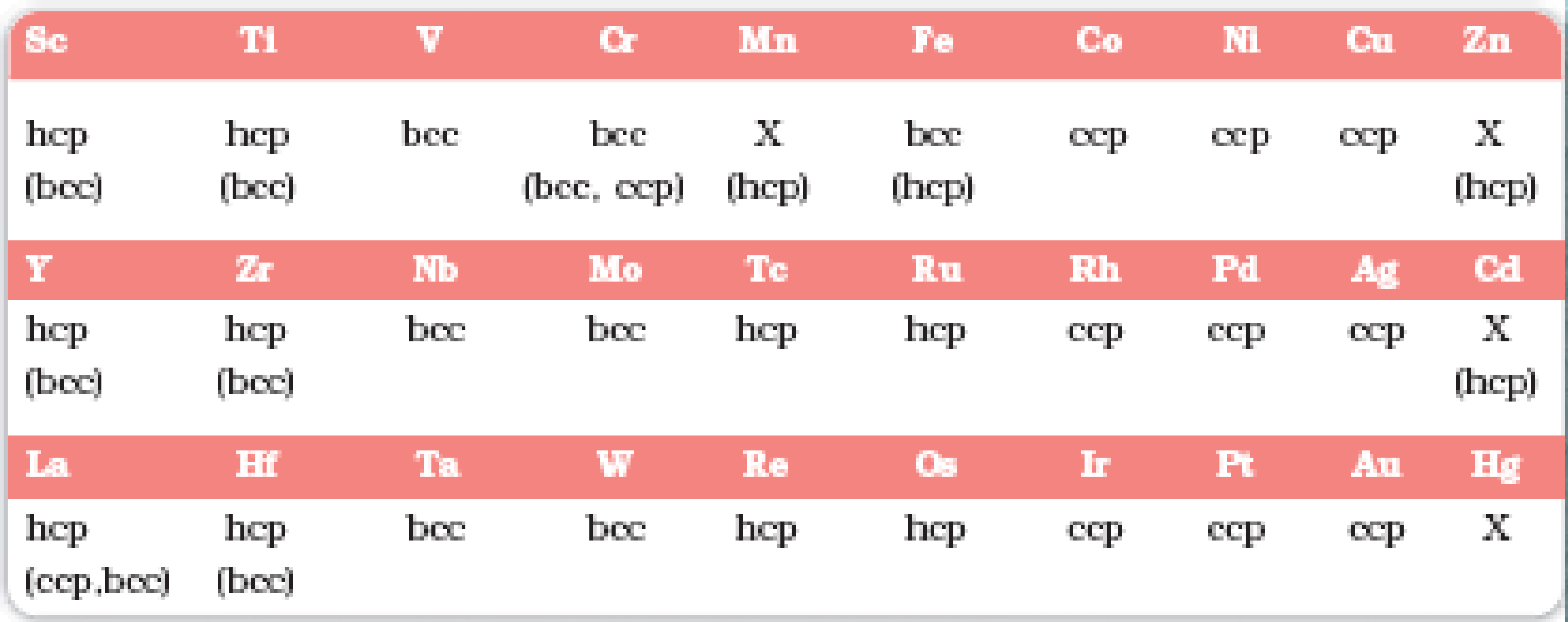
- *The orbitals in these elements are* completely filled in the ground state as well as in their common oxidation states.
- Therefore, they are not regarded as transition elements.

General Properties of the

Transition Elements (d-Block)

- Nearly all the transition elements display typical metallic properties such as
- high tensile strength,
- ductility
- malleability,
- high thermal and electrical conductivity and
- metallic lustre.
- With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

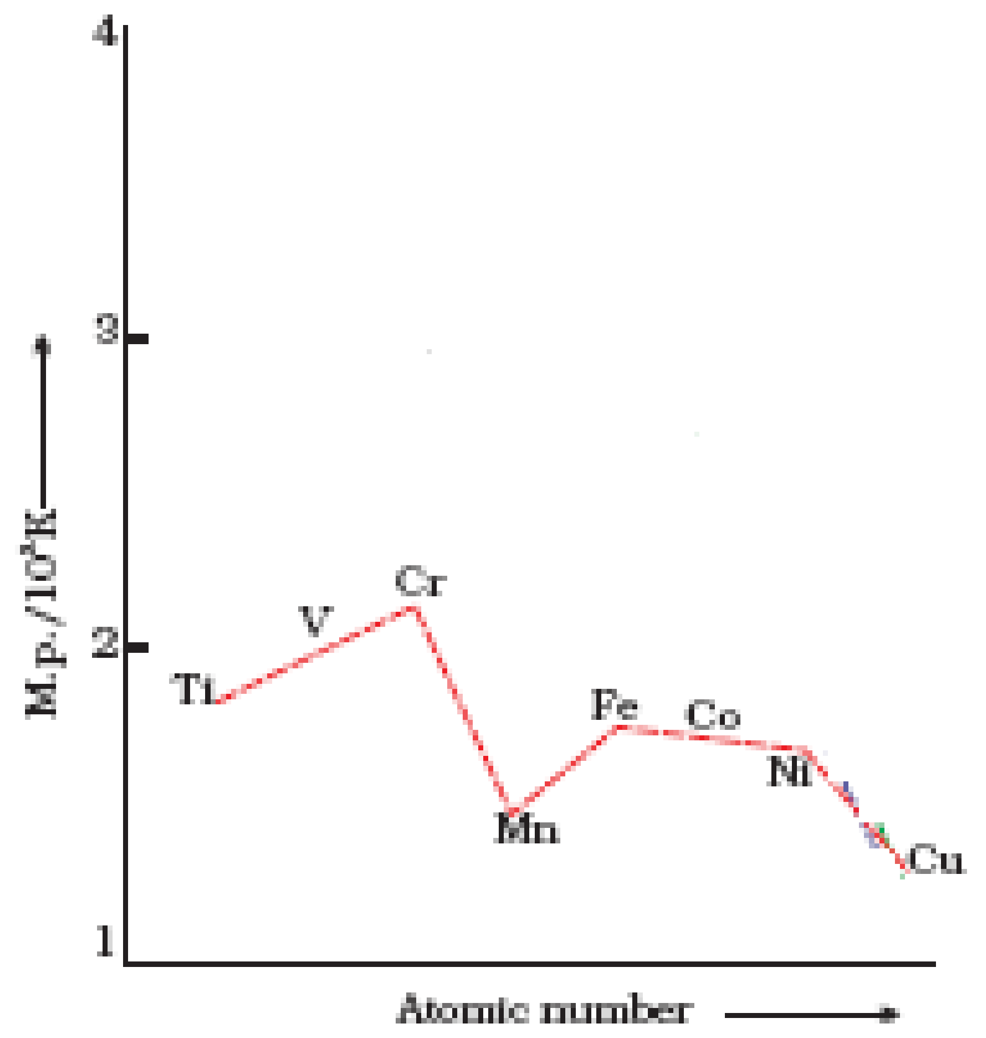
Lattice Structures of Transition Metals



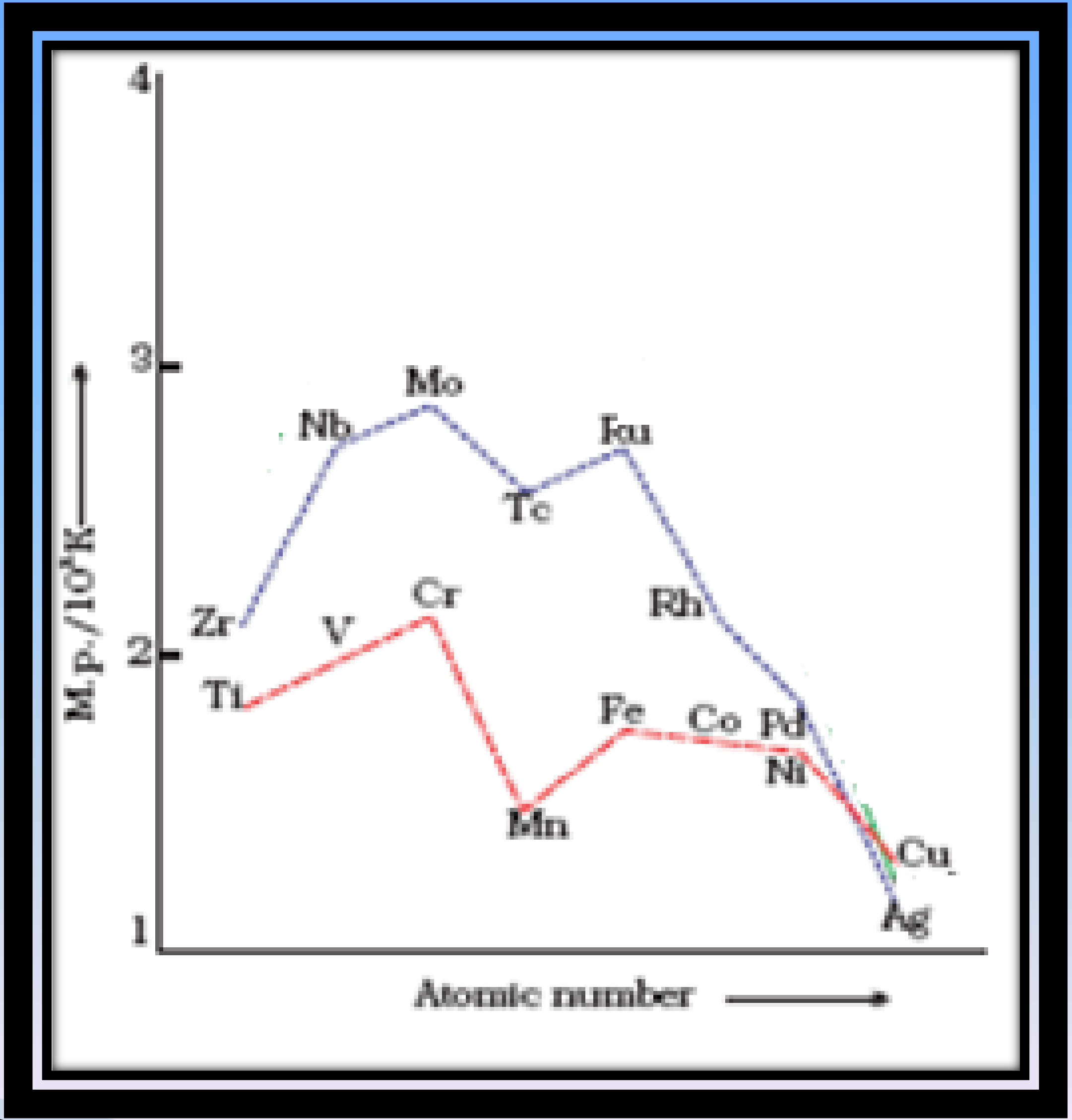
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**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

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

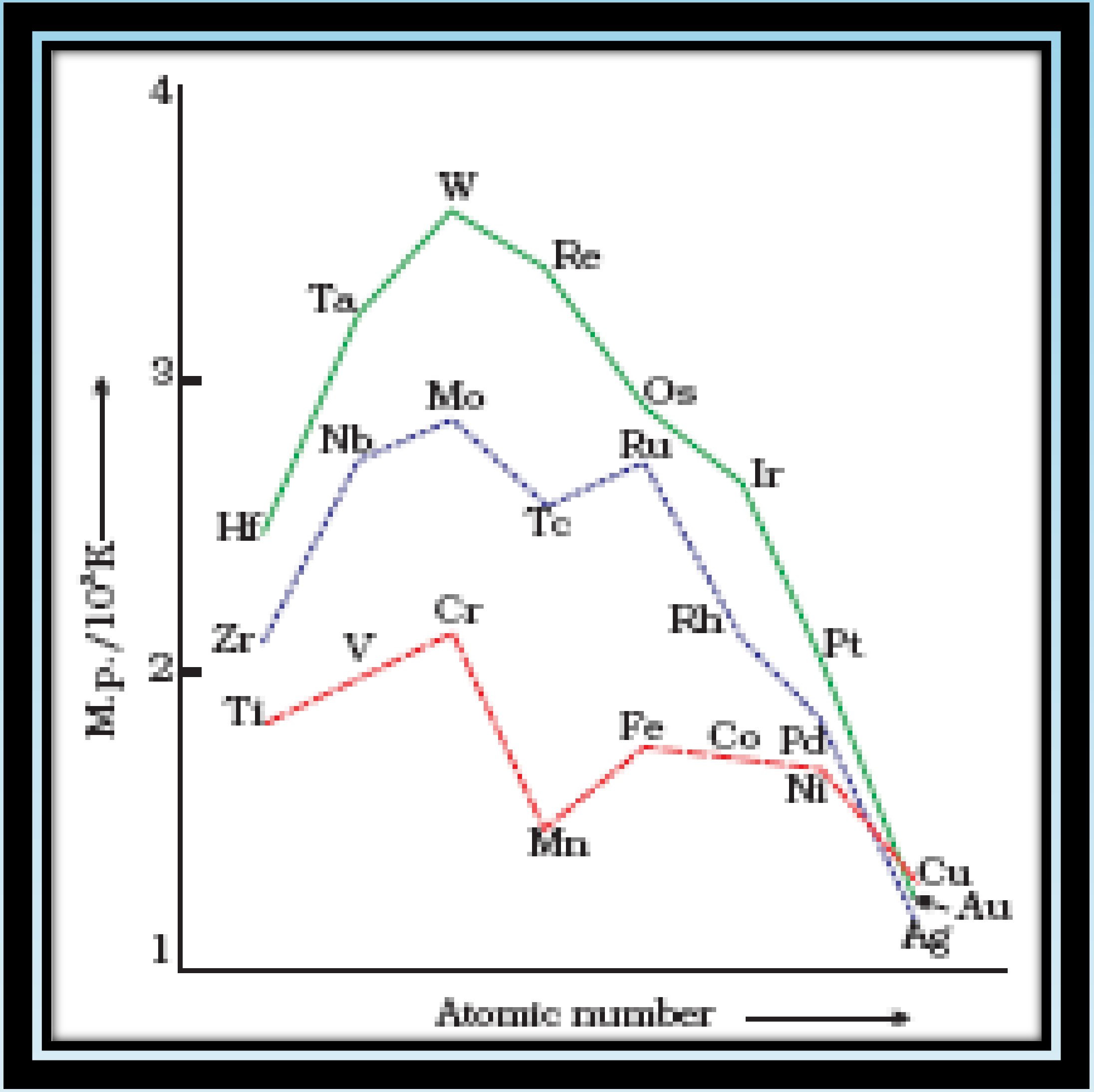
Trends in melting points of transition elements



Trends in melting points of transition elements



Trends in melting points of transition elements



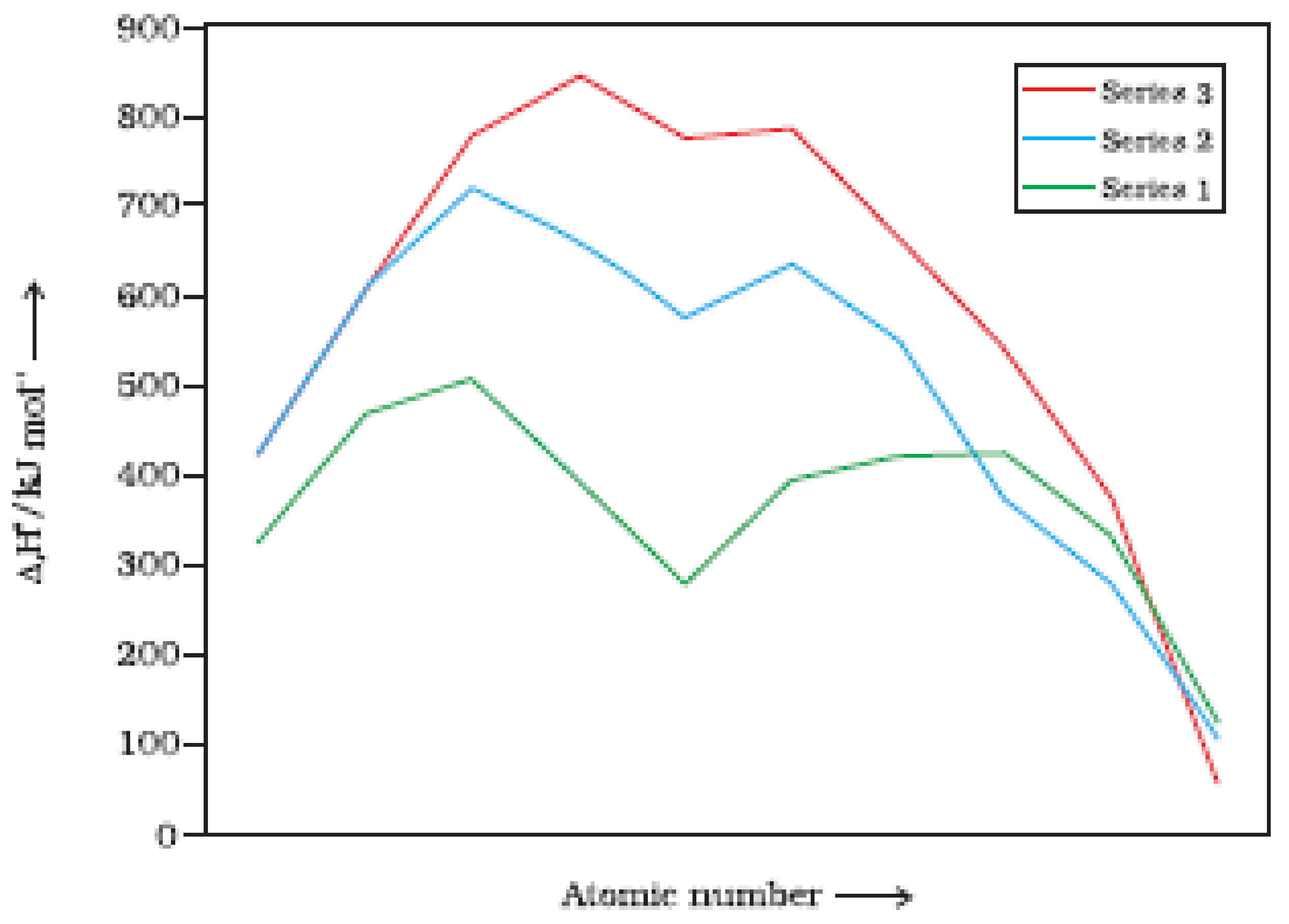
- The transition metals (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.
- **Their melting and boiling points are high.**
- High M.P and B.P - Due to strong metallic bond and the **presence of half filled d- orbitals**
- Involvement of greater number of electrons from **(n-1)*d*** in addition to the **ns** electrons in the inter atomic metallic bonding.
- Because of stronger interatomic bonding =High enthalpy of atomisation =transition elements have high M.P and B.P

- In moving along the period from left to right, the M.P of these metals first **INCREASES** to MAXIMUM and the **DECREASES** regularly towards the end of the period.
- melting points of these metals rise to a maximum at d^5 except for anomalous values of **Mn and Tc** and fall regularly as the atomic number increases.

TRENDS OF M.P OF 3- d , 4-d AND 5-d TRANSITION METALS

- The strength of interatomic bonds in transition elements is roughly related to the ***number of half filled d- orbitals***
- In the beginning the no. of half filled d- orbitals increases till the middle of the period causing increase in strength of interparticle bonds But **thereafter the pairing of electrons in d – orbitals occurs and the no. of half filled orbitals decreases** . which also cause decrease in M.P

Trends in enthalpies of atomisation of transition elements



1. Greater the number of valence electrons, stronger the inter atomic attraction, **hence stronger bonding between atoms resulting in higher enthalpies of atomization.**

2. metals of the second and third series have greater enthalpies of atomization than the corresponding elements of the first series

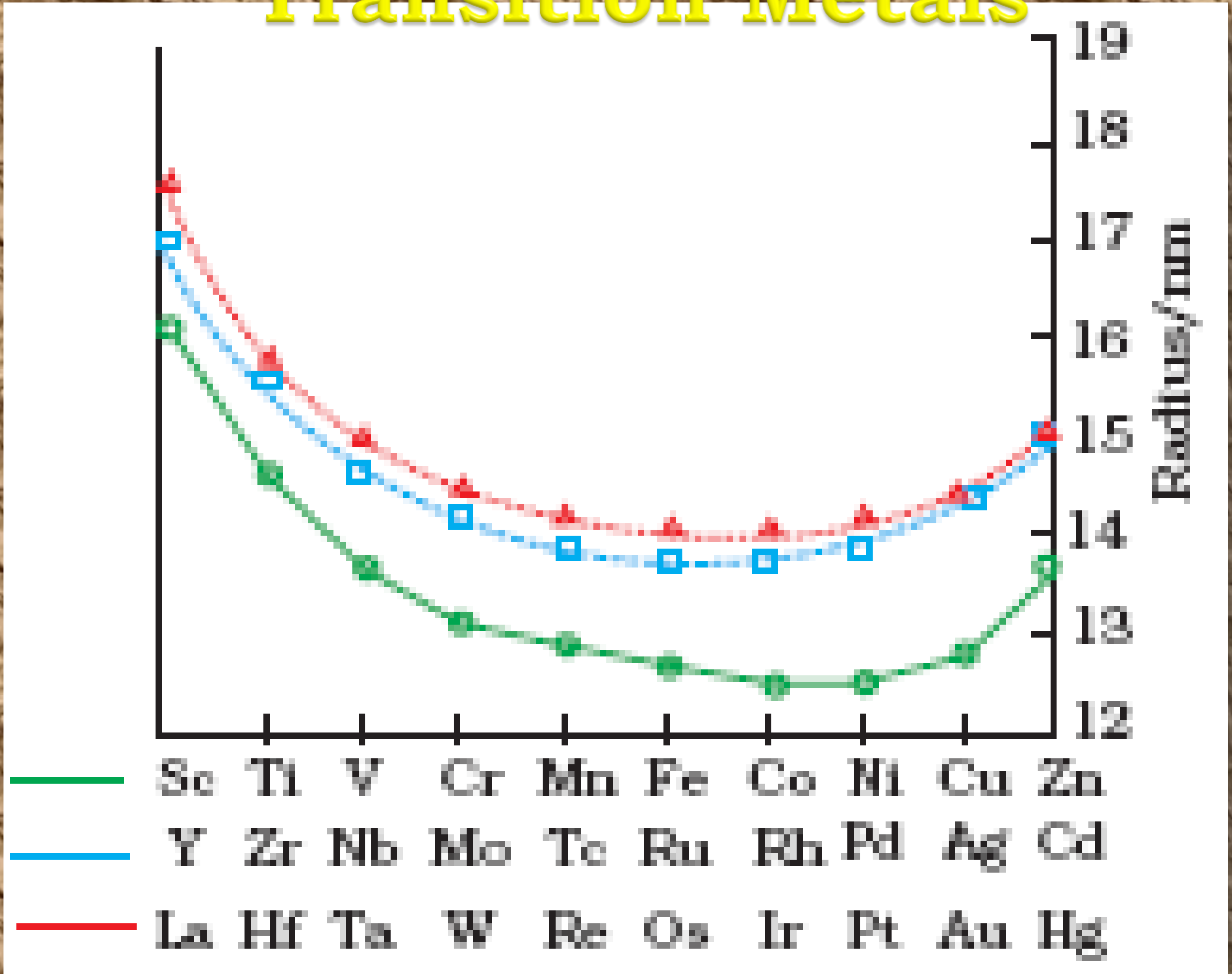
- **Why do the transition elements exhibit higher enthalpies of atomisation?**

- Because of **large number of unpaired electrons** in their atoms they have **stronger interatomic interaction** and hence **stronger bonding** between atoms resulting in higher enthalpies of atomisation.

Trends in melting points of transition elements

- In any row the melting points of these metals rise to a maximum at *d5 except for* anomalous values of Mn and Tc and fall regularly as the atomic number increases.
- They have high enthalpies of atomisation which are shown in previous slide.
- The maxima at about the middle of each series indicate that one unpaired electron per *d orbital is particularly* favourable for strong interatomic interaction.
- In general, greater the number of valence electrons, stronger is the resultant bonding.

Variation in Atomic and Ionic Sizes of Transition Metals



Atomic and ionic radii

- The Atomic/ionic radii first **DECREASES** till the middle, becomes **almost constant** and then **INCREASES** towards the end of the period.
- New electron enters a *d* orbital each time the nuclear charge increases by unity, **But the shielding effect of a *d* electron is not that effective,** hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases

- However the increased nuclear charge is partly cancelled by the **increased screening effect of electrons in the d – orbitals** of penultimate shell.
- When the increased nuclear charge and increased Screening effect balance each other, the atomic radii becomes almost constant.
- Increase in atomic radii towards the end may be attributed to the **electron – electron repulsion**.
- In fact the pairing of electrons in d – orbitals occurs after d^5 configuration.
- The **repulsive interaction** between the **paired electron** causes Increase in Atomic/ ionic radii

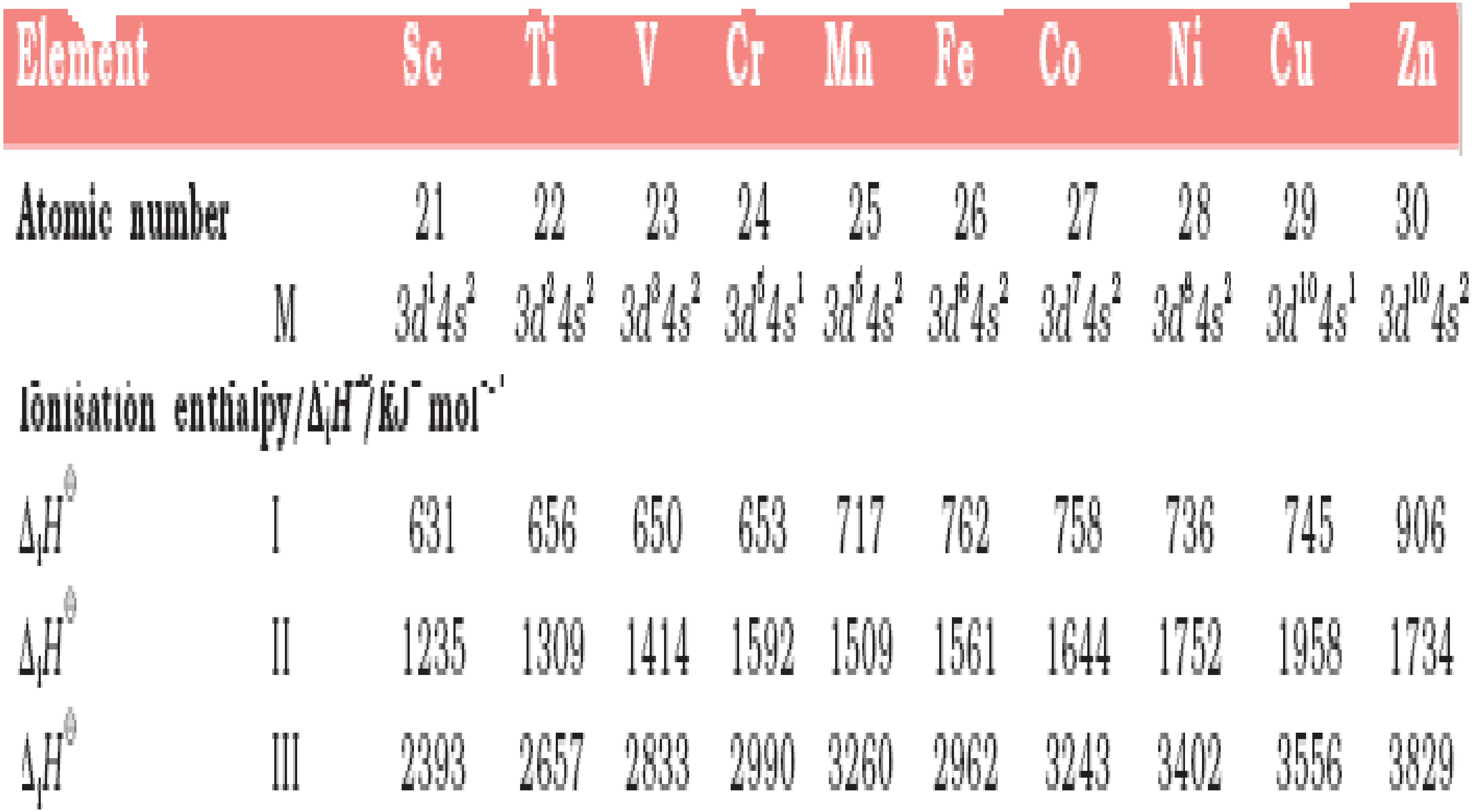
- However the increased nuclear charge is partly cancelled by the **increased screening effect of electrons in the d – orbitals** of penultimate shell.
- When the increased nuclear charge and increased Screening effect balance each other, the atomic radii becomes almost constant.
- • Increase in atomic radii towards the end may be
- attributed to the **electron – electron repulsion**.
- • In fact the pairing of electrons in d – orbitals occurs after d5 configuration.
- • The **repulsive interaction** between the **paired electron** causes Increase in Atomic/ ionic radii

- There is increase from the first (3*d*) to the second (4*d*) series of the elements.
- • But the radii of the third (5*d*) series are virtually the same as 4d
- • This is due to the **intervention of the 4*f* orbital which must be filled before the 5*d* series of elements begin.**
- • There is a steady decrease in atomic radii from La due to the poor shielding of inner core electrons (4f) is known **lanthanoid contraction.**

Ionisation Enthalpies

- Due to an **increase in nuclear charge** there is an **increase in ionisation enthalpy** along each series of the transition elements from left to right.
- • Ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states.
- • Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.
- • Mostly **IE1<IE2 <IE3 in** each group

Ionisation Enthalpies

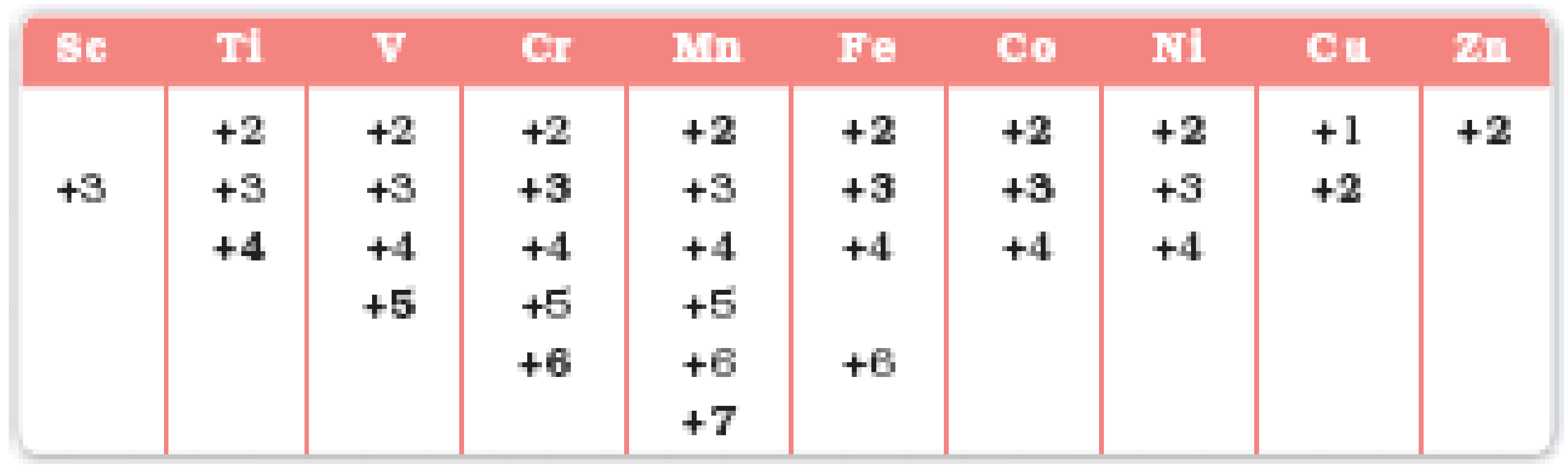


Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Ionisation enthalpy/$\Delta_i H^{\ominus}$/kJ mol^{-1}											
$\Delta_i H^{\ominus}$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^{\ominus}$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^{\ominus}$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

- The increase in IE is primarily due to **increase in nuclear charge**.
- As the transition elements involve the gradual filling of (n-1)d orbitals, the effect of increase in nuclear charge is partly cancelled by the increase in screening effect.
- Consequently, the increase in I.E along the periods of d – block elements is very small

Oxidation States

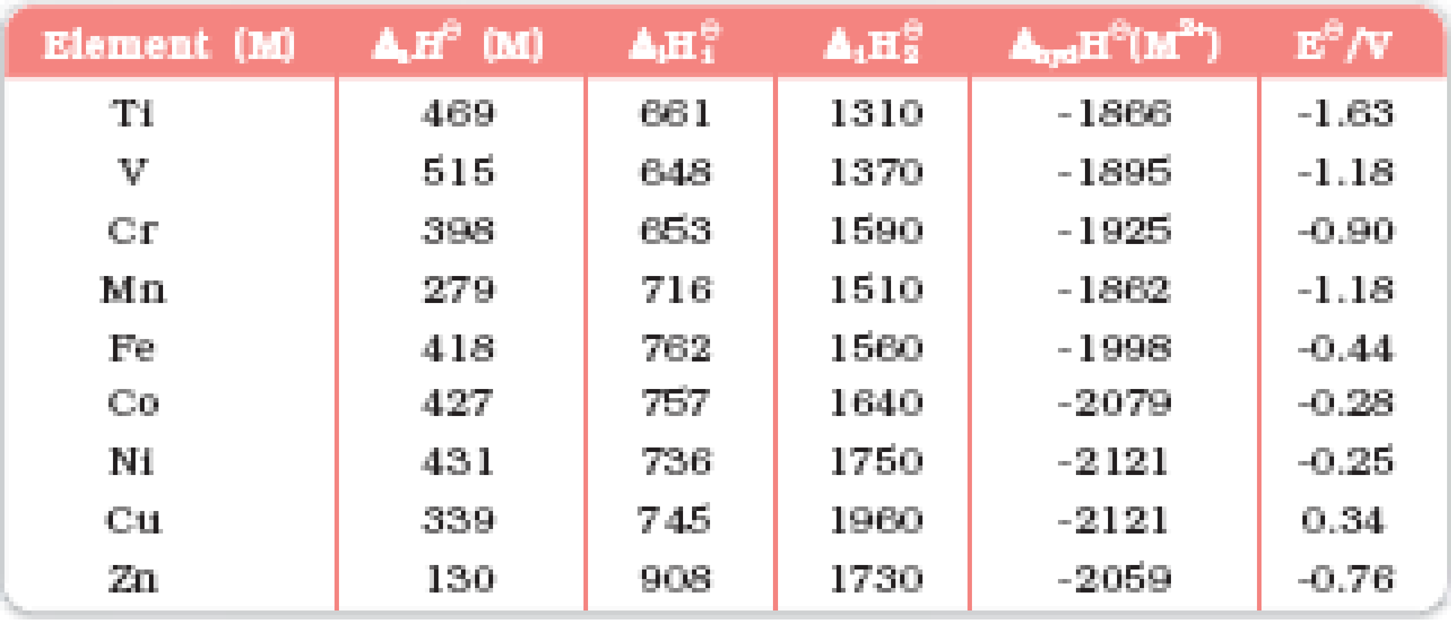
- **Oxidation States of the first row Transition Metals**



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

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.

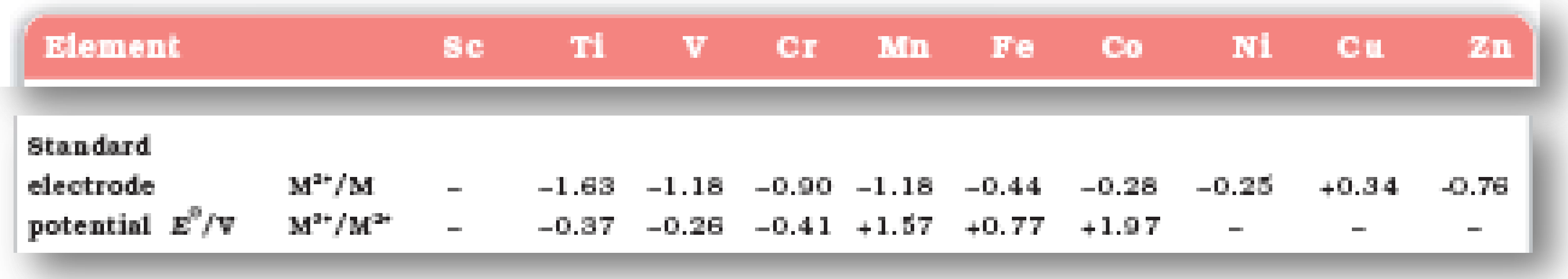
Thermochemical data (kJ mol-1) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of MII to M



Element (M)	$\Delta_a H^\circ$ (M)	$\Delta_i H_1^\circ$	$\Delta_i H_2^\circ$	$\Delta_{hyd} H^\circ(M^{2+})$	E°/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 stability of the half-filled d sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their E^0 values, whereas E^0 for Ni is related to the highest negative $\Delta_{hyd}H^0$.

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



Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Standard electrode potential E°/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	–	–	–

❑The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration.

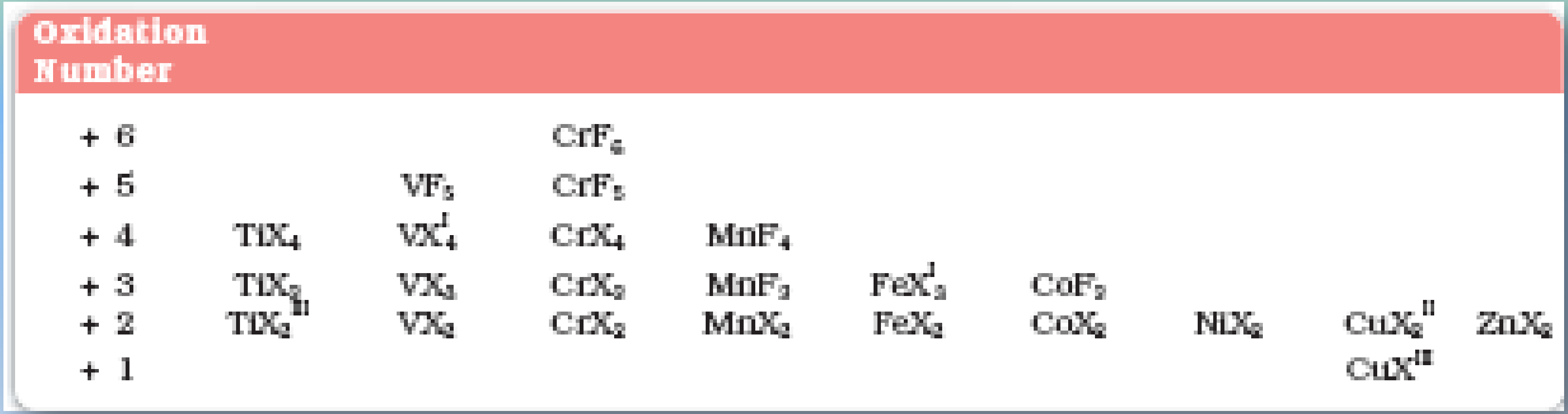
❑ The highest value for Zn is due to the removal of an electron from the stable d^{10} *configuration of* Zn^{2+}.

❑*The* comparatively high value for Mn shows that Mn^{2+}(d^5) *is particularly* stable, whereas comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5).

❑*The comparatively low value for V is related to the stability* of V^{2+}

Trends in Stability of Higher Oxidation States

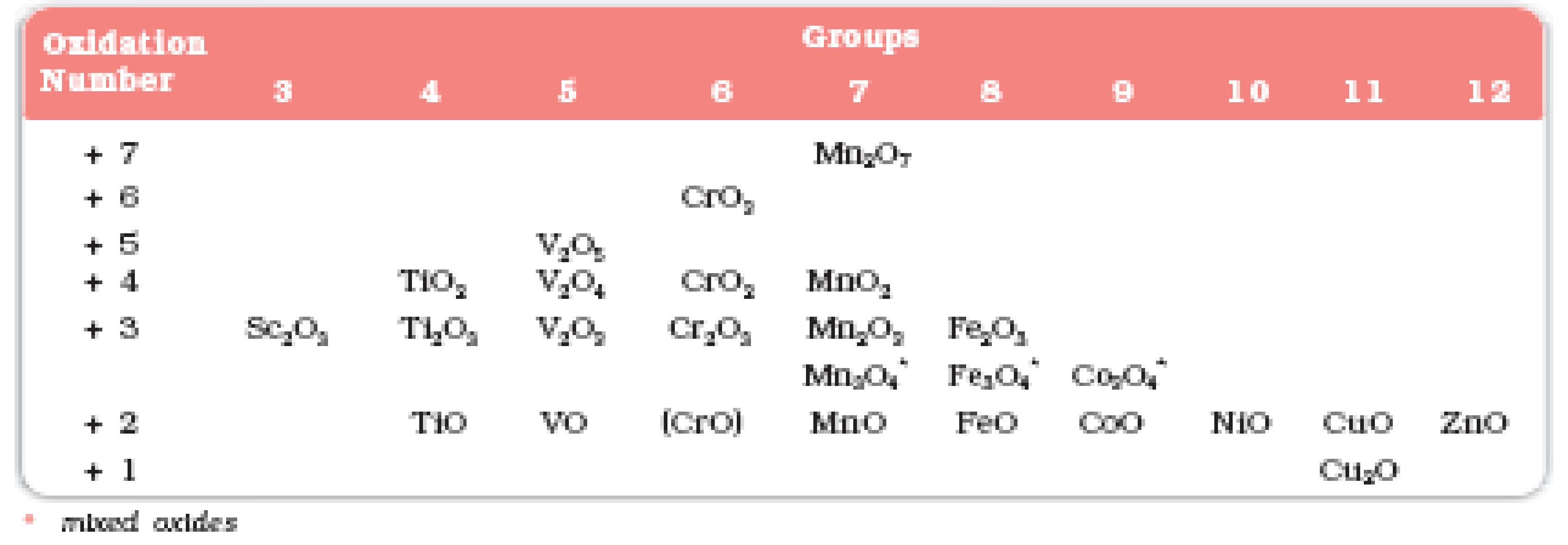
Formulas of Halides of 3*d* Metals



Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX_4^I	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3^I	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+ 1								CuX^{III}	

Key: X = F → I; XI = F → Br; XII = F, Cl; XIII = Cl → I

Oxides of 3d Metals



Oxidation Number	Groups									
	3	4	5	6	7	8	9	10	11	12
+ 7					Mn_2O_7					
+ 6				CrO_3						
+ 5			V_2O_5							
+ 4		TiO_2	V_2O_4	CrO_2	MnO_2					
+ 3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					Mn_3O_4*	Fe_3O_4*	Co_3O_4*			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu_2O	

* *mixed oxides*

The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7.

Chemical Reactivity and E^0 Values

- Transition metals vary widely in their chemical reactivity.

- Many of them are sufficiently electropositive to dissolve in mineral acids,

- Although a few are 'noble'—that is, they are unaffected by simple acids.

Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism and paramagnetism*
- **Diamagnetic** substances are repelled by the applied field while the **paramagnetic** substances are attracted.
- Substances which are attracted very strongly are said to be *ferromagnetic*. *In fact,* ferromagnetism is an extreme form of paramagnetism.
- 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.

Magnetic moment

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). A single unpaired electron has a magnetic moment of **1.73** Bohr magnetons (BM).

Magnetic moment

- The magnetic moment increases with the increasing number of unpaired electrons.
- Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion

1. Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

- Ans:
  - **$\mu = 5(5+2)$**
  - $= 5.92$BM

Magnetic Moments

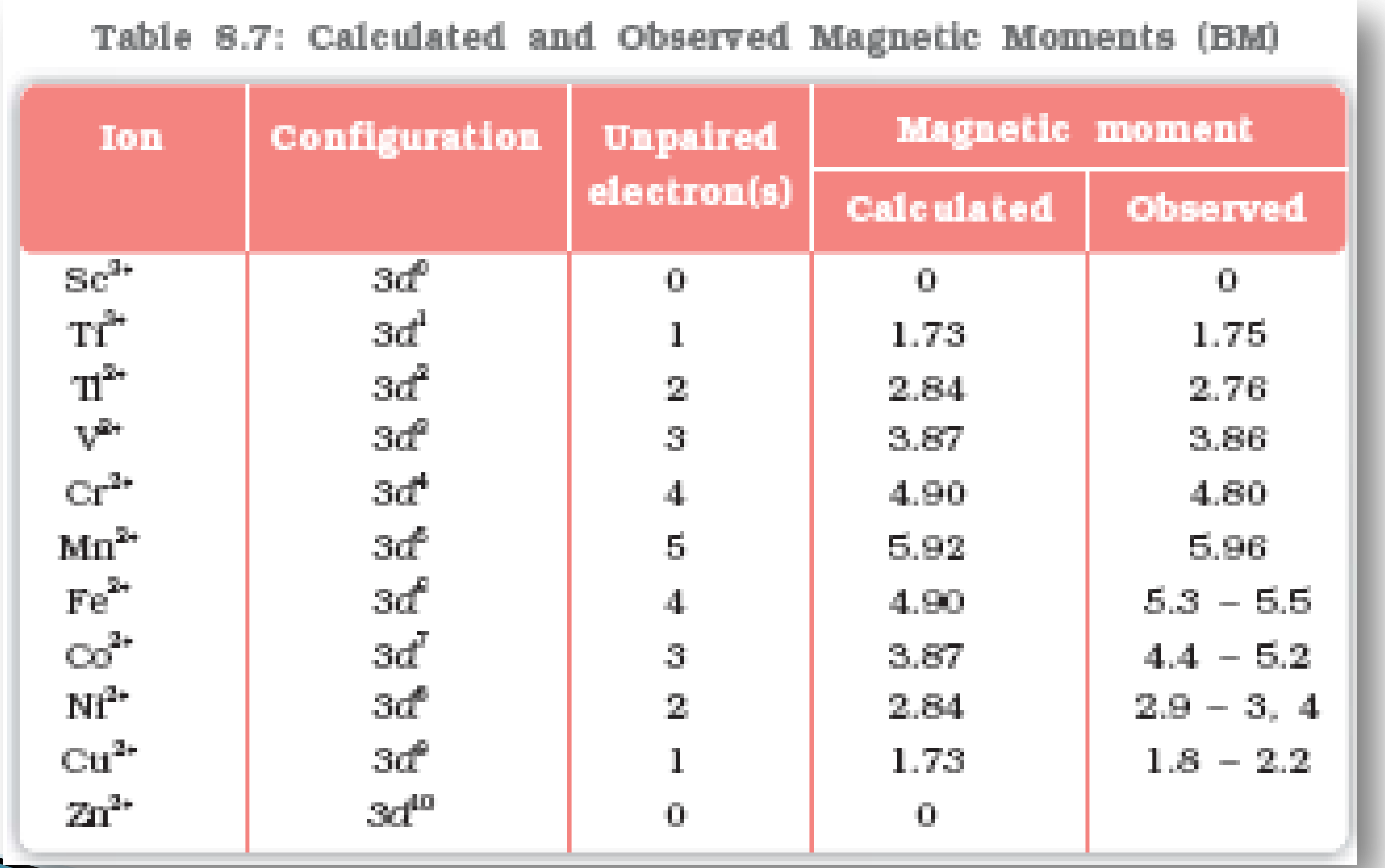


Table 8.7: Calculated and Observed Magnetic Moments (BM)

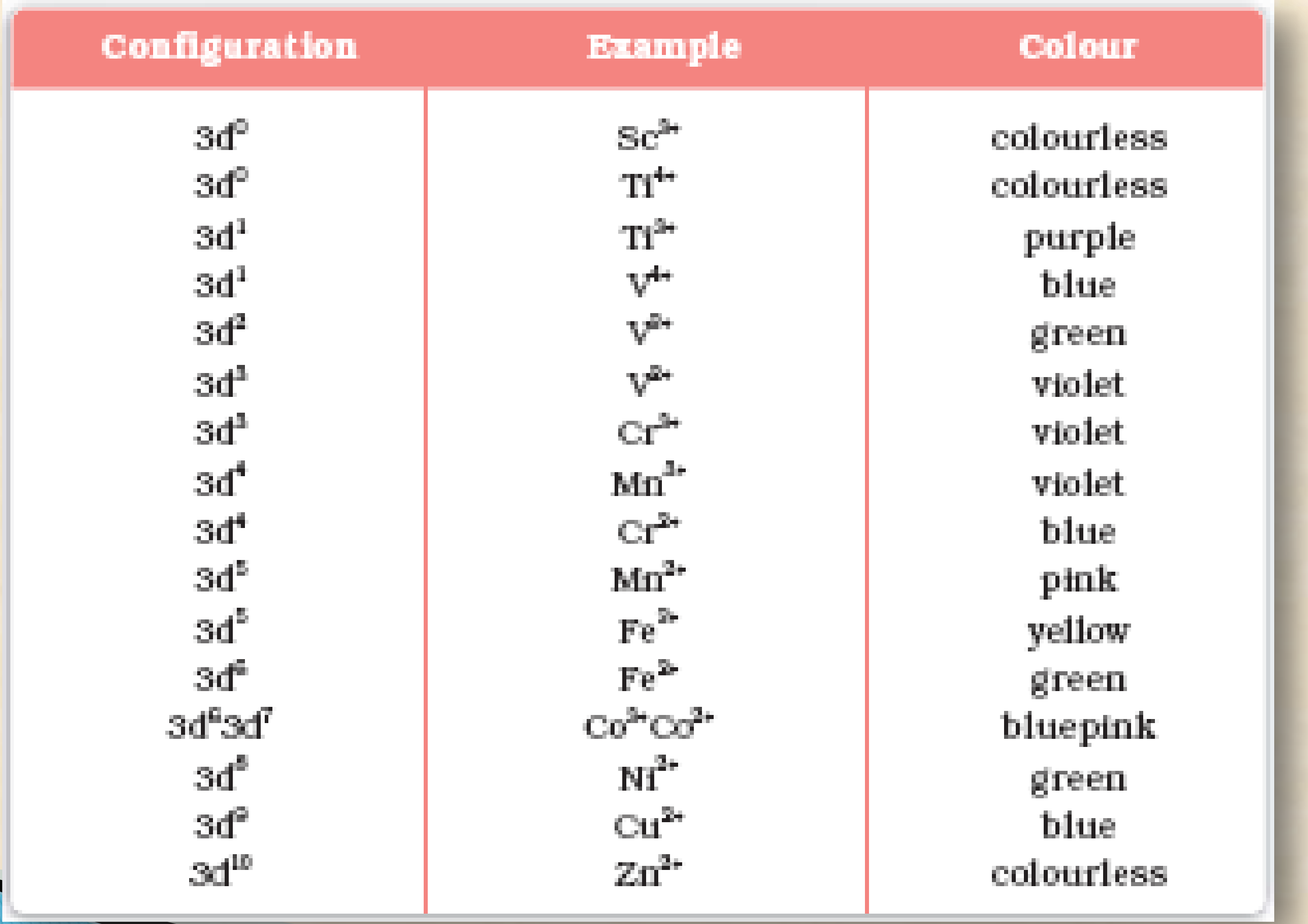
Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

Formation of Coloured Ions

Colours of some of the first row transition metal ions in aqueous solutions.

From left to right: V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} ***and*** Cu^{2+} .

Colours of Some of the First Row (aquated) Transition Metal Ions



Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+} Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

Formation of Complex Compounds

- Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties.

- A few examples are:
- $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$

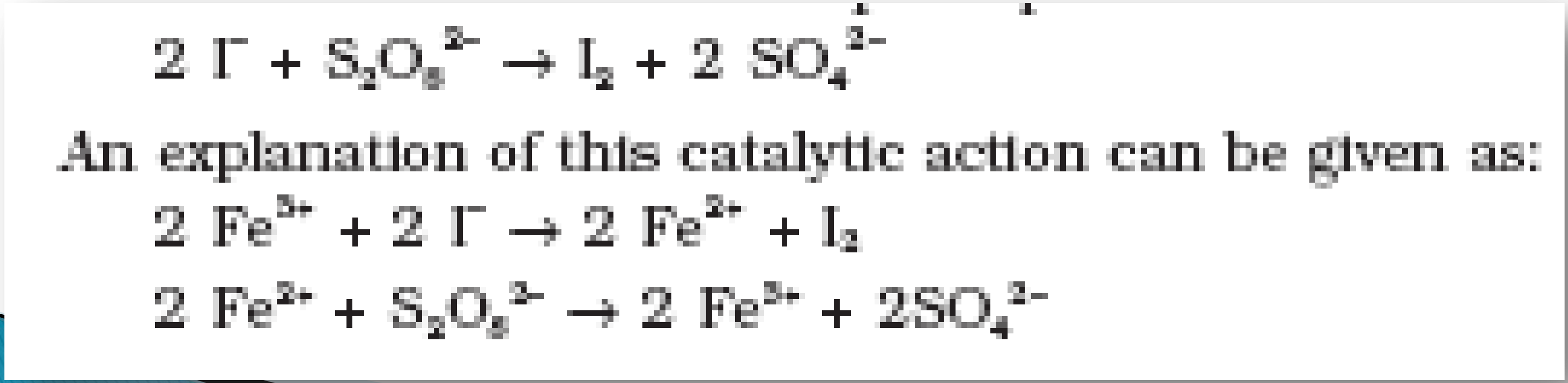
- The transition metals form a large number of complex compounds.

- 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.*

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.
- **Vanadium(V) oxide (in Contact Process),**
- **finely divided iron (in Haber's Process), and**
- **Nickel (in Catalytic Hydrogenation) are some of the examples.**
- Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d and* 4*s electrons for bonding*).

- This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).
- Also because the transition metal ions can change their oxidation states, they become more effective as catalysts.
- For example, iron(III) catalyses the reaction between iodide and persulphate ions.



$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2SO_4^{2-}$$

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, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.
- Because of the nature of their composition, these compounds are referred to as *interstitial compounds*.

Physical and chemical characteristics of Interstitial Compounds

- (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 are readily formed by these metals.
- The alloys so formed are hard and have often high melting points.
- The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel.
- 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

- **Oxides and Oxoanions of Metals**
- These oxides are generally formed by the reaction of metals with oxygen at high temperatures.
- All the metals except scandium form MO oxides which are ionic.
- The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7.

Potassium dichromate $K_2Cr_2O_7$

- Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds.

- Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air.

- The reaction with sodium carbonate occurs as follows

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

- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7 . 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

•Sodium dichromate is more soluble than potassium dichromate.

•The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

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

- Orange crystals of potassium dichromate crystallise out.

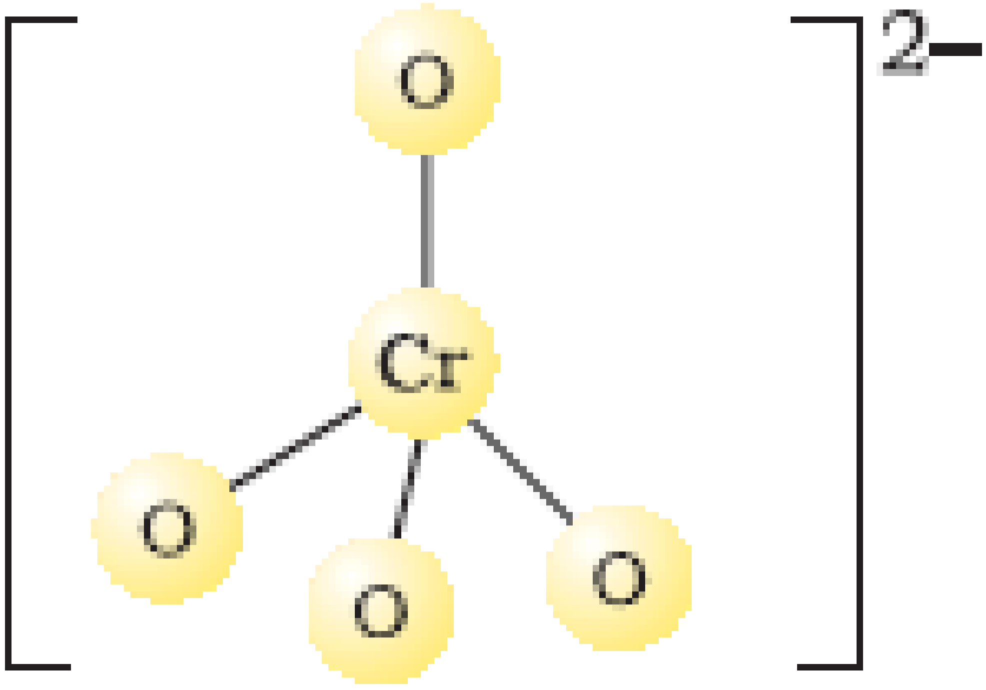
- The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

- The oxidation state of chromium in chromate and dichromate is the same.

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

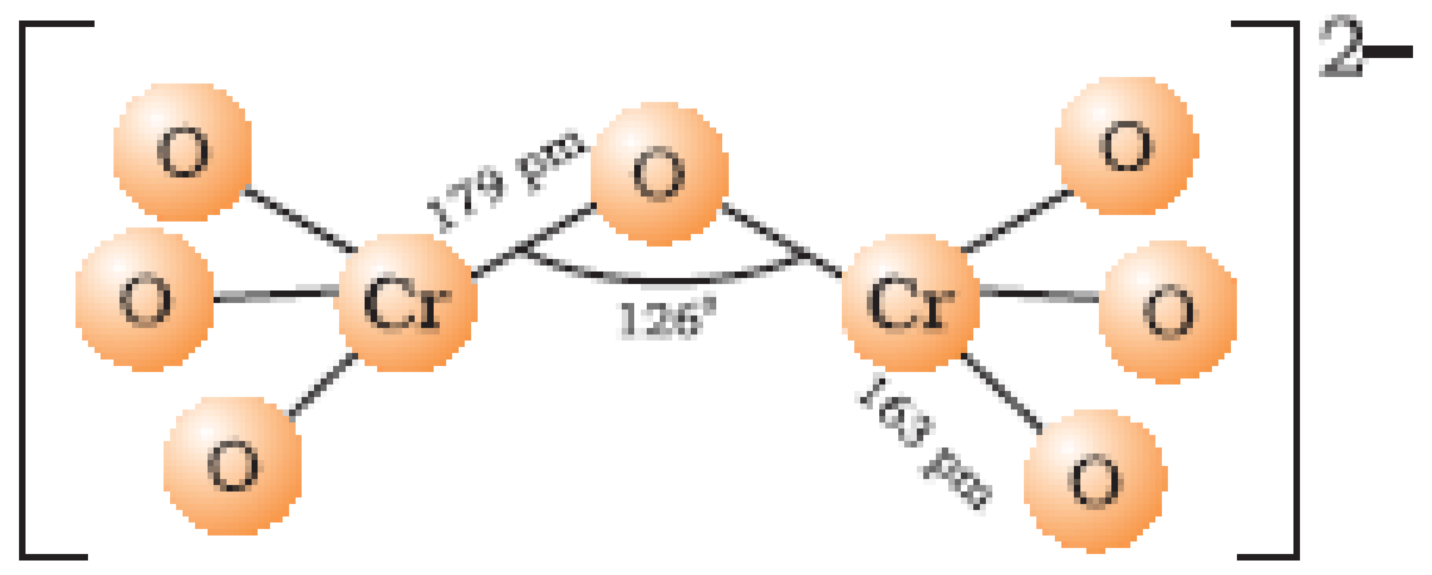
$$Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$$

The structure of chromate ion

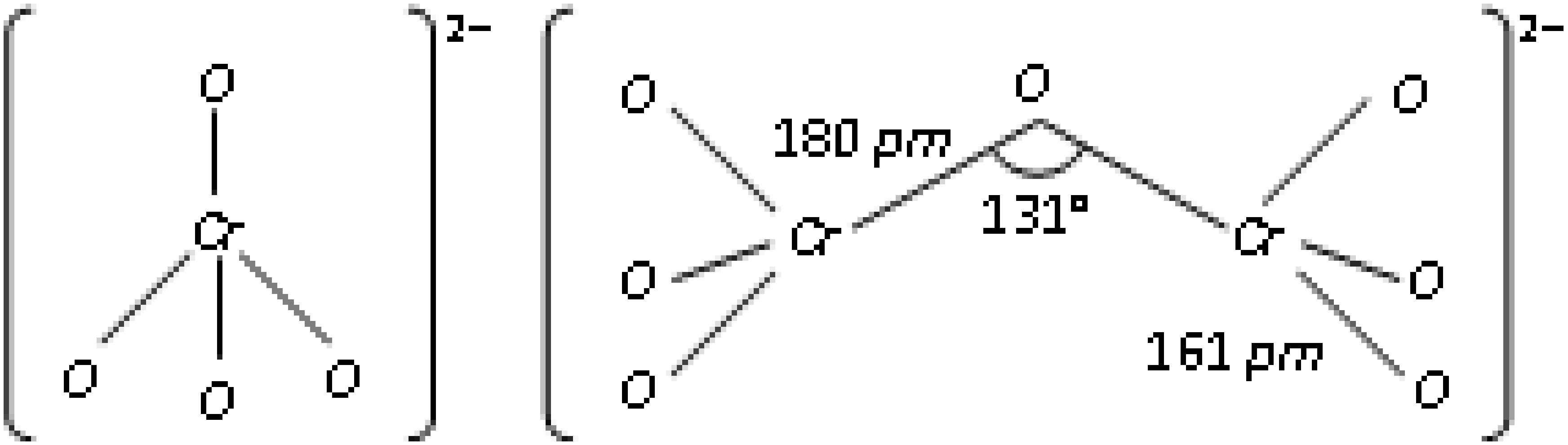


Chromate ion

The structure of dichromate ion

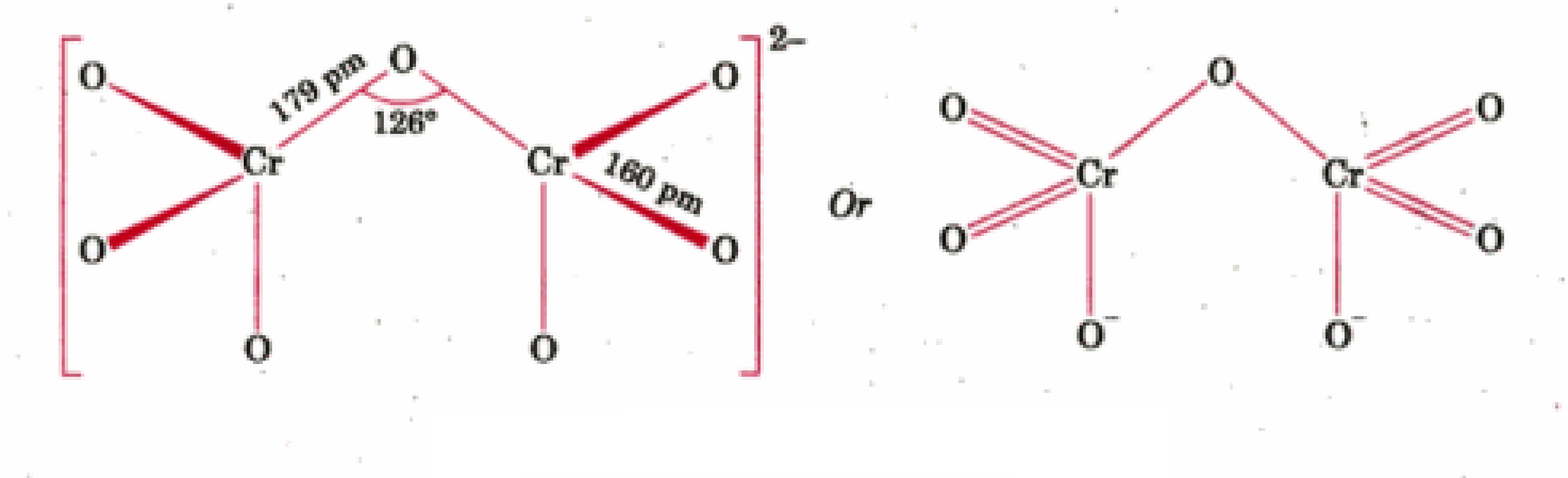


Dichromate ion



Chromate ion Dichromate ion

The structure of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions



Dichromate ion ($Cr_2O_7^{2-}$)

- The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.
- Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.
- Potassium dichromate is used as a primary standard in volumetric analysis.
- In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \ (E^\ominus = 1.33V)$$

- Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III).
- The half-reactions are noted below:

$6\ I^- \rightarrow 3I_2 + 6\ e^-$; $3\ Sn^{2+} \rightarrow 3Sn^{4+} + 6\ e^-$

$3\ H_2S \rightarrow 6H^+ + 3S + 6e^-$; $6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6\ e^-$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

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

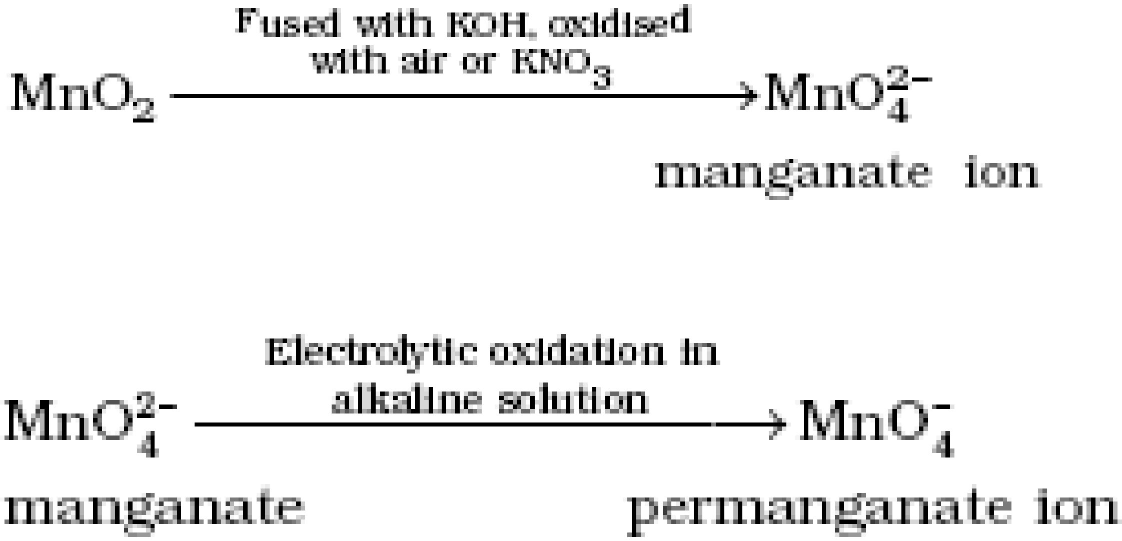
Potassium permanganate $KMnO_4$

- Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3.
- This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercial method of preparation

- Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).



$$MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH, oxidised}} \underset{\text{manganate ion}}{MnO_4^{2-}}$$

$$\underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^{-}}$$

Laboratory method of preparation

- In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

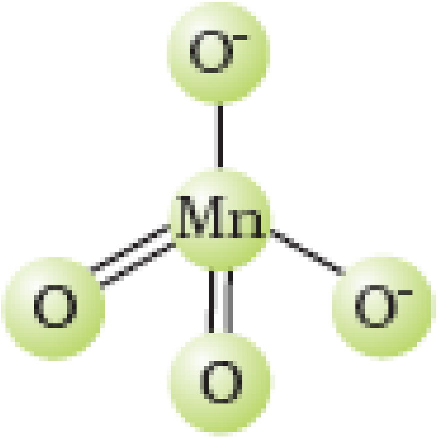
$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H^{+}$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$.

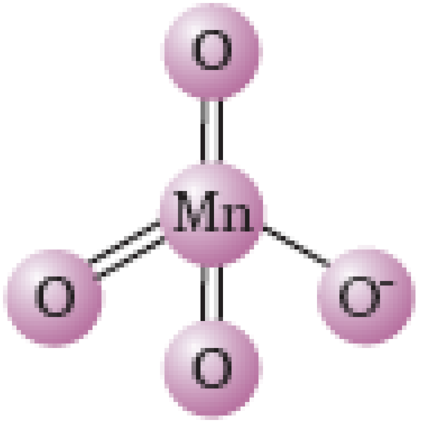
The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

manganate and permanganate ions



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

- The manganate and permanganate ions are tetrahedral;
- the green manganate is paramagnetic with one unpaired electron
- but the purple permanganate is diamagnetic.

Redox Reactions

- Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine.
- The half-reactions of reductants are:

$$5\ \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \longrightarrow 10CO_2 + 10e^-$$

$$5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5e^-$$

$$5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^-$$

$$10I^- \rightarrow 5I_2 + 10e^-$$

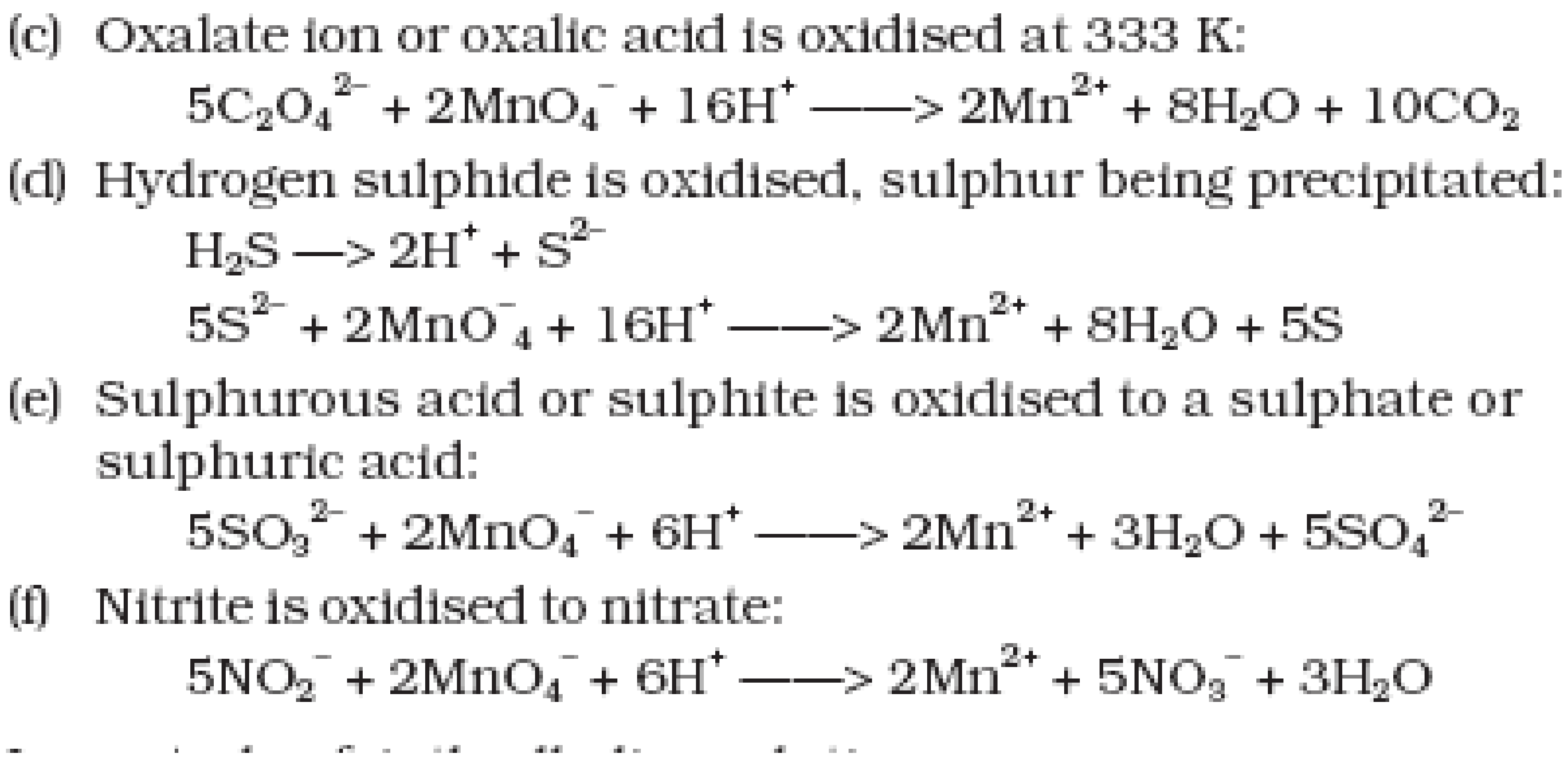
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$ $(E^\ominus = +\ 0.56\ V)$

$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ $(E^\ominus = +\ 1.69\ V)$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $(E^\ominus = +\ 1.52\ V)$

A few important oxidising reactions of $KMnO_4$ are given below:

1. In acid solutions:
   (a) Iodine is liberated from potassium iodide :
   $$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$
   (b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):
   $$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$



(c) Oxalate ion or oxalic acid is oxidised at 333 K:

$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$$H_2S \longrightarrow 2H^{+} + S^{2-}$$

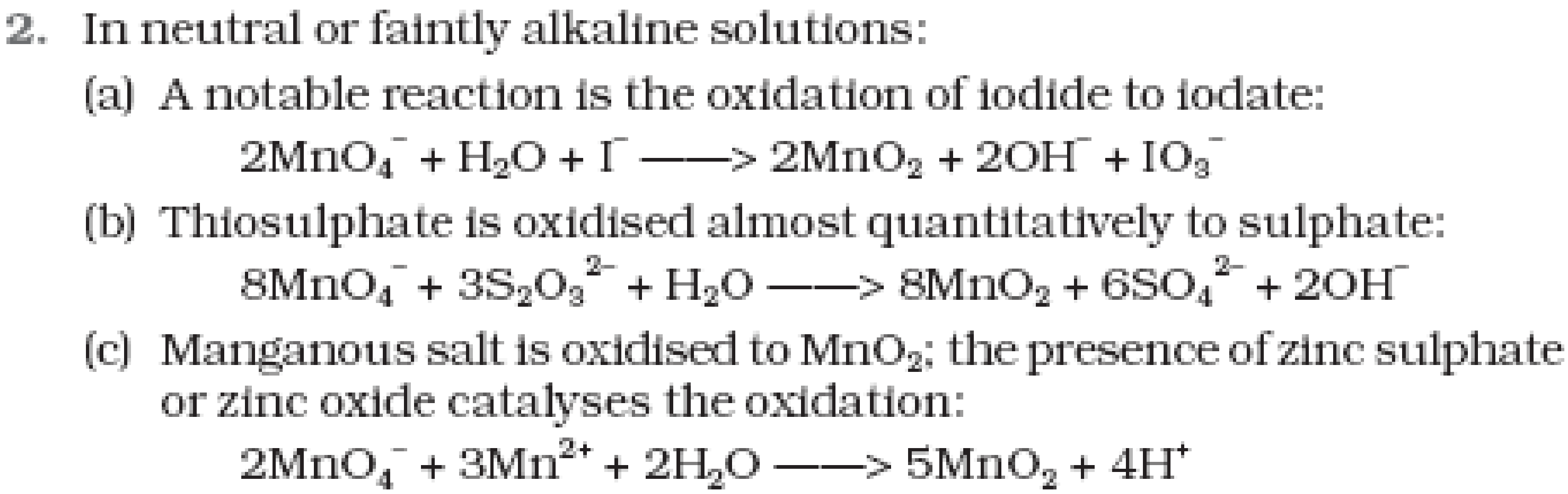
$$5S^{2-} + 2MnO^{-}_{4} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$$5SO_3^{2-} + 2MnO_4^{-} + 6H^{+} \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

(f) Nitrite is oxidised to nitrate:

$$5NO_2^{-} + 2MnO_4^{-} + 6H^{+} \longrightarrow 2Mn^{2+} + 5NO_3^{-} + 3H_2O$$



2. In neutral or faintly alkaline solutions:

   (a) A notable reaction is the oxidation of iodide to iodate:

   $$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

   (b) Thiosulphate is oxidised almost quantitatively to sulphate:

   $$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

   (c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

   $$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

Note:

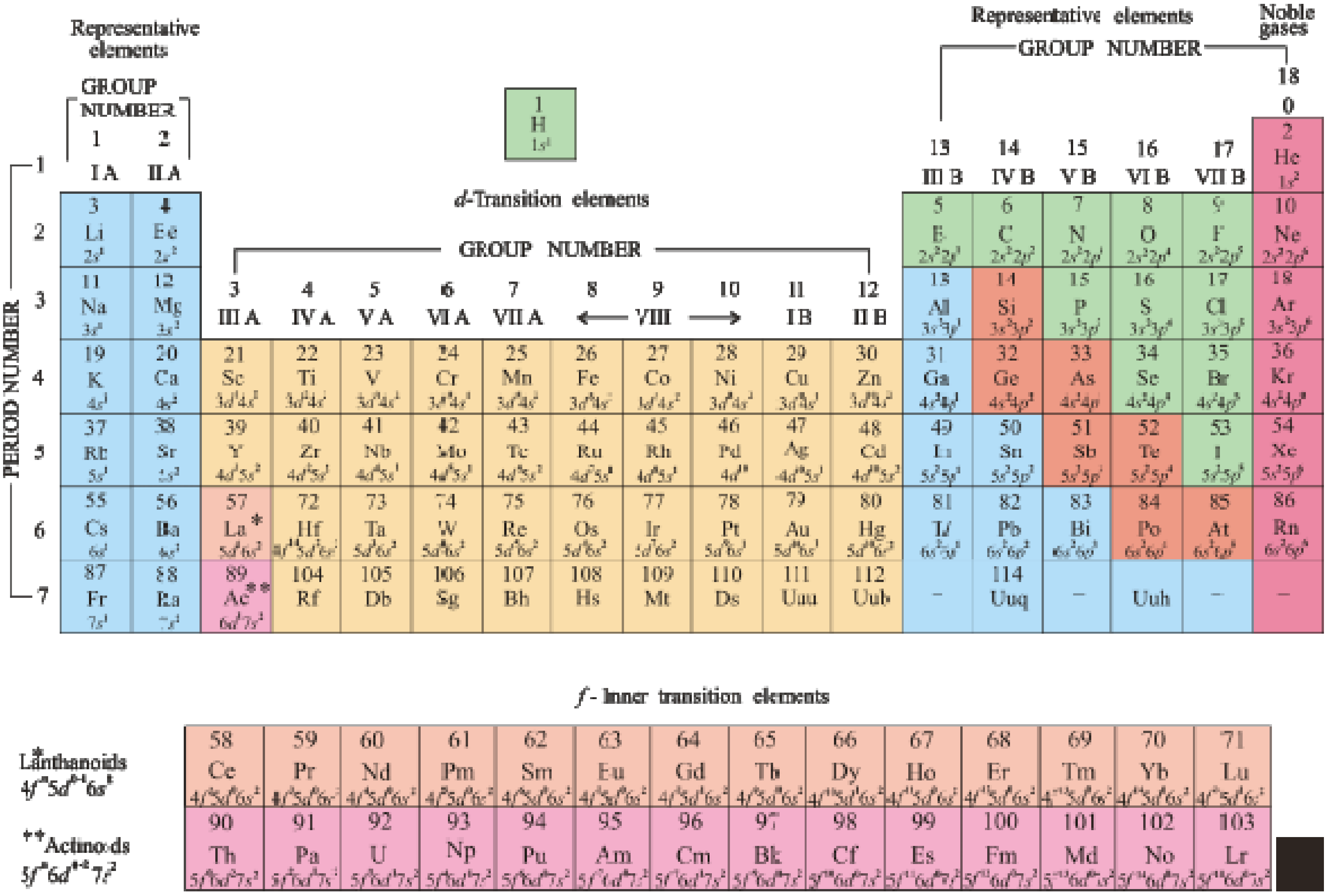
Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses of $KMnO_4$

- Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry.

- Its uses for the bleaching of wool, cotton, silk and other textile fibres and
-
- for the decolourisation of oils are also dependent on its strong oxidising power.

THE INNER TRANSITION ELEMENTS (*f-BLOCK*)



Representative elements

Representative elements

Noble gases

d-Transition elements

1
H
$1s^1$

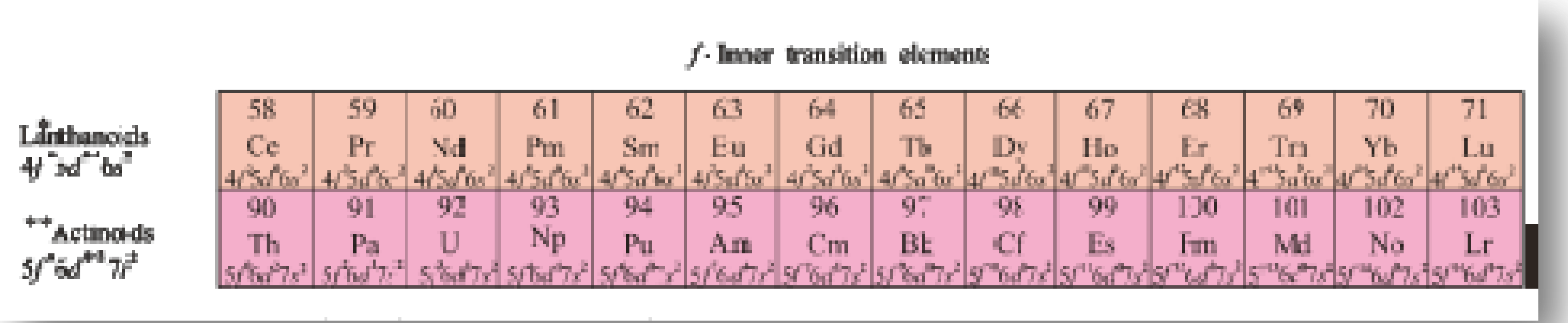
PERIOD NUMBER

	GROUP NUMBER		GROUP NUMBER										GROUP NUMBER					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	←	VIII	→	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
1																		2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	–	114 Uuq	–	Uuh	–	–

f - Inner transition elements

*Lanthanoids $4f^{n}5d^{0-1}6s^{2}$	58 Ce $4f^15d^16s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^{n}6d^{0-2}7s^{2}$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

THE INNER TRANSITION ELEMENTS (*f*-BLOCK)



f- Inner transition elements

Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

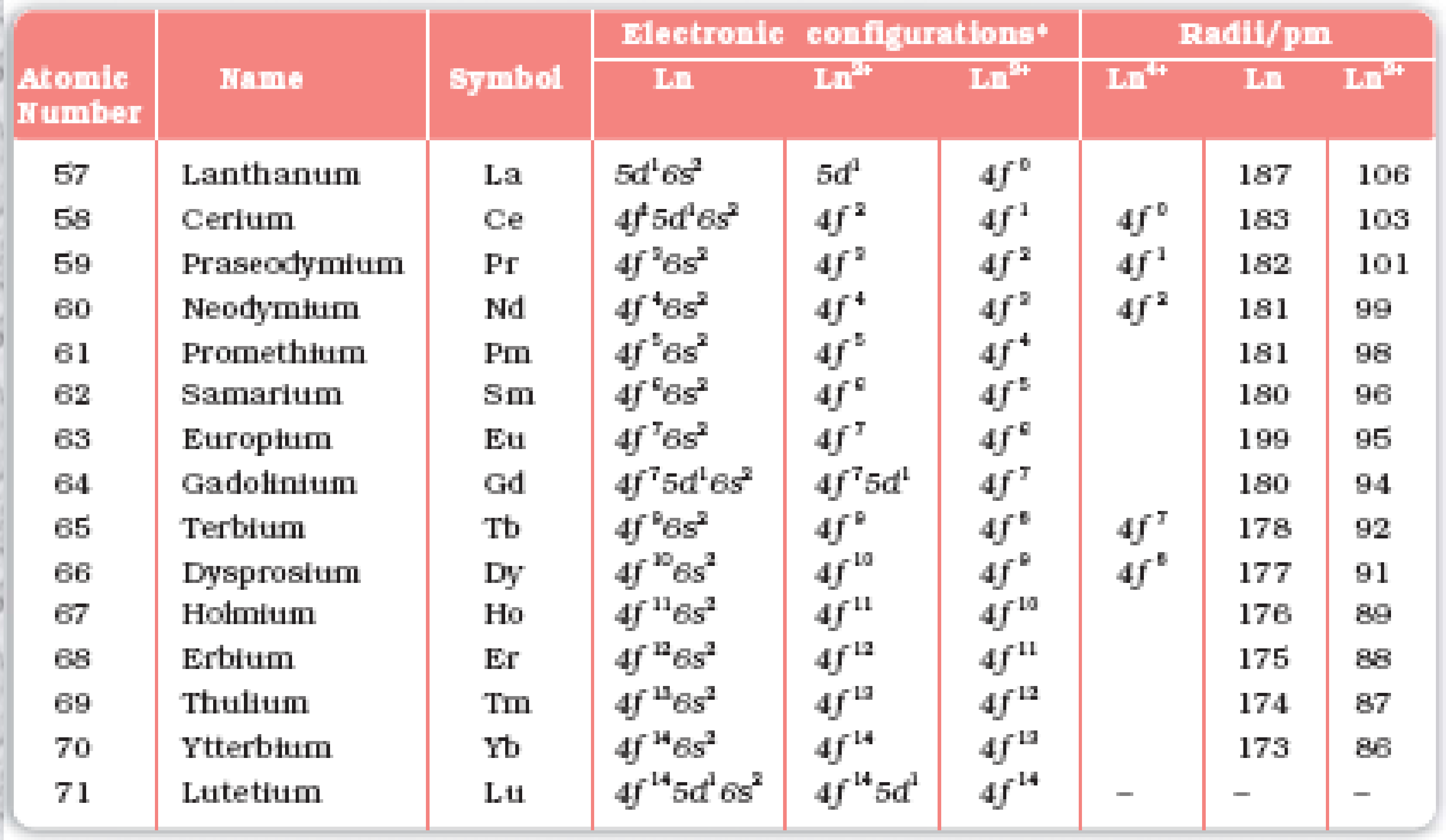
THE INNER TRANSITION ELEMENTS (*f-BLOCK)*

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

- Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol **Ln** is often used.

- Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series.

Electronic Configurations and Radii of Lanthanum and Lanthanoids



Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm		
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	–	–	–

** Only electrons outside [Xe] core are indicated*

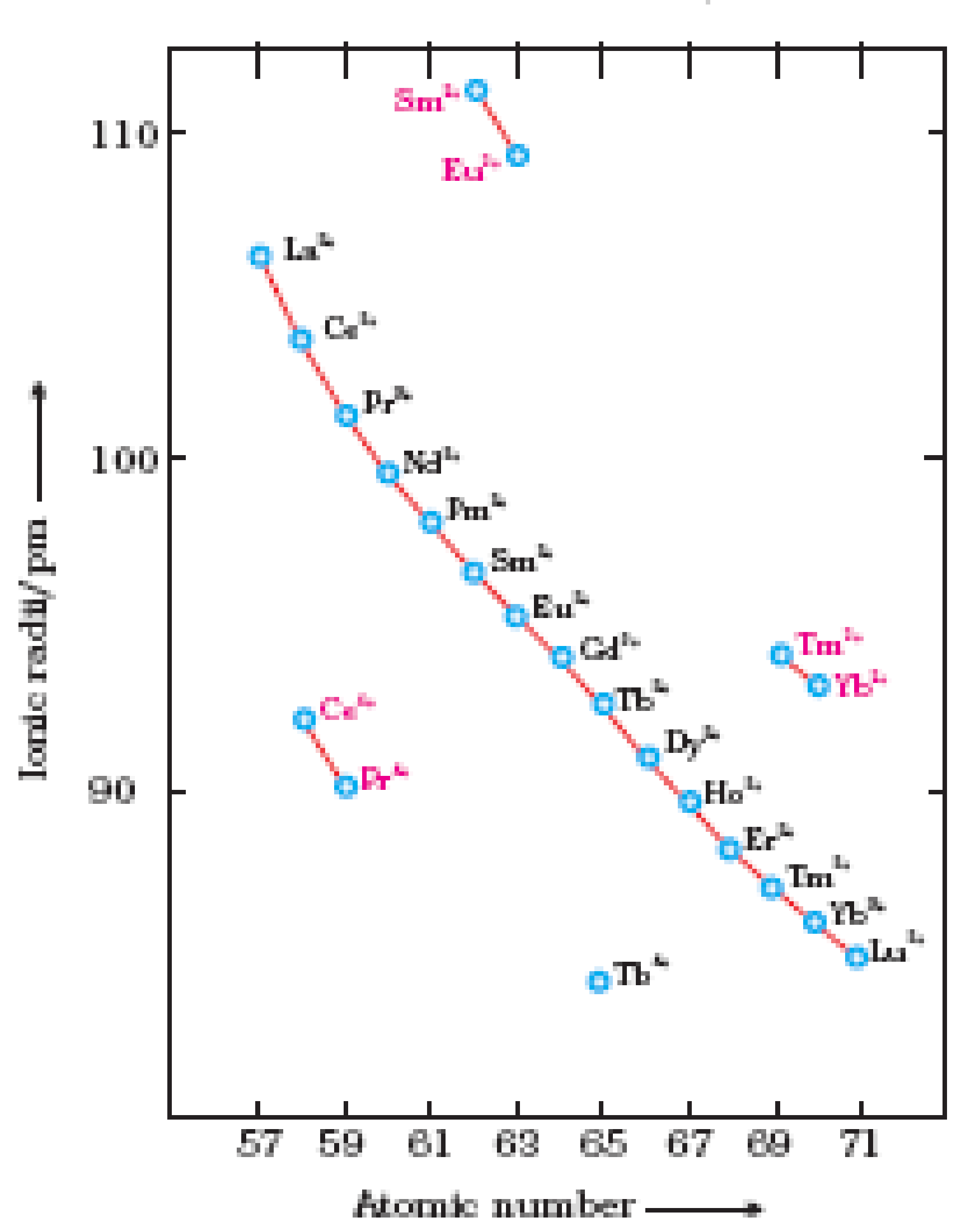
The Lanthanoids

- **Electronic Configurations**

- atoms of these elements have electronic configuration with $6s^2$ *common but with variable occupancy of 4f level*

- However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ *(n = 1 to 14 with increasing atomic number).*

Atomic and Ionic Sizes



Lanthanoid contraction

- The filling of 4*f* before 5*d orbital results in a regular decrease in atomic radii called* **Lanthanoid contraction**
- The net result of the lanthanoid contraction is that the second and the third *d series* exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship
- The factor responsible for the lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals.

Oxidation States

- In the lanthanoids, La(III) and Ln(III) compounds are predominant species.
- However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.
- This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled *f subshell.*
- Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2.
- The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states

General Characteristics

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number, samarium being steel hard.
- Their melting points range between 1000 to 1200 K but
- samarium melts at 1623 K.
- They have typical metallic structure and are good conductors of heat and electricity.
- Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions.
- Colour of these ions may be attributed to the presence of ***f*** *electrons.*
- *Neither La^{3+} nor Lu^{3+} ion shows any colour* but the rest do so.

- However, absorption bands are narrow, probably because of the excitation within ***f*** *level.*

- *The lanthanoid ions other than the* f^0 *type* (La $^{3+}$ and Ce $^{4+}$) *and the* f^{14} *type* *(Yb* $^{2+}$ *and Lu* $^{3+}$*)* *are all* paramagnetic.

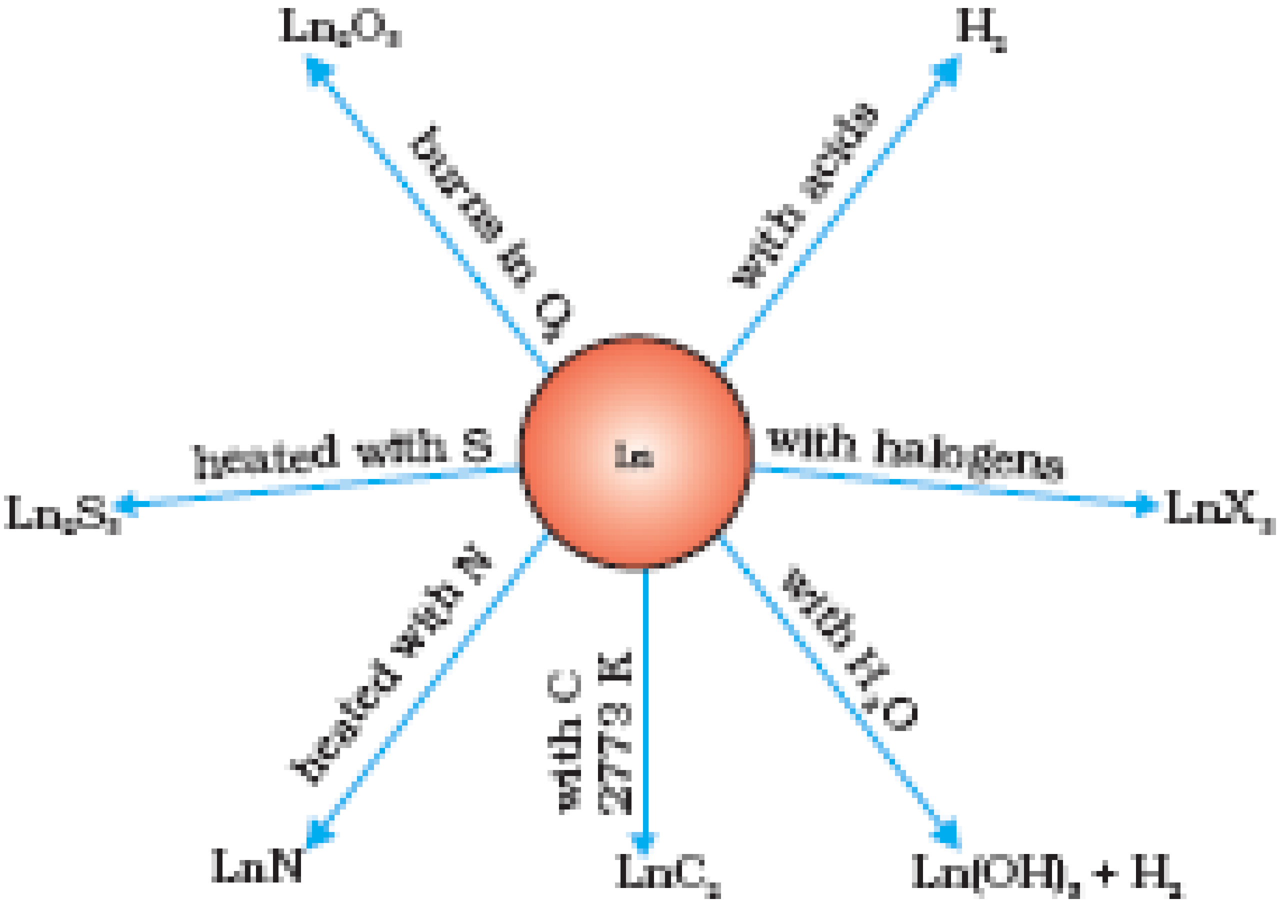
- The paramagnetism rises to maximum in neodymium.

- The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.

Chemical behavior

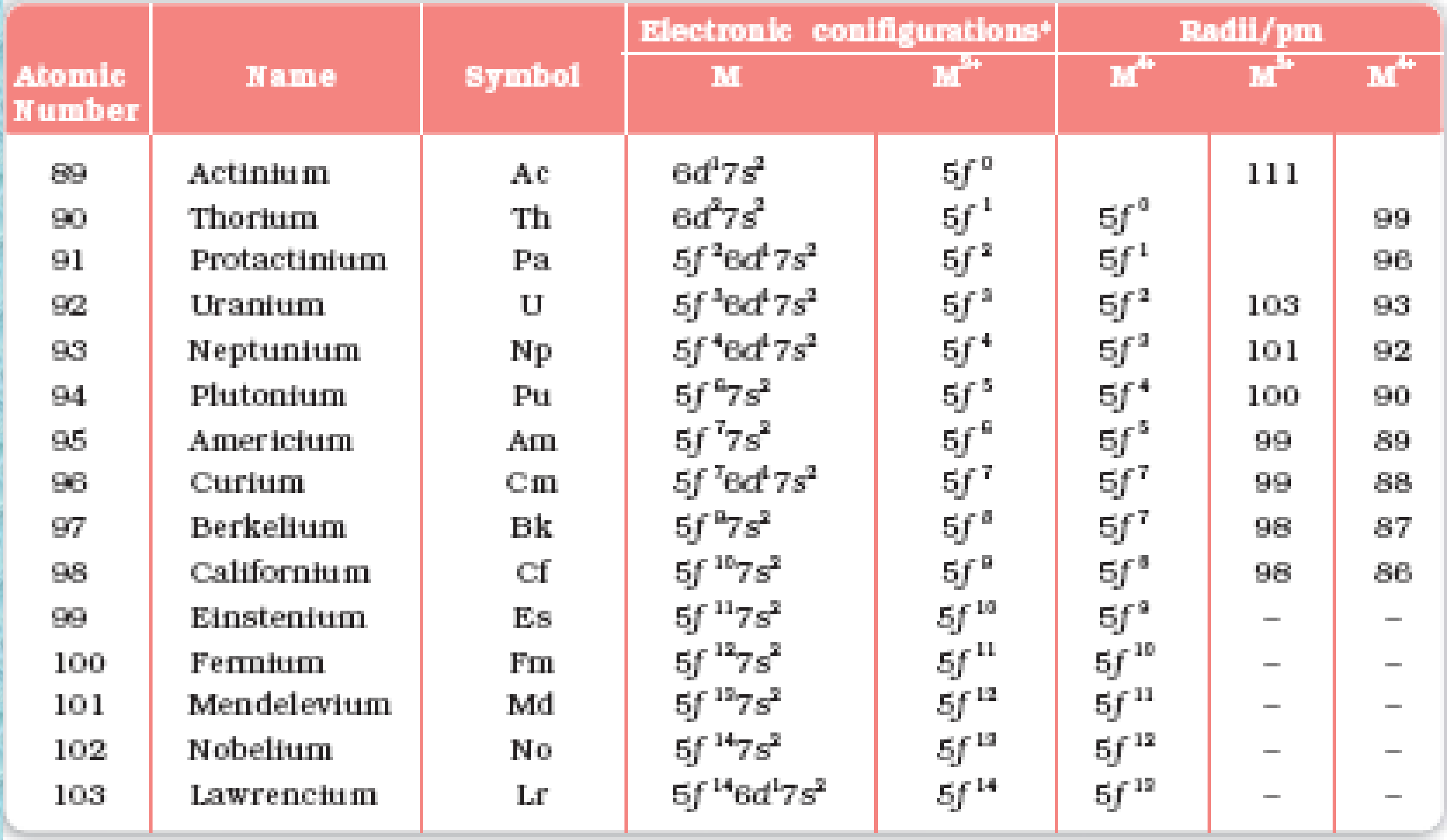
- In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium.

Chemical reactions of the lanthanoids.



The Actinoids

- The actinoids include the fourteen elements from Th to Lr.
- The names, symbols and some properties of these elements are given in next slide
- 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*).
- *The latter members could be* prepared only in nanogram quantities.



Atomic Number	Name	Symbol	Electronic configurations*		Radii/pm		
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^7$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

Electronic Configurations

- All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells.
- The fourteen electrons are formally added to 5*f, though not in thorium (Z = 90) but from Pa* onwards the 5*f orbitals are complete at element 103.*
- *The irregularities in* the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 *and* f^{14} *occupancies of the 5f* orbitals.

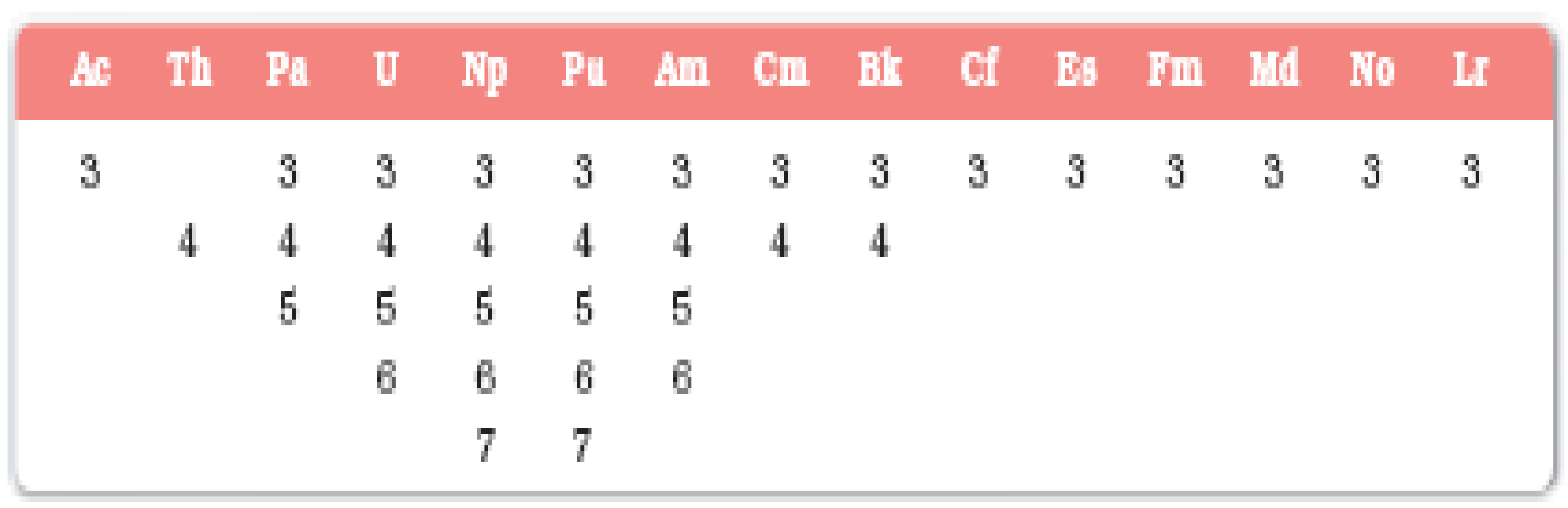
- Thus, the configurations of Am and Cm are **[Rn] $5f^{7}7s^{2}$ *and* [Rn] $5f^{7}6d1^{7}s^{2}$.**
- *Although the 5f orbitals resemble the 4f orbitals in their* angular part of the wave-function, they are not as buried as 4*f orbitals*
- and hence 5*f electrons can participate in bonding to a far greater extent.*

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 5*f electrons*.

Oxidation States

Oxidation States of Actinium and Actinoids



Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

General Characteristics and Comparison with Lanthanoids

- The actinoid metals are all silvery in appearance but display a variety of structures.

- The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

- The actinoids are highly reactive metals, especially when finely divided

- The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures.
- Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers;
- alkalies have no action.
- The magnetic properties of the actinoids are more complex than those of the lanthanoids.
- The 5*f electrons, will therefore,* be more effectively shielded from the nuclear charge than the 4*f electrons* of the corresponding lanthanoids.
- Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

Applications of d- and f-Block Elements

- Iron and steels are the most important construction materials.
- Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells.
- The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK ‘copper’ coins are copper-coated steel.

Applications of d- and f-Block Elements

- The ‘silver’ UK coins are a Cu/Ni alloy.
- Many of the metals and/or their compounds are essential catalysts in the chemical industry.
- V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid.
- $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene).
- Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures.

Applications of d- and f-Block Elements

- Nickel catalysts enable the hydrogenation of fats to proceed.
- In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.
- Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.
- The photographic industry relies on the special light-sensitive properties of AgBr.

Thank You