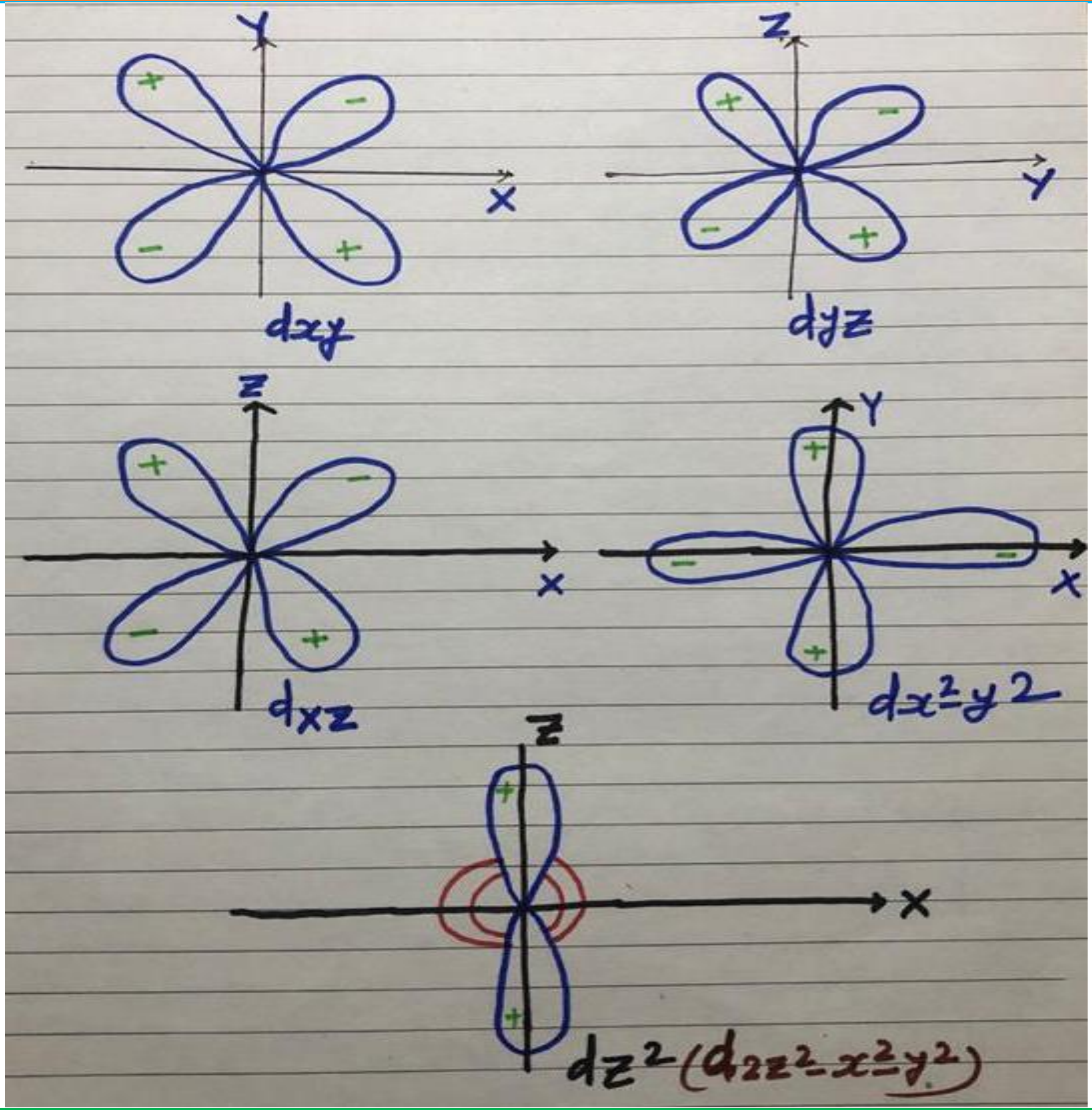
Introduction of d-Block Elements

For Life Science students

5th Semester

SY

d-Subshell



- ❖ The boundary surface of the orbital is the region of space where is there is high (typically 90%) probability of finding the electron.
- ❖ This boundary surface is what chemists draw to represent the shape of an orbital.
- ❖ The planes on which the angular wavefunction passes through zero is called angular nodes or nodal planes.
- ❖ An electron will not be found anywhere on a nodal plane.
- ❖ A nodal plane cuts through the nucleus and separates the regions of positive and negative sign of the wavefunction.

Figure: Representations of a set of five degenerate d atomic orbitals.

d- Block Elements

First T.S.	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 $3d^{10}\ 4s^2$
Second T.S.	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 $4d^{10}\ 5s^0$	47 Ag $4d^{10}\ 5s^1$	48 Cd $4d^{10}\ 5s^2$
Third T.S.	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 $5d^{10}\ 6s^2$
Fourth T.S.	89 Ac** $6d^1\ 7s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

- Three series of elements formed by filling of 3d, 4d and 5d subshells of electrons. Together these comprise the d-block elements.
- Also called as transition elements because their position in the periodic table is between the s-block and p-block elements.
- The two terms d-block metal and transition metal are often used interchangeably; however, they do not mean the same thing.

d-Block Elements vs Transition Elements

- ❖ The name transition metal originally derived from the fact that their chemical properties were transitional between those of the s and p-blocks.
- ❖ IUPAC definition of Transition Element: Element that has an incomplete d-subshell in either the neutral atom or its ions.

	3d					4s	d- Block Element	Transition Element
Sc	$3d^1$: ↑					$4s^2$: ↑↓	✓	✓
Ti	$3d^2$: ↑	↑				$4s^2$: ↑↓	✓	✓
V	$3d^3$: ↑	↑	↑			$4s^2$: ↑↓	✓	✓
Cr	$3d^5$: ↑	↑	↑	↑	↑	$4s^1$: ↑	✓	✓
Mn	$3d^5$: ↑	↑	↑	↑	↑	$4s^2$: ↑↓	✓	✓
Fe	$3d^6$: ↑↓	↑	↑	↑	↑	$4s^2$: ↑↓	✓	✓

What about Cu?

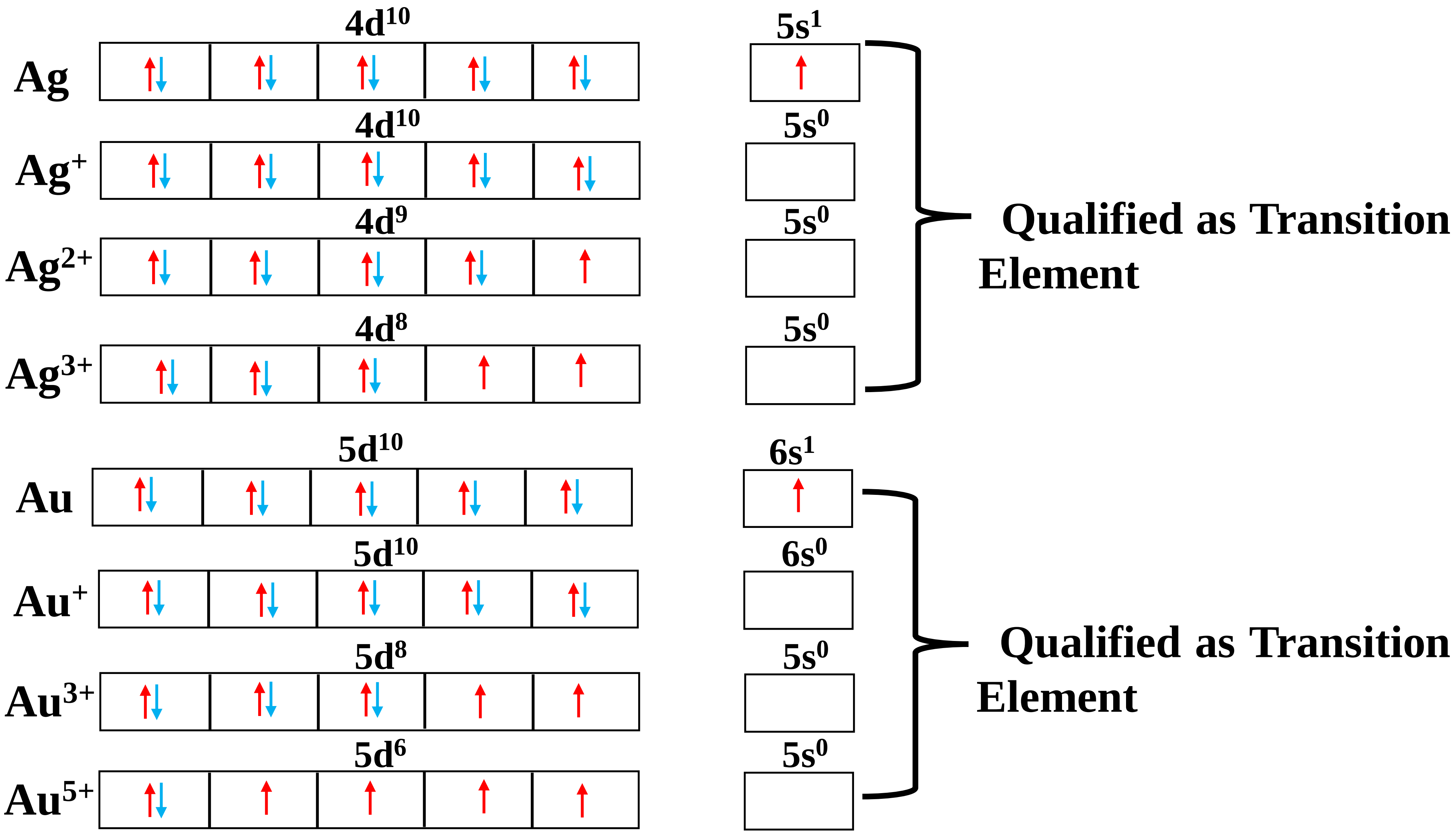
	3d	4s	d- Block Element	Transition Element
Co	$3d^7$ (↑↓ ↑↓ ↑ ↑ ↑)	$4s^2$ (↑↓)	✓	✓
Ni	$3d^8$ (↑↓ ↑↓ ↑↓ ↑ ↑)	$4s^2$ (↑↓)	✓	✓

Electronic Configuration

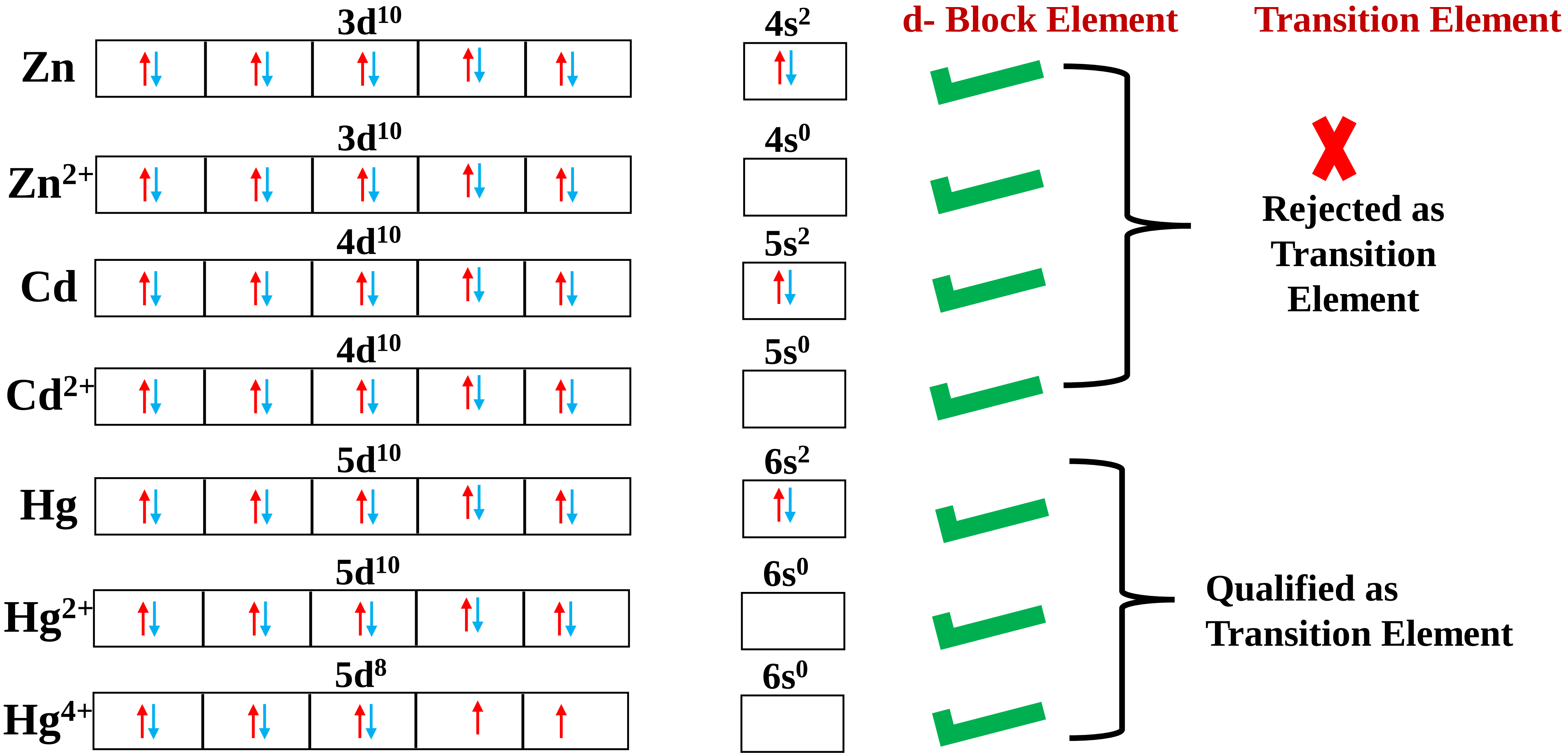
	3d	4s		
Cu	$3d^9$ (↑↓ ↑↓ ↑↓ ↑↓ ↑)	$4s^2$ (↑↓)	✗	
Cu	$3d^{10}$ (↑↓ ↑↓ ↑↓ ↑↓ ↑↓)	$4s^1$ (↑)	✓	✓
Cu^+	$3d^{10}$ (↑↓ ↑↓ ↑↓ ↑↓ ↑↓)	$4s^0$		
Cu^{2+}	$3d^9$ (↑↓ ↑↓ ↑↓ ↑↓ ↑)	$4s^0$		
Cu^{3+}	$3d^8$ (↑↓ ↑↓ ↑↓ ↑ ↑)	$4s^0$		

Incompletely filled d-orbitals are available in ionic state hence qualified as transition element.

Status of Ag and Au



What about Zn, Cd and Hg?



- Thus, two of the Group 12 elements (Zn, Cd) are members of the d block but are not transition elements as they do not have any compounds with an incomplete d subshell.
- The situation for the third Group 12 element, mercury, is different: the report of a mercury(IV) compound (HgF_4), which has the d^8 electron configuration, qualifies mercury as a transition metal.

General Properties of Transition Elements

- Electronic Configurations
- Atomic Radii
- Ionic Radii
- Metallic Character and Related Properties
- Enthalpy of Atomisation (ΔH°_{a})
- Melting and Boiling Points
- Atomic Volumes and Densities
- Ionization Energies
- Enthalpy of Hydration (ΔH_{hyd})
- Standard Oxidation Potential Values and Reducing Properties of Transition Elements in Aqueous Solution
- Variable Oxidation States
- Catalytic Properties
- Colour of Transition Metal Complex Ions
- Magnetic Properties of Transition Metal Complexes
- Electronegativity
- Complex Formation Property
- Alloy Formation
- Formation of Interstitial Compounds

General Electronic Configuration of Transition Elements

General Electronic Configuration of First Transition Series: $[Ar]_{18}\ 3d^{1-10}\ 4s^{1-2}$

V.S.C.	Sc	Ti	V	Cr*	Mn	Fe	Co	Ni	Cu**	Zn
$3d^{1-10}$	1	2	3	5	5	6	7	8	10	10
$4s^{1,2}$	2	2	2	1	2	2	2	2	1	2

Extra stability of half filled d-subshell

Extra stability of fully filled d-subshell

General Electronic Configuration of Second Transition Series: $[Kr]_{36}\ 4d^{1-10}\ 5s^{0-2}$

V.S.C.	Y	Zr	Nb*	Mo*	Tc	Ru*	Rh*	Pd*	Ag**	Zn
$4d^{1-10}$	1	2	4	5	5	7	8	10	10	10
$5s^{0-2}$	2	2	1	1	2	1	1	0	1	2

Extra stability of half filled d-subshell

Due to Nuclear-electron and Electron-electron interactions

Extra stability of fully filled d-subshell

General Electronic Configuration of Transition Elements

General Electronic Configuration of Third Transition Series: $[Xe]_{54}\ 4f^{14}\ 5d^{2-10}\ 6s^{1-2}$

V.S.C.	La**	Hf	Ta	W*	Re	Os	Ir*	Pt*	Au	Hg
$5d^{2-10}$	1	2	3	4	5	6	7	9	10	10
$6s^{0-2}$	2	2	2	2	2	2	2	1	1	2

Extra stability of fully filled d-subshell

* Due to Nuclear-electron and Electron-electron interactions.

** By definition La is a d-block element. However its physical and chemical properties resembles the lanthanide series elements which follows it. Therefore, La is considered as a member of the lanthanide series and is studied along with them.

General Electronic Configuration of Third Transition Series: for Rf_{104} to Cn_{112} $[Rn]_{86}\ 5f^{14}\ 6d^{2-10}\ 7s^{1,2}$ for Ac_{89} $[Rn]_{86}\ 5f^{0}\ 6d^{1}\ 7s^{2}$

V.S.C.	Ac**	Rf	Db	Sg*	Bh	Hs	Mt	Ds	Rg	Cn
$5d^{2-10}$	1	2	3	4	5	6	7	8	10	10
$6s^{0-2}$	2	2	2	2	2	2	2	2	1	2

Atomic Radii

Variation of Atomic Radii in a Given Period (Angstrom):

First T.S.	**Sc (1.62)**	**Ti (1.47)**	**V (1.34)**	**Cr (1.27)**	**Mn (1.26)**	**Fe (1.26)**	**Co (1.25)**	**Ni (1.24)**	**Cu (1.28)**	**Zn (1.38)**
Second T.S.	**Y (1.80)**	**Zr (1.60)**	**Nb (1.46)**	**Mo (1.39)**	**Tc (1.36)**	**Ru (1.34)**	**Rh (1.34)**	**Pd (1.37)**	**Ag (1.44)**	**Cd (1.54)**
Third T.S.	**La (1.87)**	**Hf (1.58)**	**Ta (1.46)**	**W (1.39)**	**Re (1.37)**	**Os (1.35)**	**Ir (1.36)**	**Pt (1.38)**	**Au (1.44)**	**Hg (1.57)**

(i) The atomic radii of the transition metals lie in between those of s- and p-block elements.

(ii) Generally the atomic radii of d-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway.

(iii) At the end of the period, there is slight increase in the atomic radii.

(iv) There is no major change in atomic radii on going from Fe to Cu.

At the beginning: Attractive forces > Repulsive forces

From Fe to Cu: Attractive forces = Repulsive forces

At the end: Attractive force < Repulsive force

Variation of Atomic Radii in a Given Group: Sc, Y and La increases.

Rest other have almost identical radii due to lanthanide contraction.

Ionic Radii

Same metal ion in different oxidation states:
e.g. $Ti^{2+} > Ti^{3+}$; $Cr^{2+} > Cr^{3+} > Cr^{4+} > Cr^{5+} > Cr^{6+}$; $Cu^{+} > Cu^{2+}$

Ionic radii of the cations of different element in the same oxidation state
e.g. $Ti^{2+} > V^{2+} > Cr^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$
For group 3 cations: $Sc^{3+} < Y^{3+} < La^{3+}$

Metallic Character

- **All the transition elements show metallic character**
- **Good conductor of electricity and heat**
- **Hard and brittle**
- **Crystal structure: bcc, hcp, ccp or bcc**