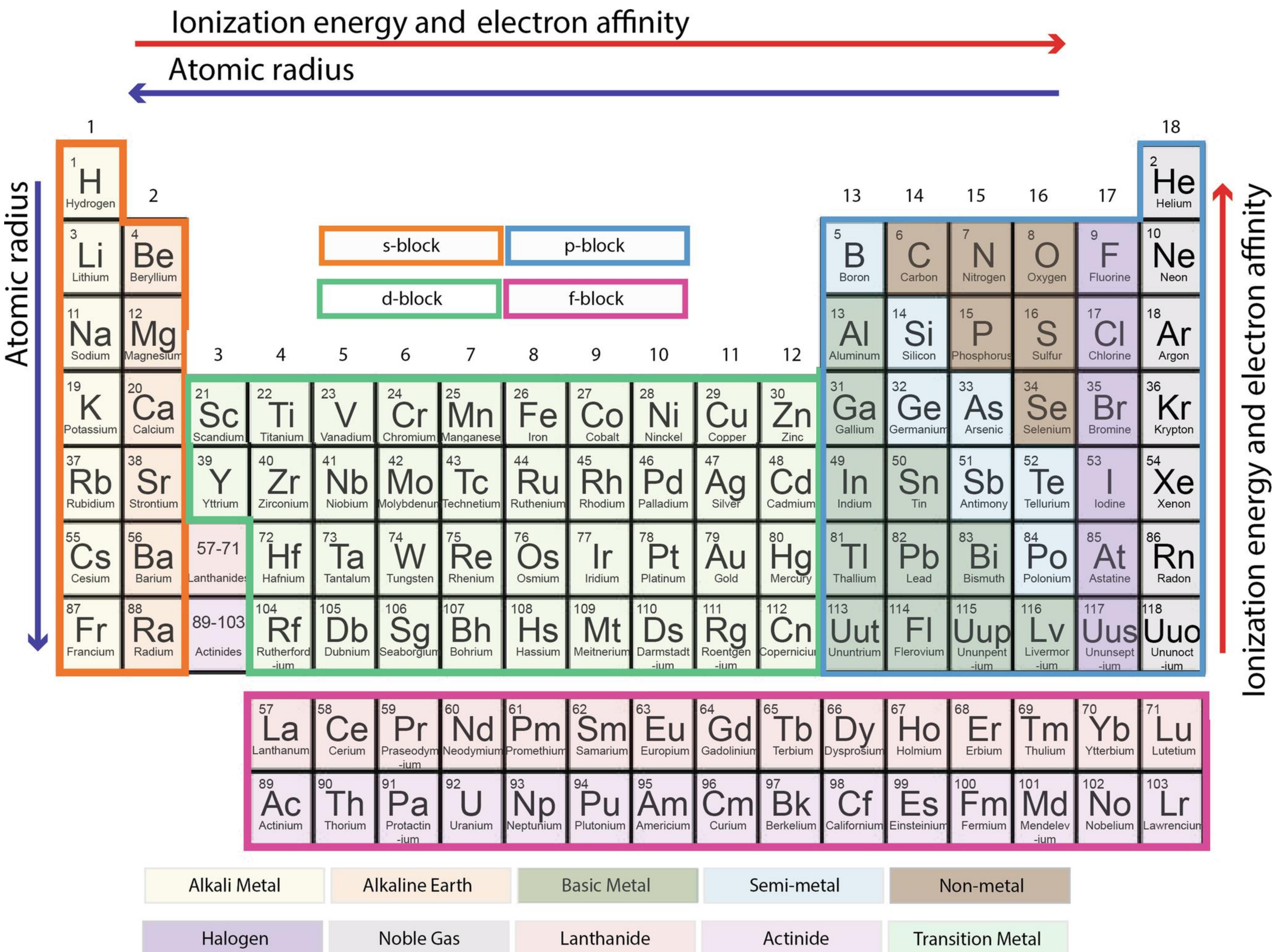
Semester II

CHE-RC/HG-2016 :CHEMISTRY2

Section A:

Topic: Transition elements (3d series)

Transition Elements



Modern Techniques and Theories

- **Transition elements** are placed in between the s-block and p-block elements in the periodic table.

- Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds, and the elements of the p-block, which are largely covalent.

- The IUPAC definition of a transition element is that it is an element that has an ***incomplete d subshell*** in either the neutral atom or its ions.

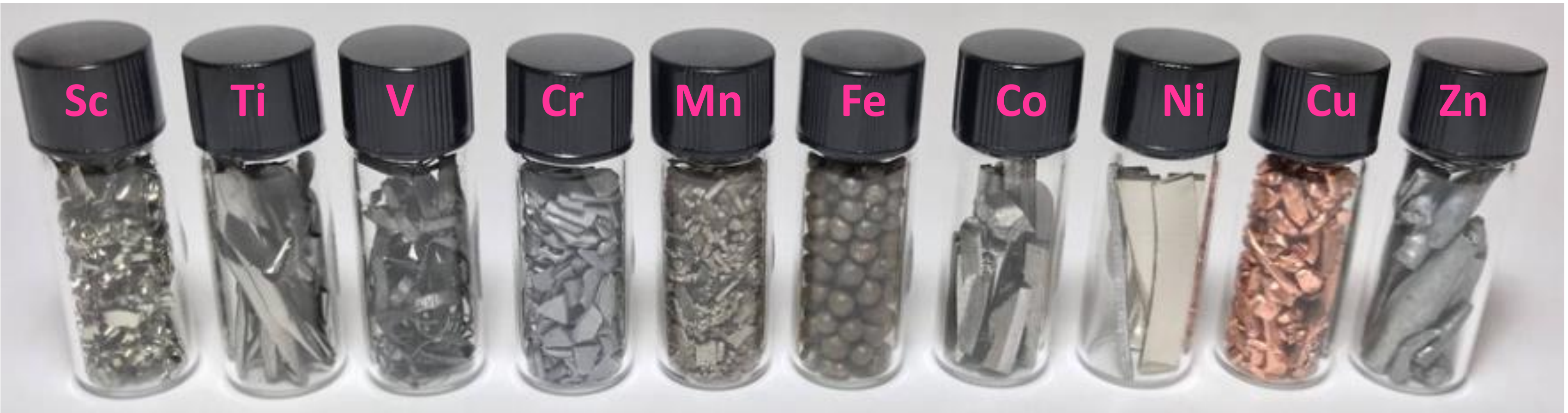
- **Group 12 (Zn, Cd, Hg) has a d^{10} configuration** and since the d shell is complete, compounds of these elements *are not regarded as transition elements*.

- All the transition elements are metals.

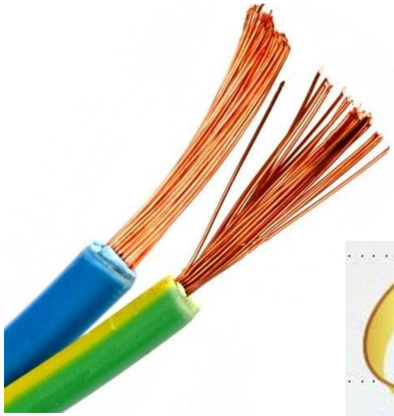
- They are therefore good conductors of electricity and heat, have a metallic lustre and are hard, strong and ductile.

- They also form alloys with other metals.

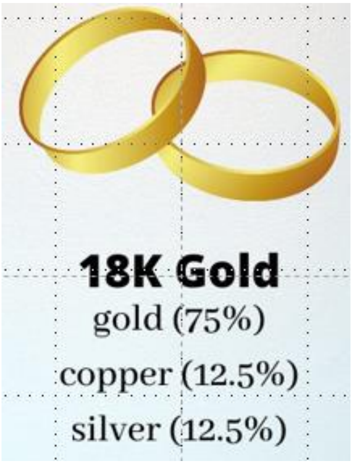
Transition Elements



Metallic state of 3d elements



Cu wire

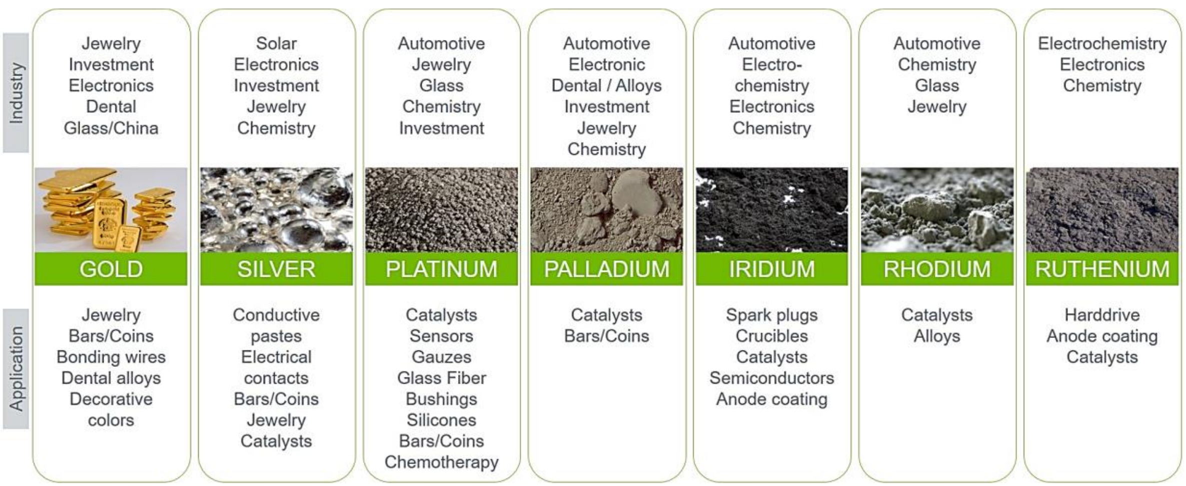


Alloy

Chemistry of colours in gemstones

Transition Elements

Group									
3	4	5	6	7	8	9	10	11	12
Sc Scandium	Ti Titanium	V Vanadium	Cr Chromium	Mn Manganese	Fe Iron	Co Cobalt	Ni Nickel	Cu Copper	Zn Zinc
Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd Cadmium
La Lanthanum	Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au Gold	Hg Mercury
Ac Actinium									



Focus of Discussion

- ✓ Electronic configuration
- ✓ Variable oxidation state
- ✓ Colour
- ✓ Magnetic properties
- ✓ Catalytic properties
- ✓ Ability to form complexes

Transition Elements

Electronic configuration

Atomic number	Element	Ground state electronic configuration
21	Sc	$[Ar]4s^2 3d^1$
22	Ti	$[Ar]4s^2 3d^2$
23	V	$[Ar]4s^2 3d^3$
24	Cr	$[Ar]4s^1 3d^5$
25	Mn	$[Ar]4s^2 3d^5$
26	Fe	$[Ar]4s^2 3d^6$
27	Co	$[Ar]4s^2 3d^7$
28	Ni	$[Ar]4s^2 3d^8$
29	Cu	$[Ar]4s^1 3d^{10}$
30	Zn	$[Ar]4s^2 3d^{10}$

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$

Variable Oxidation States

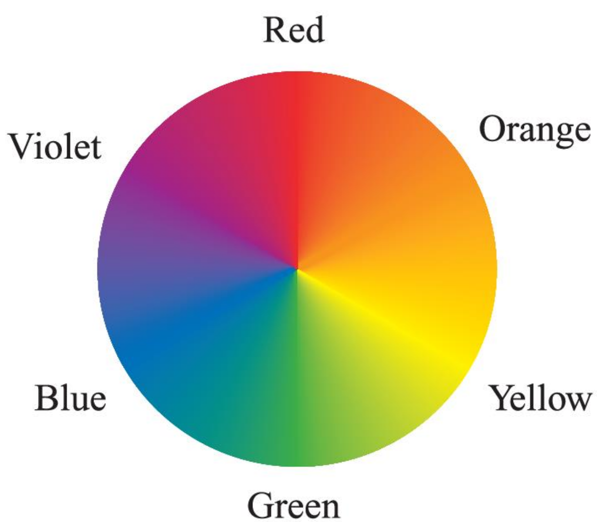
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	0	0	0	0	0	0	0	[0]	
		1	1	1	1	1	1	**1**	[1]
	2	2	**2**	**2**	**2**	**2**	**2**	**2**	**2**
3	3	**3**	**3**	3	**3**	**3**	3	3	
	4	**4**	4	4	4	4	4	[4]	
		5	5	5					
			6	6	6				
				7					

- ✓ **Elements having high oxidation states (greater than +3):** More prevalent in left side of the d-block.
- ✓ **Elements having intermediate oxidation states:** Oxidation state +3 is common to the left of the 3d series and +2 is common for metals from the middle to the right of the block.
- ✓ Once the d^5 configuration is exceeded, i.e., in the last five elements, the tendency for all the d electrons to participate in bonding decreases.
- ✓ Examples of high oxidation state 3d compounds: $KMnO_4$ and $K_2Cr_2O_7$

Transition Elements

Color

- ✓ The colors of d-block metal compounds are a characteristic feature of species with ground state electronic configurations other than d^0 and d^{10}.
- ✓ If absorption occurs in the visible region of the spectrum, the transmitted light is colored with the color complementary to the color of the light absorbed.
- ✓ Color of transition metal ions are due to d–d transitions.



The colour wheel

$Sc^{3+} \rightarrow$ colourless

$Ti^{4+} \rightarrow$ colourless

$Ti^{3+} \rightarrow$ purple

$V^{4+} \rightarrow$ blue

$V^{3+} \rightarrow$ green

$V^{2+} \rightarrow$ violet

$Cr^{2+} \rightarrow$ blue

$Cr^{3+} \rightarrow$ green

$Mn^{3+} \rightarrow$ violet

$Mn^{2+} \rightarrow$ light pink

$Fe^{2+} \rightarrow$ light green

$Fe^{3+} \rightarrow$ yellow

$Co^{2+} \rightarrow$ pink

$Ni^{2+} \rightarrow$ green

$Cu^{2+} \rightarrow$ blue

$Zn^{2+} \rightarrow$ colourless

Transition Elements

Color

Scandium chloride

Titanium chloride

Vanadium chloride

Chromium chloride

Manganese chloride

Iron chloride

Cobalt chloride

Nickel chloride

Copper chloride

$Sc^{3+} \rightarrow$ colourless

$Ti^{4+} \rightarrow$ colourless

$Ti^{3+} \rightarrow$ purple

$V^{4+} \rightarrow$ blue

$V^{3+} \rightarrow$ green

$V^{2+} \rightarrow$ violet

$Cr^{2+} \rightarrow$ blue

$Cr^{3+} \rightarrow$ green

$Mn^{3+} \rightarrow$ violet

$Mn^{2+} \rightarrow$ light pink

$Fe^{2+} \rightarrow$ light green

$Fe^{3+} \rightarrow$ yellow

$Co^{2+} \rightarrow$ pink

$Ni^{2+} \rightarrow$ green

$Cu^{2+} \rightarrow$ blue

$Zn^{2+} \rightarrow$ colourless

Transition Elements

Magnetic Properties

- When a substance is placed in an external magnetic field of strength *H,* the intensity of the magnetic field in the substance may be greater than or less than *H.*
- If the field in the substance is greater than H, the substance is paramagnetic. Paramagnetic materials tend to attract magnetic lines of force. Paramagnetism arises as a result of unpaired electron spins in the atom.
- If the field in the substance is less than H, the substance is diamagnetic. Diamagnetic materials tend to repel magnetic lines of force. All substances show diamagnetism.
- Some transition elements such as Fe, Co and Ni are ferromagnetic in which the moments on individual atoms become aligned at all point in the same direction.
- Many transition elements are paramagnetic, because they contain partially filled electron shells.
- Measurement of magnetic moments can distinguish between high-spin and low-spin transition metal octahedral complexes.

Transition Elements

Magnetic Properties

Neodymium

Nd-Fe-B magnetic material known as “Magnet King”

Ferrite

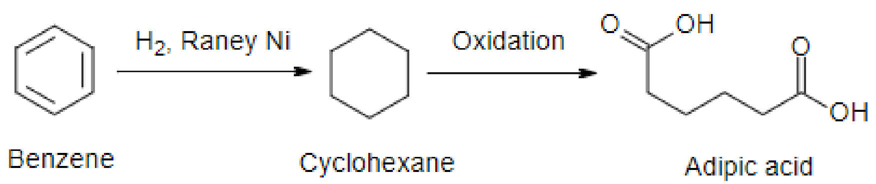
Iron(III) oxide (Fe_2O_3, rust) blended with small proportions of one or more additional metallic elements, such as Sr, Ba, Mn, Ni, and Zn

Source: *Wikipedia*

Transition Elements

Catalytic Properties

$TiCl_3$	Used as the Ziegler–Natta catalyst in the production of polythene.
V_2O_5	Converts SO_2 to SO_3 in the Contact process for making H_2SO_4.
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.
$FeSO_4$ 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 $CH_3CHO + 2HCl + Pd$.
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone).
$PtO_2 \cdot H_2O$	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 oxidize NH_3 to NO.
Cu	Direct process for manufacture of $(CH_3)_2SiCl_2$ used to make silicones.
$CuCl_2$	Deacon process of making Cl_2 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).
	Reppe synthesis (polymerization of alkynes, e.g. to give benzene or cyclooctatetraene).



$$Al + Ni \xrightarrow{1200\text{-}1500\ ^{o}C} Al\text{-}Ni$$

$$Al\text{-}Ni + NaOH \xrightarrow[-NaAlO_2]{} Ni$$

Catalytic Properties: Examples

1. *Ostwald process* of manufacturing HNO_3

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow[\text{5 atm 850 °C}]{\text{platinum/rhodium catalyst}} 4NO_{(g)} + 6H_2O_{(g)}$$

2. *Haber process* of NH_3 synthesis

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Catalyst: The catalyst is made by fusing Fe_3O_4 with KOH and a refractory material such as MgO, SiO_2 or Al_2O_3.

3. *Contact process* of manufacture H_2SO_4

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Catalyst: vanadium pentoxide (V_2O_5)

4. *Monsanto acetic acid synthesis*

$$CH_3OH + CO \xrightarrow[\text{HI}]{\text{Rh catalyst}} CH_3COOH$$

Transition Elements

Ability to form complexes

- The transition elements have an unparalleled tendency to form coordination compounds with Lewis bases, i.e. with groups which are able to donate an electron pair. These groups are called ligands.
- This ability to form complexes is in marked contrast to the *s*- and *p*-block elements which form only a few complexes.
- The reason transition elements are so good at forming complexes is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands.
- Complexes where the metal is in the (+III) oxidation state are generally more stable than those where the metal is in the (+II) state.

Definition of Stability

Compounds are regarded as stable if they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures.