|          |     |          | sb       | olo | ck        |           |           |          | d <b>a</b> ta 1 | -         | 11        | 1         |           |           |            |           | blog       | 3         |            |            |
|----------|-----|----------|----------|-----|-----------|-----------|-----------|----------|-----------------|-----------|-----------|-----------|-----------|-----------|------------|-----------|------------|-----------|------------|------------|
| X        |     | 1<br>H   |          | l   |           | th        | le        | t        | -b              | 0         | C         | K         |           |           |            |           | V          | -         |            | 2<br>He    |
| C        |     | 3<br>Li  | 4<br>Be  |     |           |           |           | Ī        |                 |           |           |           |           |           | 5<br>B     | 6<br>C    | 7<br>N     | 8<br>0    | 9<br>F     | 10<br>Ne   |
| SLO      | S   | 11<br>Na | 12<br>Mg |     |           |           |           |          | ື               |           | S         |           |           |           | 13<br>Al   | 14<br>Si  | 15<br>P    | 16<br>S   | 17<br>Cl   | 18<br>Ar   |
|          | IN  | 19<br>K  | 20<br>Ca |     | 21<br>Sc  | 22<br>Ti  | 23<br>V   | 2.<br>C  | 25<br>Mn        | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn  | 31<br>Ga   | 32<br>Ge  | 33<br>As   | 34<br>Se  | 35<br>Br   | 36<br>Kr   |
|          | (E) | 37<br>Rb | 38<br>Sr |     | 39<br>Y   | 40<br>Zr  | 41<br>Nb  | 42<br>Mo | 43<br>Tc        | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd  | 49<br>In   | 50<br>Sn  | 51<br>Sb   | 52<br>Te  | 53<br>I    | 54<br>Xe   |
| <b>N</b> | EN  | 55<br>Cs | 56<br>Ba | *   | 71<br>Lu  | 72<br>Hf  | 73<br>Ta  | 74<br>W  | 75<br>Re        | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl   | 82<br>Pb  | 83<br>Bi   | 84<br>Po  | 85<br>At   | 86<br>Rn   |
| D        | EL  | 87<br>Fr | 88<br>Ra | t   | 103<br>Lr | 104<br>Rf | 105<br>Db | 10<br>50 | 107<br>Bh       | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112<br>Cn | 113<br>Uut | 114<br>Fl | 115<br>Uup | 116<br>Lv | 117<br>Uus | 118<br>Uuo |
| HE       |     |          |          | *   | 57<br>La  | 58<br>Ce  | 59<br>Pr  | 60<br>Nd | 61<br>Pm        | 62<br>Sm  | 63<br>Eu  | 64<br>Gd  | 65<br>Tb  | 66<br>Dy  | 67<br>Ho   | 68<br>Er  | 69<br>Tm   | 70<br>Yb  | )          |            |
| I        |     |          |          | +   | 89<br>Ac  | 90<br>Th  | 91<br>Pa  | 92<br>U  | 93<br>Np        | 94<br>Pu  | 95<br>Am  | 96<br>Cm  | 97<br>Bk  | 98<br>Cf  | 99<br>Es   | 100<br>Fm | 101<br>Md  | 102<br>No | J          |            |
|          |     |          |          |     |           |           |           |          |                 |           |           |           |           |           |            |           |            |           |            |            |

CHAPTER - 8

# **THE D AND F BLOCK ELEMENTS**



### **Introduction to d-Block Elements**

The d-block elements are defined as the elements from periodic table in which, last electron enters into the 'd-orbital' of the penultimate shell i.e. (n-1)d orbital. Where 'n' is the last shell.

The d-block elements are also called transition elements, because their properties are intermediate between the properties of highly electropositive s-block elements and highly electronegative p-block elements. Transition elements have partly or incompletely filled (n-1)d orbital in their elementary states.

### **D-block elements:**

The d-block elements are called transition metals (belonging to group 3 to 12) and have valence electrons in the d-orbitals. Its standard electronic configuration is  $(n-1) d^{1-10} ns^{1-2}$  where (n-1) represents the front shell (last but only one).

**Definition:** initially they were named 'transition elements' because their properties were found to be transitional between s and p block elements.

However, IUPAC definition is as follows,

Transition metals are metals which have incomplete d subshell either which have one or more unpaired d electrons in their ground state or in their common oxidation state can be called transition elements.

### Note

group-12 elements i.e., Zn, Cd and Hg have completely filled d-orbital both in their ground state and in their oxidation state thus they are not considered transition elements but nonetheless are studied under d-block. A lot of elements do not possess unpaired electrons in their ground state but definition helps identify them as transition elements. Eg. – Copper

Electronic configuration of is:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ . As we can see, it has a completely filled d-orbital in its ground state but in its common oxidation state i.e., +2,

Electronic configuration of  $Cu^{2+}$  is:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^9$ and it has an unpaired electron thus it can be called a transition element. A similar case is observed for silver.

The possession of unpaired d and f electrons makes transition elements different from s and p block elements and hence there study is carried out separately.

### Some important concepts

### **Enthalpy of Atomisation:**

Enthalpy of atomization,  $\Delta aH0$ , is the change in enthalpy when one mole of bonds is completely broken to obtain atoms in the gas phase. For example: atomization of methane molecule.

 $CH_4(g) \rightarrow C(g) + 4H(g)$   $\Delta_a H^0 = 1665.0 \text{ kJ mol-1}$ For diatomic molecules, the enthalpy of atomization is equal

to the enthalpy of bond dissociation. For example: the atomization of dihydrogen molecule.

 $H_2(g) \rightarrow 2H(g); \qquad \Delta_a H^0 = 435.0 \text{ kJ mol-}1$ 

### **Metallic Bonding:**

Metallic bonding is a type of chemical bonding that arises from the electrostatic attractive force between conduction electrons (in the form of an electron cloud of delocalized electrons) and positively charged metal ions.

### Lanthanoid contraction:

Lanthanides are the rare earth elements of the modern periodic table, i.e. the elements with atomic numbers from 58 to 71, following the element Lanthanum.

The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering the inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called lanthanoid contraction. Lanthanoid contraction is also known as lanthanide contraction

### **Standard Electrode Potential:**

Under standard conditions, the standard electrode potential occurs in an electrochemical cell say the temperature = 298K, pressure = 1atm, concentration = 1M. The symbol ' $E^{\circ}_{cell}$ ' represents the standard electrode potential of a cell.

### **Oxidation and Reduction:**

According to Classical or earlier concept oxidation is a process which involves the addition of oxygen or any electronegative element or the removal of hydrogen or any electropositive element.

According to electronic concept oxidation is defined as the process in which an atom or ion loses one or more electrons.

According to Classical or earlier concept reduction is a process which involves the addition of hydrogen or any electropositive element or the removal of oxygen or any electronegative element.

According to electronic concept reduction is defined as the process in which an atom or ion gains one or more electrons.

### Why are d-Block elements called transition elements?

The position of d-block elements are in between s-block and p-block elements in periodic table. These d-block elements are called transition elements because they exhibit transitional behaviour between s- and p-elements.

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

### **F-Block Elements:**

The elements of f block are lanthanides and actinides and are called genetic mutations due to their placement in the periodic table due to the activation of electrons. The orbitals of the electron shell are filled with "n-2." There are a high number of fourteen electrons that can reside in orbitals.

### Lanthanoids:

The 14 elements that immediately follow lanthanum, namely, Cerium (58) to Lutetium (71) are called lanthanoids. They belong to the first series of inner-transition elements. Lanthanum (57) has similar properties. Therefore, they called as lanthanoids.

### Actinoids:

The 14 elements immediately after actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They are in the second phase of inner-transition elements. Actinium (89) has similar features. Therefore, they called as actinoids.

# Why are f-block elements called inner transition elements?

F block elements are called inner transition elements because the last electron enters the anti-penultimate shell, which is inner to the penultimate shell in which the last electron of dblock elements enters.

### **Electronic Configuration d-Block Elements**

General electronic configuration of four series of d-block elements are given below.

3d series: [Ar]  $3d^{1-10} 4S^{1-2}$ 4d series : [Kr]  $4d^{1-10} 5S^{0-2}$ 5d series : [Xe]  $5d^{1-10} 6S^2$ 6d series : [Rn]  $6d^{1-10} 7S^2$ Abnormal Electronic Configuration of Chromium And Copper among d Block Elements Chromium(24Cr) has electronic configuration (Expected): [Ar]  $3d^4 4S^2$ (Observed): [Ar]  $3d^5 4s^1$ Copper (29Cu) has electronic configuration (Expected): [Ar]  $3d^9 4s^1$ (Observed): [Ar]  $3d^{10} 4s^1$ 

### Explanation

due to more stability of half –filled and completely filled orbital.

### **Physical Properties**

The transition metals are hard and tough. They have low volatility but Zn, Cd and Hg are an exception.

They have high melting and boiling points due to the greater quantity of electrons from (n-1) d along with the ns electrons metallic



Metals possessing high boiling point are noble in their

The metals belonging to second and third series have greater enthalpies of atomisation than the elements belonging to first series.



### **Four Transition series**

First transition series (or) 3d series

1. 3d - Transition series. Transition elements with an atomic number 21 (Sc) to 30 (Zn) and with an incomplete 3d orbital are called the first series of mutations.

| Element       | Atomic<br>number | Symbo<br>l | Electronic configuration              |  |  |
|---------------|------------------|------------|---------------------------------------|--|--|
| Scandium      | 21               | Sc         | [Ar] 3d <sup>1</sup> 4s <sup>2</sup>  |  |  |
| Titanium      | 22               | Ti         | [Ar] 3d <sup>2</sup> 4s <sup>2</sup>  |  |  |
| Vanadium      | 23               | v          | [Ar] 3d <sup>3</sup> 4s <sup>2</sup>  |  |  |
| Chromiu<br>m  | 24               | Cr         | [Ar] 3d <sup>5</sup> 4s <sup>1</sup>  |  |  |
| Manganes<br>e | 25               | Mn         | [Ar] 3d <sup>5</sup> 4s <sup>2</sup>  |  |  |
| Iron          | 26               | Fe         | [Ar] 3d <sup>6</sup> 4s <sup>2</sup>  |  |  |
| Cobalt        | 27               | Co         | [Ar] 3d <sup>7</sup> 4s <sup>2</sup>  |  |  |
| Nickel        | 28               | Ni         | [Ar] 3d <sup>8</sup> 4s <sup>2</sup>  |  |  |
| Copper        | 29               | Cu         | [Ar] 3d <sup>10</sup> 4s <sup>1</sup> |  |  |
| Zine          | 30               | Zn         | [Ar] 3d <sup>10</sup> 4s <sup>2</sup> |  |  |

**2. 4d** - **Transition series.** It contains elements with an atomic number 39 (Y) to 48 (Cd) and has an incomplete 4d orbital. It is called the second version of the version.

Second transition series (or) 3d series

| Element    | Atomic Number | Symbol | Electronic configuration              |
|------------|---------------|--------|---------------------------------------|
| Ytterium   | 39            | Y      | [Kr] 4d <sup>1</sup> 5s <sup>2</sup>  |
| Zirconium  | 40            | Zr     | [Kr] 4d <sup>2</sup> 5s <sup>2</sup>  |
| Niobium    | 41            | Nb     | [Kr] 4d <sup>4</sup> 5s <sup>1</sup>  |
| Molybdenum | 42            | Мо     | [Kr] 4d <sup>5</sup> 5s <sup>1</sup>  |
| Technetium | 43            | Tc     | [Kr] 4d <sup>5</sup> 5s <sup>2</sup>  |
| Ruthenium  | 44            | Ru     | [Kr] 4d <sup>7</sup> 5s <sup>1</sup>  |
| Rhodium    | 45            | Rh     | [Kr] 4d <sup>8</sup> 5s <sup>1</sup>  |
| Palladium  | 46            | Pd     | [Kr] 4d <sup>10</sup> 5s <sup>0</sup> |
| Silver     | 46            | Ag     | [Kr] 4d <sup>10</sup> 5s <sup>1</sup> |
| Cadmium    | 48            | Cd     | [Kr] 4d <sup>10</sup> 5s <sup>2</sup> |

**3. 5d - Transition series.** Transition elements with atomic numbers 57 (La), 72 (Hf) to 80 (Hg) and with an incomplete orbital 5d are called the third transformation series.

## Third transition series (or) 3d series

| Element   | Atomic number    | Symbol | Electronic configuration                               |
|-----------|------------------|--------|--|
| Lanthanum | 57               | La     | [Xe] 5d <sup>1</sup> 6s <sup>2</sup>                   |
| Hafnium   | 72               | Hf     | [Xe] 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>  |
| Tantalum  | 73               | Ta     | [Xe] 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>  |
| Tungstun  | 74               | W      | [Xe] 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>  |
| Rhenium   | 75               | Re     | [Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>  |
| Osmium    | 76               | Os     | [Xe] 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>  |
| Iridium   | 77               | Ir     | [Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>  |
| Platinum  | 78               | Pt     | [Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>  |
| Gold      | 79               | Au     | [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup> |
| Mercury   | <mark>8</mark> 0 | Hg     | [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> |

**4. 6d - Transition series**. Transition elements have an atomic number 89 (Ac), 104 (Rf) to 112 (Uub) and have an incomplete 6d orbital. It is called the fourth revolution series.

### **Common features of transition elements**

### Metallic Character -

All the transition metals have high thermal as well as electrical conductivity and having very high melting and boiling points compared to those of representative elements due to their closed-packed structure.

On-going across the period melting points first increase, attain maximum value and then steadily decreases as atomic number.

The strength of metallic bond depends upon the number of unpaired electrons, it increases up to middle i.e., up to  $(n-1)d^5$  hence accordingly melting and boiling points also increases.

After (n-1) d<sup>5</sup> configuration, the electrons start pairing, hence metallic strength, melting and boiling points decreases with increase in atomic number.

### Atomic radii

The atomic radii of the elements of 3d-series decreases as the atomic number increases.

The atomic radii increase from 3d to 4d, the atomic radii of the 4d and 5d transition series are very close due to lanthanoid contraction. For example, Zirconium and Hafnium.

This decrease in the metallic radius due to increase in the atomic mass leads to an increase in the density of elements. Consequently the density increases from titanium to copper.



**Ionic radii** - In the first row of transition elements ionic radii decreases with the increase in the number of atoms. The amount of ionic radii also depends on the oxidation state of the metals. As the oxidation state increases ionic radii decrease and as the oxidation state decreases ionic radii increase.

**Melting point**: generally, transition metals have a high melting and boiling point because of strong metallic bonds that they form using the ns and (n - 1)d electrons.

In a row, generally increases from the first element to the element with  $d^5$  electronic configuration and then falls regularly from there to last.

The reason attributed to this is that because the  $d^5$  configuration forms the strongest metallic bonding, melting point becomes very high.

Metals with very high enthalpy of atomisation tend to be noble in their reactions.

**Exception**: Mn and Tc's melting point is less than the previous element in their respective period despite having a d^5 configuration. This is because these elements have a stable half-filled configuration due to which these electrons do not participate in bonding, thus the atom-atom attraction of these metals is weaker and hence its easier to break their metallic bonds leading to a low melting point and hence the metals preceeding these (Cr and Mo) have the highest melting points.

**Lanthanoid Contraction** - The continuous depletion of the atomic and ionic radiation of the transition metals as the number of atoms increases. This is due to filling of 4f orbital before 5d orbitals. This size limit is normal. This is called lanthanoid contraction. It is because of the lanthanoid array that the atom of the second-line radio of genetic mutations is almost identical to that of the third-line mutation gene.

**Ionization enthalpy** - Transition elements have small size which results in high ionization energy.

They exhibit less electro positivity than the s-block elements due to their ionization potentials lying between S and P block elements.

They form covalent compounds.

The d-block elements exhibit an increase in the ionization potentials from left to right due to the screening effect of the new electrons added into the (n-1) d subshell.

The first transition series exhibit an increase in the second ionisation energies with the increase in atomic number due to stable electronic configuration.

Ionization energy decreases down the group.

Ionization energy increases across the period.

**Oxidation state** - The transition metal exhibit variable oxidation states and form compounds showing more than one (variable) oxidation states because energies levels of ns and (n-1)d are nearly similar. The oxidation state of 3d series is from +2 to +7 (except Cr and Cu).

The lowest oxidation states of these elements are +1 or +2 which is due to their 4s electrons.

As the number of unpaired electrons in 3d orbital increases the number of oxidation state also increases form Sc to Mn and after that electrons starts pairing in 3d orbital hence oxidation states decreases form Fe to Zn.

The highest oxidation state of transition elements is +8 which shown by Os and Ru.

### Standard hydrogen electrode

The electrode is connected to a standard hydrogen electrode (SHE) to constitute a cell

It consists of a platinum electrode coated with a layer of platinum black.

 $H^+(aq) + e^- \rightarrow \frac{1}{2} H2 (g)$ 



The electrode is immersed in an acidic solution and the pure hydrogen gas is bubbled through it.

The concentration of the reduced form and the oxidized form of hydrogen is sustained at unity with following conditions:

Pressure of hydrogen gas = 1 bar

Concentration of hydrogen ion in the solution = 1 molar

 $E_{cell} = E_{cathode} - E_{anode}$ 

 $E_{cell} = E_{cathode} - 0 = E_{cathode}$ 

The measured Emf of the cell: Pt|  $H_2$  (1 bar)|  $H^+$  (1M) ||  $Cu^{2+}$  (1M)| Cu is 0.34 V.

The positive value of the standard electrode potential signifies the easy reduction of  $Cu^{2+}$  ions than H+ ions. T he measured Emf of the cell

Pt| H<sub>2</sub> (1 bar)| H<sup>+</sup> (1M) || Zn<sup>2+</sup> (1M)| Zn is -0.76 V.

The negative value of the standard electrode potential signifies that the hydrogen ions oxidizes the zinc (or it can be said that zinc can reduce hydrogen ions).

An electrode with standard electrode potential greater than zero is stable in its reduced form compared to hydrogen gas.

Whereas an electrode with negative standard electrode potential is less stable in its reduced form compared to hydrogen gas.

This decreases the standard electrode potential which in turn decreases the oxidizing power of the specific electrode on the left and increases the reducing power of the electrode to the right of the reaction.

**Magnetic Properties -** Due to presence of unpaired electrons in the (n-1)d orbital, most of the transition metal ions and their compounds are paramagnetic i.e. they are attracted by magnetic field.

The transition element and their ions having all electrons paired are diamagnetic i.e. they are repelled by magnetic field.

Metals like Fe, Co and Ni possess very high paramagnetic and acquire permanent magnetic moment hence, they are ferromagnetic.

Alnico is an alloy of Al(12%), Ni(20%),Co(50%) and remaining Fe(18%). It is used to make permanent magnets. Bohr magneton (B.M) is unit of magnetic moment:  $1B.M = eh/4\pi mec$ 

The effective magnetic moment  $\mu$ eff, of a paramagnetic substance is given by 'spin only' formula.

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

Where n is the number of unpaired electrons.

**Catalytic Properties -** Many transition metals are used as catalysts which influence the rate of chemical reaction.

A catalytic substance is capable of forming an unstable intermediate compound which readily decomposes yielding the products and regenerating the catalyst.  $A+B + C \longrightarrow [A-B-C] \longrightarrow A-B + C$ (reactant) (catalyst) (intermediate) (product) (catalyst)

The commonly used transition metals as a catalyst are Fe, Co, Pt, Cr, Mn etc.

### Example

 $MnO_2$  acts as a catalyst for decomposition of  $KClO_3$  to  $O_2$ .

In manufacture of ammonia, Fe with Mo is used as catalyst.

Nickel acts as a catalyst in hydrogenation of oils to fats.

Transition metals and their compounds exhibiting catalytic properties in various processes are given below.

#### In general, the colour of transition ions can be related to -

- Presence of unpaired d electrons.
- d-d transition.
- Nature of groups i.e. ligands linked to metal ions.
- Geometry of the complexes formed by the metal ion

- (a)  $V_2O_5$  is used in the contact process for the manufacture of  $H_2SO_4$ .
- (b) Fe is used in Haber's process for the manufacture of  $NH_3$ .
- (c) Ni is used in the hydrogenation of oils.
- (d) FeSO<sub>4</sub> is used in the oxidation of Benzene with  $H_2O_2$ .
- (e) Cu is used in the dehydrogenation of alcohols.
- (f)  $TiCl_4$  is used as a catalyst in Vinyl polymerisation.
- (g) Pt is used in Ostwald's process of nitric acid.

**Formation of coloured compounds** - Most of the compounds of transition metals are coloured in their solid or solution form. Colour of the compound of the transition metals may be attributed to the presence of incomplete (n-1)d orbital and the number of unpaired electrons.

Transition metal ions with no unpaired electrons are colourless because there is possibility of d-d transition. e.g.  $Sc^{+3}(3d^0)$ ,  $Ti^{+4}(3d^0)$ ,  $Cu^+(3d^{10})$ . Ions with unpaired electrons are coloured i.e. ions with electronic configuration 3d1 to 3d9 are coloured.

| Configuration                   | Example                            | Colour     |
|---------------------------------|------------------------------------|------------|
| 3d°                             | Sc <sup>3+</sup>                   | colourless |
| 3d°                             | Ti4+                               | colourless |
| 3d <sup>1</sup>                 | T1 <sup>3+</sup>                   | purple     |
| 3d <sup>1</sup>                 | V <sup>4+</sup>                    | blue       |
| 3d <sup>2</sup>                 | V <sup>3+</sup>                    | green      |
| 3d <sup>3</sup>                 | V <sup>2+</sup>                    | violet     |
| 3d <sup>3</sup>                 | Cr <sup>a+</sup>                   | violet     |
| 3d*                             | Mn <sup>3+</sup>                   | violet     |
| 3d*                             | Cr <sup>2*</sup>                   | blue       |
| 3d <sup>5</sup>                 | Mn <sup>2*</sup>                   | pink       |
| 3d <sup>5</sup>                 | Fe <sup>3</sup> *                  | yellow     |
| 3d <sup>6</sup>                 | $Fe^{2*}$                          | green      |
| 3d <sup>6</sup> 3d <sup>7</sup> | Co <sup>3</sup> *Co <sup>2</sup> * | bluepink   |
| 3d <sup>s</sup>                 | Ni <sup>2+</sup>                   | green      |
| 3d <sup>9</sup>                 | Cu <sup>2+</sup>                   | blue       |
| 3d <sup>10</sup>                | Zn <sup>2+</sup>                   | colourless |

**Formation of complexes -** The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands.

The bonds involved in the formation of complexes are coordinate and hence the complexes are called coordinate complexes. The structure of these complex ions is linear, square, planar, tetrahedral, octahedral depending upon nature of hybridization of metal ions.

The weak ligand like CO, NO forms complexes only when transition metals are in zero due to the availability of vacant orbitals in the donor atom of the ligand in addition to lone pair. The highly electronegative and basic ligand like F-, Cl<sup>-</sup> can form complexes with transition metals even though there are in high oxidation states due to the presence of small, highly charged or neutral ligands with lone pair of electrons that can form strong sigma bond by donating a lone pair of electrons.

In a transition series the stability of complexes increases with the rise in atomic number.

The transition metal atom reveals multiple oxidation state; the higher valent ion forms more stable complexes.

A few examples are: [Fe (CN)<sub>6</sub>]<sup>3-</sup>



Octahedral Geometry



**Formation of Interstitial Compounds -** Transition elements in combination with small atoms like H, B, C, N etc. leads to the formation of interstitial compounds that are non-stoichiometric in composition. E.g.: TiH<sub>1.3</sub>, VH<sub>0.5</sub>

The interstitial compounds so formed are chemically inert having higher melting points as compared to pure metals. These compounds are hard and tough and keep metallic conductivity.



**Alloy Formation** - The transition metals can form large number of alloys among themselves having high melting points.

In the molten state, transition metals are miscible with one another, which forms solid alloy on cooling.

Transition metals can form alloy with non-transition metals such as brass (Cu-Zn) and bronze (Cu-Sn).

# Transition metals have the following physical characteristics:

- They are good heat and electricity conductors.
- They can be hammered or bent easily.
- They have high melting points (but mercury is a liquid at room temperature)
- They are usually strong and durable.
- They have high density.

### **Non-stoichiometric Compounds**

The compounds in which the there is no conformity in chemical composition with the ideal chemical formula are called non-stoichiometric compounds.

These compounds are formed due to variable valency in transition metals and also due to the defects arising in solid state.

The compounds formed with O, S, Se, Te, Fe, Zn etc. are the examples of such compounds.



### Preparation of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>):

Prepared by a combination of chromate ore (FeCr $_2O_4$ ) and sodium carbonate over air:

Potassium dichromate,  $(K_2Cr_2O_7)$  is an orange-ish inorganic chemical reagent. In different laboratory or industry it is basically used as an oxidizing agent usually for alcohols.

It can be prepared through the following process:

At first the fusion of chromite ore  $FeCr_2O_4$  with sodium or potassium carbonate in the presence of access of air.

 $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 --> 8Na_2CrO_4 + 2FeO_3 + 8CO_2$ 

Solution of sodium chromate is first filtered and then acidified with a solution of sulfuric acid which results in an orange sodium dichromate solution  $Na_2Cr_2O_7.2H_2O$  can be crystallized.

 $2Na_2CrO_4 + 2H^+ --> Na_2Cr_2O_7 + 2Na^+ + H_2O$ 

Sodium dichromate is more soluble than potassium dichromate and therefore it is fused with KCl that leads to the formation of orange crystals of potassium dichromate.

 $Na_2Cr_2O_7 + 2KCl --> K_2Cr_2O_7 + 2NaCl$ 

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

 $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$ 

Sodium

Sodium

Chromate Dichromate

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

Potassium Dichromate exists as orange red crystals and is soluble in water.

### Action of Alkali

Alkali (KoH) reacts with potassium dichromate to give yellow coloured solution of potassium chromate.  $K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$ 

### Properties of potassium dichromate Oxidizing Properties

Potassium Dichromate is good oxidizing agent in acidic medium. Potassium dichromate (oxidation number of Cr = +6) is reduced to chromium sulphate (oxidation number of Cr = +3)

 $Cr_2 O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O.$ 

By gaining six electrons dichromate ions acts as an oxidizing agent.



### Preparation of potassium permanganate (KMnO<sub>4</sub>):

It oxidizes iodides to iodine.  $Cr_2O_7 \ ^{2-} + 14H^+ + 6I^- --> 2Cr \ ^{3+} + 7H_2O + 3I_2$ It oxidizes ferrous salts to ferric salts.  $Cr_2O_7 \ ^{2-} + 14H^+ + 6 \ Fe^{2+} --> 2Cr \ ^{3+} + 7H_2O + 6Fe^{3+}$ It oxidizes stannous salts to stannic salts.  $Cr_2O_7 \ ^{2-} + 14H^+ + 3Sn \ ^{2+} --> 2Cr \ ^{3+} + 7H_2O + 3Sn \ ^{4+}$ It oxidizes H2S to sulphur.  $Cr_2O_7 \ ^{2-} + 8H^+ + 3H_2S --> 2Cr \ ^{3+} + 7H_2O + 3S$ 

**Effect of pH on chromate and dichromate ions:** Chromates and dichromates are converted into aqueous solution depending on the pH of the solution. The oxidation status of chromium in chromate and dichromate is similar.

 $2\mathrm{Cr}\mathrm{O}_{4^{2^{*}}}+2\mathrm{H}^{\scriptscriptstyle +} \xrightarrow{\phantom{*}} \mathrm{Cr}_{2}\mathrm{O}_{7^{2^{*}}}+\mathrm{H}_{2}\mathrm{O}$ 

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

Potassium dichromate acts as a strong oxidizing agent in an acidic environment.  $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ 

### **Uses of Potassium Dichromate**

- It is used as an oxidizing agent.
- Used in a dyeing.
- In manufacture of lead chromate and chrome alum.
- Used in the detect ion of chloride ion.
- In the tanning of leather.
- In manufacture of pigments and inks.
- **A.** Potassium permanganate is prepared by the combination of MnO<sub>4</sub> with alkali metal hydroxide (KOH) in the presence of O<sub>2</sub> or an oxidizing agent similar to KNO<sub>3</sub>. It produces a dark green K<sub>2</sub>MnO<sub>4</sub> that gets oxidation and reduces the neutral or acidic solution to give permanganate.

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

**B.** Commercially prepared by alkaline oxidative fusion of MnO<sub>2</sub> followed by electrolytic oxidation of manganite (VI).



### **Properties of KMnO**<sub>4</sub>

It is crystalline solid having deep purple colour. It is soluble in water at room temperature. When heated it decomposes giving oxygen at 473K.  $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ At red heat, it further decomposes to K<sub>2</sub>MnO<sub>3</sub> and oxygen. Heated solid KMnO<sub>4</sub> gives KOH, MnO and water vapour in current of H<sub>2</sub>.

### Uses of KMnO<sub>4</sub>

- It is used as –
- Disinfectant.
- An oxidizing agent.
- Baeyer's reagent.
- For detecting halides in qualitative analysis.

### **F-block Elements**

Elements whose f orbital getting filled up by electrons are called f block elements. These elements have electrons, (1 to 14) in the f orbital, (0 to 1) in the d orbital of the penultimate energy level and in the outermost's orbital.

There are two series in the f block corresponding to the filling up of 4f and 5f orbitals. The elements are 4f series of Ce to Lu and 5f series of Th to Lw. There are 14 elements filling up the 'f' orbital in each series.

### Lanthanides:



The electronic Configuration of lanthanoid is [Xe]  $4f^{n+1} 5d^{\circ} 6s^2$ or [Xe]  $4f^n 5d^1 6s^2$  with their valence shell electronic configuration as  $4f^{1-14} 6s^2$ .

They exhibit the oxidation state of +3, +2 and +4.

The initial members of this series are somewhat reactive towards calcium which resembles their behaviour to that of aluminium with the gradual increasing atomic number.

On application of gentle heat Lanthanides combine with hydrogen.

Heating them with carbon leads to the formation of carbides and halides (in presence of halogens while burning).

Reaction of Lanthanides with dilute acids releases hydrogen gas.

They form basic alkaline earth metal oxides and hydroxides like  $N_2O_3$  and  $M(OH)_3$ .

### **Oxidation States of Lanthanoids**

The common oxidation state of all lanthanoids is +3. It is characteristics of series.

Lanthanum, gadolinium and lutetium shows only +3 oxidation state by losing two 6s and one 5d electrons giving stable outer electronic configuration  $4f^{0}$ ,  $4f^{7}$  and  $4f^{14}$  respectively.

In +4 oxidation state cerium, terbium attains  $4f^0\ and\ 4f^7$  respectively.

Europium (Eu) as well as ytterbium (Yb) attains  $4f^7$  and  $4f^{14}$  respectively in +2 oxidation state.

Chemical Reactivity of Lanthanoids

Earlier members of lanthanoids are quite reactive, behaves like calcium but as atomic number increases, they behaves more like aluminium.

Lanthanoids forms carbides, hydrides, oxides, nitrides, halides, etc.

### **Carbides-**

Ln + C  $\rightarrow$  Lanthanoid Carbide Hydrides-  $2Ln + 3H_2 \rightarrow 2LnH_3$ Oxides-  $2Ln + 3O_2 \rightarrow 2Ln_2O_3$ Nitrides-  $2Ln + N_2 \rightarrow 2LnN$ Halides-  $2Ln + 6HCl \rightarrow 2LnCl_3 + 3H_2$ Sulphides- $2Ln + 3S \rightarrow Ln_2S_3$ 

### Lanthanoid Contraction

The gradual decrease in atomic and ionic size of lanthanoids with increases in atomic number is called lanthanoid contraction.

As we move along the lanthanoid series, the atomic number gradually increases by one or we can say number of electrons and protons increases by one.

Addition of electrons to the same shell increases the effective nuclear charge.

Increase in atomic number also increases the number of electrons in the 4f orbital having poor shielding effect due to which the effective nuclear charge upon the outer electrons also increases.

Therefore the size of lanthanoids steadily decreases with the increase in the atomic number and phenomenon is called lanthanoid

As a result of lanthanoid contraction there is a similarity in the properties of second and third transition series.



# Effects of Lanthanoid Contraction Decrease in Basicity

Due to lanthanoid contraction the size of the tri-positive lanthanoid ion (M3+) regularly decreases with increase in atomic number i.e. from  $La^{3+}$  to  $La^{3+}$ . It results into decrease of basic from  $La^{3+}$  to  $Lu^{3+}$ .

### Ionic Radii of the Post Lanthanoids

The elements which follow the lanthanoids in the third transition series are known as post lanthanoid. As a result of

lanthanoid contraction the atomic radii (size) of the elements which follow lanthanum (Hf, Ta, W, etc) are similar to that of the elements of 4d series. Since Zr-Hf, Nb-Ta, Mo-W and Tc-Re have almost identical sizes, similar number of valence electrons and similar properties these pairs of elements are called chemical twins.

### **Oxidation States of lanthanoids**

The elements belonging to lanthanide series exhibit an oxidation state of +3. For example, Praseodymium (Pr) shows +3 oxidation state.

### **Actinides Series**

Some elements exhibit +2 oxidation states in their complexes in solutions. For example, Samarium (Sm), Europium (Eu), Thulium (Tm) and Ytterbium (Yb) show +2 oxidation state. Some elements exhibit +4 oxidation states due to high stability of empty, half-filled or fully filled f-subshells. Praseodymium (Pr), Neodymium (Nd), Terbium (Tb) and Dysprosium (Dy) exhibits +4 oxidation state in their oxides. Cerium (Ce) shows both +3 as well as +4 state.



The series of fourteen elements 90Th to 103Lr which follows actinium (89Ac) and in which last electrons are progressively filled in 5f orbital in pre-penultimate shell are called actinoid series or 5f series.

The elements which are synthetically or artificially prepared by man having atomic number higher than uranium (z=92) are called as trans-uranic elements (Np-93 to Uno-118).

### **Position of Actinoids**

The actinoids belongs to third group of the periodic table in the seventh period.

Actinoids are placed at the bottom of the periodic table below the lanthanoid series because it interrupts fourth transition series of d-block elements.

**Electronic Configuration** The general electronic configuration of 5f elements is represented as 5f1-14  $6d^{0-1}$   $7s^2$ .

The electronic configuration of actinoids is not definite. Actinium and thorium does not contain any 4f electron.

### **Oxidation state in Actinoids**

In general the oxidation state of these elements is +3 (similar to lanthanides).

They also exhibit +4 oxidation states.

Some of the elements also exhibit higher oxidation states.

The oxidation state initially rises to the middle of the series (+4 for Th to +5, +6 and +7 for Pa, V and Np) and then descends in the succeeding elements.

#### **Actinide Contraction**

The atomic size/ ionic radii of tri positive actinides ions decrease steadily from Th to Lw due to increasing nuclear charge and electrons entering the inner (n-2) f orbital.

This gradual decrease in the size with an increasing atomic number is called actinide contraction like lanthanide contraction. Because of the very poor shielding by 5f electrons, contraction is larger along the period.

### **Formation of Coloured Ions**

Actinides like lanthanides ions have electrons in f-orbital and also empty orbitals like the d-block elements. When a

frequency of light is absorbed, the f-f electron transition produces a visible colour.

### **Ionization of Actinides**

The actinides have lower ionization enthalpies than lanthanides because 5f electrons are more effectively shielded from nuclear charge than 4f.

### **Formation of Complexes**

Actinides are better complexing agents than lanthanides due to the smaller size but higher nuclear charge. They can form  $P\pi$  – complexes as well.

Degree of complexion decreases in the order  $M^{4+} > MO_2{}^{2+} > M{}^{3+} > MO_2{}^{2+.}$ 

### **Chemical Reactivity of Actinides**

Because of the lower ionization energy, actinides are electropositive than lanthanides and most reactive. They react with hot water. React with oxidizing agents and form a passive coating. Form halides and hydrides. Actinides are strong reducing agents.

#### **Properties of Lanthanides**

- Lanthanides are soft metals with a silvery white colour.
- Their colour dulls and their brightness reduces rapidly when exposed to air.
- They have melting points ranging from 1000K to 1200K (Except Samarium, 1623K).
- Lanthanides are good conductors of heat and electricity.
- They are non-radioactive in nature except Promethium
- A decrease in atomic and ionic radii from lanthanum to lutetium is observed. This is called the lanthanoid contraction.

#### **Properties of Actinoids:**

- They all have radiation.
- Actinides are very electropositive.
- Metals decompose easily in air.
- Actinides are very dense metals with different properties.
- Reacts with boiling water or purifying acid to release hydrogen gas.
- Actinide iron is usually soft.

### **Difference between Lanthanides and Actinides**

- Lanthanoids are involved in the filling of 4f- orbitals whereas actinoids are involved in the filling of 5f- orbitals. The binding energy of 4f electrons is comparatively less than that of 5f-electrons. The shielding effect of 5f-electrons is less effective as compared to that of 4f-electrons.
- The paramagnetic properties of lanthanoids can be easily explained but this explanation is difficult in the case of actinoids.
- Lanthanides are non-radioactive in nature except promethium whereas all actinide series elements are radioactive.
- Lanthanides do not have a tendency to form oxo-cations, but several oxo-cations of actinide series exist. The compounds formed by lanthanides are less basic on the other hand the compounds of actinides are highly basic.

### Uses of Lanthanides:

It is used as a catalyst in the manufacture of petroleum and synthetic products.

Thoria and Ceria are used in lamps, magnets, lasers, motion picture projectors, and X-ray intensify screens.

Alloys of Lanthanides are used in the instrumental steels, stainless steel, and heat resistance.

It is used for the metallothermic reaction.

Ceria salts are used in lead storage batteries.

# Q. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

**Sol.** In actinoids, 5f orbitals are filled having poorer shielding effect than 4f orbitals (in lanthanoids) due to which the effective nuclear charge experienced by the electrons in valence shells of actinoids is more than what is experienced by lanthanoids. Therefore, the size of contraction in actinoids is greater as compared to that in lanthanoids. They are termed as inner transition elements due to their occurence inside the series of transition elements.

Q. What is the significance of formation of coloured ions by transition metals?

Coloured compounds of transition Sol. elements are associated with partially filled (n-1)d orbitals. The transition undergoes electronic unpaired delectrons undergo an electronic transition from one -d- orbital to another. During this d-d transition process, the electrons absorb certain energy from the radiation and emit the remainder of energy as coloured light. The colour of the ion is complementary to the colour absorbed by it. Hence, the coloured ion is formed due to d-d transition which falls in the visible region for all transition elements.

### Why do d-block element form complexes?

**Q**.

**Sol.** The d-block elements are smaller in size and have high electropositive density and they consist of (n-1)d free orbitals to accept the free electrons from the ligand and it forms complexes easily.

**Mischmetal**: Mischmetal is an alloy of rare earth elements with iron and traces of S, C, Ca and Al. The composition is 50% cerium and 25% lanthanum, with small amounts of neodymium and praseodymium. It improves workability of steel. It is used in the ferrocerium "flint" ignition device of many lighters and torches.

It is also used in the preparation of rare earth elements.

### **Question For You**

Why F-block elements are placed separately? Are all F-block elements radioactive?

Why are F-block elements called inner transition elements?

### **SUMMARY**



The d-block consisting of group 3-12 occupies the large middle section of the periodic table. In these elements are filled in d-orbitals. The f-block is at the bottom and the electrons are filled in 4f and 5f orbitals.

All the transition elements exhibit typical metallic properties such as high tensile strength, ductility, malleability, thermal and electrical conductivity. Their melting and boiling points are high because the elements were go into the (n-1) d subshell resulting into strong interatomic bonding. The maxima of all the properties will occur at the middle of each series which indicates that one unpaired electron per d orbital is particularly a favourable configuration for strong interatomic interaction.

Successive ionisation enthalpies do not increase as gradually as in the group elements with increasing atomic number. Hence, the loss of variable number of electrons form (n-1) d orbitals is not energetically unfavourable. The transition elements exhibit certain different characteristics because of involvement of (n-1)d subshell. Thus, in addition to variable oxidation state, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

Transition elements varies in their chemical behaviour also. Many of them are sufficiently electropositive and remaining are noble. With the exception of copper, all the first transition elements are relatively reactive. Transition metals react with a number of non-metals like oxygen, nitrogen, sulphur etc. to form binary compounds. The first transition series is generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolved in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore is used for the preparation of potassium permanganate. Both are strong oxidising agent.

The two series of inner transition elements lanthanoids and actinoids are called the f- block elements. With the successive filling of the inner orbitals 4f, there is a gradual decrease in the atomic and ionic size of these metals. Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although+4, +2 oxidation states are also exhibited by some occassionally. The chemistry of the actinoids is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoids elements are radioactive which make the study of these elements rather difficult.

There are many useful applications of the d and f-block elements and their compounds.

# **MIND MAP**

Characteristics properties

Acts as catalyst due to variable

Coloured compounds due to d-d

Interstitial compounds due to

Formation of complex due to

Alloy formation due to similar size

oxidation state

transition

vacant space

vacant d orbitals

Physical properties Show metallic properties High melting and boiling point Higher value of enthalpy of atomization

Oxides of oxoanions of metals Potassium dichromate Potassium permanganate

 $\begin{array}{c} Electronic \ configuration \\ (n-1) \ d^{1-10} \ ns^{1-2} \end{array}$ 

d-Block elements (Between s and p-block Uses Conductor, catalyst, paint and construction materials etc.

Trends

Atomic and ionic size decreases with the increasing atomic number for a given series. Increase in ionization enthalpy from left to right. Variable oxidation state Trends in M2+/M Standard electrode Potential irregular Chemical reactivity irregular Magnetic moment increases with increasing atomic number

Lanthanides [Xe] 4f<sup>1-14</sup> 5d<sup>0-1</sup> 6s<sup>2</sup> General characteristics of Lanthanides Silvery in appearance Tarnish in air Hardness increases with atomic number Good conductor of electricity Good reducing agents

Trends in Lanthanides Atomic and ionic size decreases from La to Lu. Oxidation state = common oxidation state +3. They also shows +2 and +4. Ionisation enthalpies of Lanthanides is higher than actinides.

f-Block elements

General characteristics of actinides Silvery in appearance Display a variety of structures Highly reactive metals Complex magnetic property Trends in actinides Atomic and ionic radii decreases along the series. Oxidation state – common state +3. They also shows +4, +5, +6 and +7.

> Actinides [Rn] 5f<sup>1-14</sup> 6d<sup>0-1</sup> 7s<sup>2</sup>

# **QUESTIONS FOR PRACTICE**

**Q1.** In which of the following pairs, both the ions are **Q11.** The oxidation state of Cr in final product formed by coloured in aqueous solutions? reaction of KI and acidified dichromate solution is (a) Sc<sup>3+,</sup> Ti (b) Sc<sup>3+</sup>, CO<sup>2+</sup> (a) +4 (b) +6 (c) Ni<sup>2+</sup>, Cu<sup>+</sup> (d) Ni<sup>2+</sup>, Ti<sup>3+</sup> (c) + 2(d) +3 Q2. The number of moles of KMnO<sub>4</sub> that will be needed to **012.** KMnO<sub>4</sub> gets reduced to react with one mole of SO32- in acidic solution. (a) K<sub>2</sub>MnO<sub>4</sub> in neutral medium (a) 1 (b) 3/5 (b) MnO<sub>2</sub> in acidic medium (c) 4/5 (d) 2/5 (c) Mn<sup>2+</sup> in alkaline medium (d) MnO<sup>2</sup> in neutral medium Q3. The correct order of decreasing second ionisation enthalpy of Ti(22), V(23), Cr(24) Mn(25) **Q13.** The electronic configuration of Cu(II) is 3d9 whereas (a) V > Mn > Cr > Tithat of Cu(I) is 3d<sup>10</sup>. Which of the following is correct? (b) Mn > Cr > Ti > V[NCERT Exemplar] (c) Ti > V > Cr > Mn(a) Cu(II) is more stable (d) Cr > Mn > V > Ti(b) Cu(II) is less stable **Q4.** Which of the following pairs has the same ionic size? (c) Cu(I) and Cu(II) are equally stable (b) Zn<sup>2+</sup>, Hf<sup>4+</sup> (a) Zr<sup>4+</sup>, Hf<sup>4+</sup> (d) Stability of Cu(I) and Cu(II) depends on nature of (d) Zr4+, Ti4+ (c) Fe<sup>2+</sup>, Ni<sup>2+</sup> copper salts Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution turns green when SO2 gas is 05. **Q14.** Generally transition elements form coloured salts due passed through it due to formation of to the presence of unpaired electrons. Which of the (b)  $CrO_{4^{2}}$ (a)  $Cr_2(SO_4)_3$ following compounds will be coloured in solid state? (c) Cr<sub>2</sub>(SO<sub>3</sub>)<sub>3</sub> (d) CrSO<sub>4</sub> (a)  $Ag_2SO_4$ (b)  $CuF_2$ (c) ZnF<sub>2</sub> (d)  $Cu_2Cl_2$ The stability of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Cr^{2+}$ ,  $Co^{2+}$  is in order of (At 06. No. of Mn = 25, Fe = 26, Cr = 24, Co = 27) **Q15.** On addition of small amount of KMnO<sub>4</sub> to concentrated (a)  $Mn^{2+} > Fe^{2+} > Cr^{2+} > Co^{2+}$ H<sub>2</sub>SO<sub>4</sub>, a green oily compound is obtained which is (b)  $Fe^{2+} > Mn^{2+} > Co^{2+} > Cr^{2+}$ highly explosive in nature. Identify the compound from (c)  $Co^{2+} > Mn^{2+} > Fe^{2+} > Cr^{2+}$ the following. (d)  $Cr^{2+} > Mn^{2+} > Co^{2+} > Fe^{2+}$ (a)  $Mn_2O_7$ (b)  $MnO_2$ **Q7.** Which of the following lanthanoid ion is diamagnetic? (c) MnSO<sub>4</sub> (c)  $Mn_2O_3$ (At No. of Ce = 58, Sm = 62, Eu = 63 Yb = 70) Q16. Anomalous electronic configuration in the 3d series (a) Eu<sup>2+</sup> (b) Yb<sup>2+</sup> are of (c) Ce<sup>2+</sup> (d) Sm<sup>2+</sup> (a) Cr and Fe (b) Cu and Zn Magnetic moment of 2.83 BM is given by which of the **Q8**. (d) Cr and Cu (c) Fe and Cu following ion? **Q17.** Which of the following are d-block elements but not (a) Ti<sup>3+</sup> (b) Ni<sup>2+</sup> regarded as transition elements? (c) Cr<sup>3+</sup> (d) Mn<sup>2+</sup> (a) Cu, Ag, Au (b) Zn, Cd, Hg **Q9.** KMnO<sub>4</sub> is not acidified by HCl instead of H<sub>2</sub>SO<sub>4</sub> because (c) Fe, Co, Ni (a) H<sub>2</sub>SO<sub>4</sub> is stronger acid than HCl (d) Ru, Rh, Pd (b) HCl is oxidised to Cl2 by KMnO<sub>4</sub> (c) H<sub>2</sub>SO<sub>4</sub> is dibasic acid **018.** CuSO<sub>4</sub>.5H<sub>2</sub>O is blue is colour because (d) rate is faster in presence of H<sub>2</sub>SO<sub>4</sub> (a) It contains water of crystallization. **Q10.** Out of  $Mn_2O_7 V_2O_3$ ,  $V_2O_5$ , CrO,  $Cr_2O_3$ , the basic oxides (b)  $SO_4^{2-}$  ions absorb red light. are (c) Cu<sup>2+</sup> ions absorb orange red light. (a)  $Mn_2O_7, V_2O_3$ (b) V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> (d)  $Cu^{2+}$  ions absorb all colours except red from the (d)  $V_2O_3$  and CrO (c) V<sub>2</sub>O<sub>5</sub>, CrO white light.

| Q19. | Transition elements form   | alloys easily because they  |              | (c) Yb   | (d) Ho.  |       |
|------|--|---|--------------|--|--|-------|
|      | have<br>(a) Same atomic number<br>(b) Same electronic config<br>(c) Nearly same atomic siz<br>(d) None of the above  | uration<br>e  | Q28.         | The anomalous e<br>shown by<br>(a) Cr, Cu<br>(c) Cr, Zn  | electronic configuration in 3d-sea<br>(b) Sc, Cr<br>(d) Cr, Mn                       | ries  |
| Q20. | Which one of the follow<br>transition metals is asso-<br>activity?   | wing characteristics of the<br>ciated with higher catalytic   | Q29.         | Which element is<br>point.<br>(a) Ti<br>(c) Zn   | s having lowest melting and boil<br>(b) Cu<br>(d) Mn                                 | ing   |
|      | <ul><li>(b) Paramagnetic behavior</li><li>(c) Colour of hydrate ions</li><li>(d) Variable oxidation stat</li></ul>   | es  | Q30.         | In 1st transition s<br>(a) V<br>(c) Cu   | eries which has low melting poin<br>(b) Mn<br>(d) Zn                                 | t     |
| Q21. | The property which is no<br>metals is<br>(a) Variable oxidation stat<br>(b) Tendency to form com   | t characteristic of transition<br>es.<br>plexes.  | Q31.<br>Q32. | The lowest densit<br>(a) Copper<br>(c) Sc<br>Which one of the  | y d-block element is<br>(b) Nickel<br>(d) Zinc<br>following metals is used as a cata | lyst  |
|      | <ul><li>(c) Formation of coloured</li><li>(d) Natural radioactivity.</li></ul>   | compounds.  |              | (a) Tungsten<br>(c) Chromium   | (b) Molybdenum<br>(d) iron containing Mo.  |       |
| Q22. | <ul> <li>Which of the following is used as an oxidising agent</li> <li>(a) HCl cannot be use consumed in the rea</li> <li>(b) Nitric acid is not u because it itself acts</li> </ul> | a incorrect for KMnO <sub>4</sub> to be<br>?<br>d because some KMnO <sub>4</sub> is<br>action.<br>used for the above purpose<br>as a self-oxidising agent and | Q33.         | When manganese<br>gives<br>(a) potassium per<br>(b) potassium man<br>(c) manganese hyd<br>(d) Mn304. | e dioxide is fused with KOH in air<br>manganate<br>nganate<br>droxide                | r. It |
|      | <ul> <li>(c) The equivalent w<br/>medium is 158.</li> <li>(d) The number of elect</li> </ul>   | eight of KMnO <sub>4</sub> in basic   | Q34.         | Which metal has l<br>(a) Cs<br>(c) Hg  | lowest melting point?<br>(b) Na<br>(d) Sn  |       |
| Q23. | KMnO <sub>4</sub> in acidic me<br>Transition metals, despite<br>reducing agents. The incon   | dium is 3.<br>e high E° oxidation, are poor<br>rect reason is   | Q35.         | Which is the first<br>(a) Sc<br>(c) Tc   | man-made element?<br>(b) Os<br>(d) Zr  |       |
|      | <ul><li>(b) High ionization energie</li><li>(c) Low heats of hydration</li><li>(d) Complex forming natu</li></ul>  | es.   | Q36.         | Which transition<br>state?<br>(a) Sc   | (b) Ti   | ion   |
| Q24. | Which of the following ha<br>5.9?<br>(a) Fe <sup>2+</sup><br>(c) Ni <sup>2+</sup>  | s magnetic moment value of<br>(b) Fe <sup>3+</sup><br>(d) Cu <sup>2+</sup>  | Q37.         | (c) 05<br>In KMnO4 oxidati<br>(a) +2<br>(c) + 6  | (d) 2n<br>on number of Mn is<br>(b) + 4<br>(d) + 7                                   |       |
| Q25. | Which of the following act<br>upto +7?<br>(a) Am<br>(c) U  | inoids show oxidation states<br>(b) Pu<br>(d) Np  | Q38.         | When KMnO <sub>4</sub> ac<br>medium, the oxida<br>(a) 1<br>(c) 3                                     | cts as oxidising agent in alka<br>ation number of Mn decreases by<br>(b) 2<br>(d) 5. | ine   |
| Q26. | General electronic config<br>2) $f^{1-14}$ (n – 1) $d^{0-2}$ ns <sup>2</sup> .Whithave one electron in 6d or   | uration of actionoids is (n –<br>ch of the following actinoids<br>bital?  | Q39.         | Ag+ ion is isoelect<br>(a) Au <sup>3+</sup><br>(c) Zn <sup>2+</sup>                                  | ric with<br>(b) Cd <sup>2+</sup><br>(d) Pd <sup>2+</sup>                             |       |
|      | <ul><li>(a) U (Atomic no. 92)</li><li>(c) Pu (Atomic no. 94)</li></ul>   | (b) Np (Atomic no. 93)<br>(d) Am (Atomic no. 95)  | Q40.         | The transition ele<br>(a) Scandium<br>(c) Zinc   | ement with lowest atomic number<br>(b) Titanium<br>(d) Lanthanum                     | is is |
| Q27. | Which of the following lar<br>state besides the character<br>lanthanoids?<br>(a) Ce  | athanoids show +2 oxidation<br>eristic oxidation state +3 of<br>(b) Eu  | Q41.         | Which of the follo<br>(a) CaO<br>(c) SiO <sub>2</sub>  | wing oxides is amphoteric in natu<br>(b) CO <sub>2</sub><br>(d) SnO <sub>2</sub>     | re?   |

- (b) Cd<sup>2+</sup> (d) Pd2+
- t with lowest atomic number is (b) Titanium (d) Lanthanum

- (b) Ti (d) Zn
- (b) + 4 (d) + 7
- umber of Mn is
- (b) 0s (d) Zr

Q42. The equivalent mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, when it acts as oxidising agent in acidic medium, is equal to
(a) M (b) M/2

| (d) M/5 |
|---------|
|         |
|         |

- Q43. Rutile is an ore of<br/>(a) Scandium<br/>(c) Manganese(b) Titanium<br/>(d) Chromium
- Q44. If two compounds have the same crystal structure and analogous formula, they are called(a) Isomers(b) Isotopes
  - (c) Isobars (d) Isomorphous.
- Q45. Which of the following would be diamagnetic? (a)  $Cu^{2+}$  (b)  $Ni^{2+}$ (c)  $Cd^{2+}$  (d)  $Ti^{3+.}$
- Q46. Which of the following would be paramagnetic? (a)  $Zn^{2+}$  (b)  $Cu^+$ (c)  $Ag^+$  (d)  $Ni^{2+}$
- Q47. Which of the following is not an actinide?(a) curium(b) californium.(c) uranium(d) terbium.
- Q48. Least paramagnetic property is shown by (a) Fe (b) Mn (c) Ni (d) Cu
- **Q49.** Vanadium (III) oxide is a strong
  - (a) Drying agent (b) Oxidizing agent
  - (c) Reducing agent (d) Witting agent
  - (e) Precipiting agent.
- **Q50.** The value of spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is (a) d4 (in strong ligand field)
  - (b) d4 (in weak ligand field)
  - (b) d4 (in weak ligand field)
  - (c)  $d^3$  (in weak as well as strong fields)
  - (d) d5 (in strong ligand field)

# ASSERTION AND REASONING

**Q1. Assertion:** Magnetic moment values of actinides are lesser than the theoretically predicted values.

**Reason:** Actinide elements are strongly paramagnetic

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- **Q2.** Assertion: Cuprous ion (Cu<sup>+</sup>) has unpaired electrons while cupric ion (Cu<sup>++</sup>) does not.

**Reason:** Cuprous ion  $(Cu^+)$  is colourless whereas cupric ion  $(Cu^{++})$  is blue in the aqueous solution.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is incorrect but Reason is correct

### Q3. Assertion: Transition metals show variable valency.

- **Reason:** Transition metals have a large energy difference between the  $ns^2$  and (n 1)d electrons.
  - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
  - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
  - (c) If the Assertion is correct but Reason is incorrect.
  - (d) If both the Assertion and Reason are incorrect.
  - (e) Assertion is incorrect but Reason is correct
- **Q4.** Assertion: Transition metals are good catalysts. **Reason:** V<sub>2</sub>O<sub>5</sub> or Pt is used in the preparation of H<sub>2</sub>SO<sub>4</sub> by contact process.
  - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
  - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
  - (c) If the Assertion is correct but Reason is incorrect.
  - (d) If both the Assertion and Reason are incorrect.
  - (e) Assertion is incorrect but Reason is correct.

# TRUE/FALSE

- **Q1.** Interstitial compounds have high melting points, higher than those of pure metals.
  - (a) True
  - (b) False
- **Q2.** Permangnate titrations in presence of hydrochloric acid are unsatisfactory.
  - (a) True
  - (b) False
- **Q3.** KMnO<sub>4</sub> does not act as an oxidising agent in strong alkaline medium.
  - (a) True
  - (b) False

# **QUESTIONS FOR PRACTICE**

| Q1.  | Transition metals are generally coloured because<br>(a) they absorb electromagnetic radiations<br>(b) their penultimate d-subshells are fully filled<br>(c) of d-d transition<br>(d) none of the above |   |  |  |  |
|------|--|---|--|--|--|
| Q2.  | Paramagnetism is commor<br>(a) s-block elements<br>(c) d-block elements  | i in<br>(b) p-block elements<br>(d) any of them                                 |  |  |  |
| Q3.  | Transition elements exhib<br>they release electrons from<br>(a) ns orbitals<br>(c) (n-1)d orbitals   | it variable valency because<br>1<br>(b) np orbitals<br>(d) (n-1)d & ns orbitals |  |  |  |
| Q4.  | In industrial processes, tra<br>oxides are used as<br>(a) Surfactants<br>(c) Catalyst  | <ul><li>(b) Insecticides</li><li>(d) any of them</li></ul>                      |  |  |  |
| Q5.  | What is the nature of the transition elements?<br>(a) Varies from element to element<br>(b) Metallic<br>(c) Non-metallic<br>(d) Metalloid  |   |  |  |  |
| Q6.  | How many series' of transi<br>the periodic table?<br>(a) One<br>(c) Three  | tion elements are present in<br>(b) Two<br>(d) Four                             |  |  |  |
| Q7.  | Which of the following ele<br>transition series of the per<br>(a) Nb<br>(c) Au   | ment belongs to the second<br>iodic table?<br>(b) Ni<br>(d) La                  |  |  |  |
| Q8.  | Which of the following element belongs to the third transition series of the periodic table?<br>(a) Tc (b) Sc<br>(c) Re (d) Rh   |   |  |  |  |
| Q9.  | Which of the following e<br>element?<br>(a) Fe<br>(c) Zn   | lement is not a transition<br>(b) Mn<br>(d) Ag                                  |  |  |  |
| Q10. | Which of the following is u<br>(a) Uranium<br>(c) Zinc   | sed as a nuclear fuel?<br>(b) Cobalt<br>(d) Iron                                |  |  |  |
| Q11. | What is the end product for with HCl?  | ormed when KMnO4 reacts   |  |  |  |

| (a) Dense white fumes | (b) Brown fumes         |
|-----------------------|-------------------------|
| (c) Dark green gas    | (d) Greenish yellow gas |

|          | Q12. | What is the colour of KMn                                  | 04?  |
|----------|------|--|--|
|          |      | (a) Colourless   | (b) Green                                  |
|          |      | (c) Purple   | (d) Blue                                   |
|          | Q13. | Which property of actinoi<br>(a) Acidic                    | ds cannot be explained?<br>(b) Radioactive |
|          |      | (c) Oxidation  | (d) Magnetic                               |
|          | Q14. | Actinoids are mostly attac                                 | ked by which acid?                         |
|          | -    | (a) Hydrochloric acid                                      | (b) Nitric acid                            |
| 3        |      | (c) Sulphuric acid   | (d) Boric acid                             |
|          | Q15. | Which of the following is a                                | amphoteric?                                |
|          |      | (a) CrO  | (b) Cr <sub>2</sub> O <sub>3</sub>         |
| r        |      | (c) CrO <sub>5</sub>                                       | (d) CrO <sub>3</sub>                       |
|          | Q16. | What happens to the ato                                    | omic size of the lanthanides               |
|          |      | (a) The radius remains up                                  | changed                                    |
|          |      | (a) The radius decreases                                   | lenangeu                                   |
|          |      | (c) The radius increases                                   |  |
|          |      | (d) The radius first increa                                | ses and then decreases                     |
|          | Q17. | Which of the following                                     | is not a consequence of                    |
| ı        |      | lanthanide contraction?                                    |  |
| -        |      | (a) The atomic radii of 40                                 | and 5d series is similar                   |
|          |      | (b) From La+3 to Lu+3, $106 \text{ nm}$ to $95 \text{ nm}$ | the ionic radii changes from               |
|          |      | (c) As the size of the la                                  | nthanide ions decreases the                |
| ł        |      | basic strength incre                                       | eases                                      |
|          |      | (d) The basic character                                    | r of oxides and hydroxides                 |
|          |      | decreases with incr  | ease in atomic number                      |
|          | Q18. | Which of the following is n                                | ot a property of lanthanides?              |
| 1        |      | (a) The melting point o                                    | f the metal ranges from 500-               |
|          |      | 1000K  |  |
|          |      | (b) They are soft metal                                    | s with white silvery color                 |
| <b>,</b> |      | (c) They tarnish rapidly                                   | y by air                                   |
| 1        |      | (d) The hardness of  | the metals increases with                  |
|          | 010  | Which of the following                                     | is the correct order of                    |
|          | Q19. | arrangement of the first f                                 | ive lanthanides according to               |
|          |      | atomic number?   | ive faithainaes according to               |
|          |      | (a) La, Ce, Pr, Pm, Nd                                     |  |
|          |      | (b) La, Ce, Pr, Nd, Pm                                     |  |
| -        |      | (c) La, Pr, Ce, Pm, Nd                                     |  |
| 5        |      | (d) La, Pr, Ce, Nd, Pm                                     |  |
|          | Q20. | Which is the last element                                  | of lanthanides?                            |
|          |      | (a) Ytterbium  | (b) Lutetium                               |
|          |      | (c) Thulium  | (d) Erbium                                 |

- **Q21.** What is the nature of the transition elements?
  - (a) Varies from element to element
  - (b) Metallic
  - (c) Non-metallic
  - (d) Metalloid
- **Q22.** Why there is an increase in the atomic radius of transition elements at the end of the period?
  - (a) Increased electron-electron repulsions
  - (b) Decreased electron-electron repulsions
  - (c) Increase in nuclear charge
  - (d) Increase in atomic mass
- **Q23.** Why the atomic radii of the second and third transition series are almost same?
  - (a) Actinoid contraction
  - (b) Radioactive nature
  - (c) Lanthanoid contraction
  - (d) Filled d-orbital
- Q24. Group VIB of transition elements contains
  - (a) Zn Cd Hg
  - (b) Fe Ru Os
  - (c) Cr Mo W
  - (d) Mn Te Re
- **Q25.** What is the formula of hematite?
  - (a) Fe<sub>3</sub>O<sub>4</sub>
  - (b) FeSO<sub>4</sub>.7H<sub>2</sub>O
  - (c) Fe<sub>2</sub>O<sub>3</sub>
  - (d) FeCl<sub>3</sub>
- **Q26.** Which of the following is Baeyer's reagent?
  - (a) Acidified KMnO<sub>4</sub>
  - (b) Alkaline KMnO<sub>4</sub>
  - (c) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  - (d) Aqueous KMnO<sub>4</sub>
- **Q27.** Which of the following metal is used as a thermometric liquid?
  - (a) Iron
  - (b) Copper
  - (c) Mercury
  - (d) Potassium
- **Q28.** Which of the following test does AgCl not answer? (a) Chromyl chloride test
  - (a) Chi oniyi chioi lu
  - (b) Baeyer's test(c) Alkaline test
  - (d) Acidic test
  - Which commoned formed
- **Q29.** Which compound forms double salt with sulpahtes of alkali metals?
  - (a) Ferric oxide
  - (b) Silver nitrate

- (c) Ferric chloride
- (d) Ferrous sulphate
- $\label{eq:Q30.Which compound is used in Ultra-violet calibration?} \textbf{Q30.} \\$ 
  - (a) Hg<sub>2</sub>Cl<sub>2</sub>
  - (b) HgCl<sub>2</sub>
  - (c) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  - (d) KMnO<sub>4</sub>

# ASSERTION AND REASONING

**Q1. Assertion:** Transition metals are efficient catalysts. **Reason:** Transition metals usually contain incomplete d-orbitals and provide larger surface area for adsorption.

Transition metals are efficient catalysts.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is incorrect but Reason is correct
- **Q2.** Assertion: In transition elements, the ns orbital is filled up first and (n-1)d afterwards. During ionization, ns electrons are lost prior to (n-1)d electrons.

**Reason:** The effective nuclear charge felt by (n-1) d electrons is higher as compared to that by ns electrons.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is incorrect but Reason is correct
- $\label{eq:Q3.Assertion: It is not possible to obtain anhydrous ZnCl_2 by heating ZnCl_2.2H_2O.$

**Reason:** ZnCI<sub>2</sub>.2H<sub>2</sub>O. undergoes hydrolysis to produce Zn(OH)<sub>2</sub> and HCI.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is incorrect but Reason is correct

**Q4.** Assertion: Copper metal gets readily corroded in an acidic aqueous solution.

**Reason:** Free energy change for this process is negative.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) Assertion is incorrect but Reason is correct

**Q5.** Assertion: Promethium is a man-made element. **Reason:** It is radioactive and has been prepared by artificial means.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

# (c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

(e) Assertion is incorrect but Reason is correct.

### TRUE/FALSE

- Q1. Mn<sup>2+</sup> compounds more stable than Fe<sup>2+</sup> towards oxidation to their +3 states.
  (a) True
  (b) False
- Q2. Titanium and copper both in the first series of transition metal exhibits +1 oxidation state most frequently(a) True(b) False
- **Q3.** Elements belonging to the d -block of the periodic table are transition elements.

(a) True (b) False

Q4. The second transition series involves the filling of 3d - subshell.(a) True(b) False

# SOLUTION FOR PRACTICE QUESTIONS

- **S1.** (d) Ni<sup>2+</sup>, Ti<sup>3+</sup> are coloured due to presence of unpaired electrons.
- S2. (d)  $2 \text{ MnO}_{4^-} + 5\text{SO}_{3^{2^-}} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_{4^{2+}} + 8\text{H}_2\text{O}$ 5 moles of SO<sub>3<sup>2-</sup></sub> needs 2 moles of KMnO<sub>4</sub> 1 mole of SO<sub>3<sup>2-</sup></sub> needs 2/5 moles of KMnO<sub>4</sub>
- **S3.** (d) :: Cr<sup>+</sup>(4s°3d<sup>5</sup>), Mn<sup>+</sup> 4s<sup>1</sup>3d<sup>5</sup>, V<sup>+</sup>(4s<sup>1</sup>3d<sup>3</sup>), Ti<sup>+</sup>4s<sup>1</sup>3d<sup>2</sup>
- **S4.** (a) Zr4<sup>+</sup>, Hf have similar size due to lanthanoid contraction.
- **S5.** (a) It is due to formation of chromium sulphate.
- **S6.** (a) Mn<sup>2+</sup>(3d<sup>5</sup>) is most stable, Fe<sup>2+</sup>(3d<sup>6</sup>), Cr<sup>2+</sup>(3d<sup>4</sup> Co<sup>2+</sup>(3d<sup>1</sup>)
- **S7.** (b) Yb<sup>2+</sup>(4f<sup>14</sup>) does not have unpaired election, therefore, diamagnetic.
- **S8.** b Ni<sup>2+</sup> has 2 unpaired electrons.
- **S9.** (b)  $2KMnO_4 + 16 HCl \rightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 2H_2O$
- **S10.** (d) V<sub>2</sub>O<sub>3</sub> and CrO are basic oxides due to lower, oxidation states.
- **S11. (d)** Cr<sup>3+</sup> is formed.
- S12. (a)
- **S13. (a)** Cu(II) is more stable due to higher hydration energy.
- **S14. (b)** CUF<sub>2</sub> is coloured due to presence of unpaired electron in d-orbital.
- **S15.** (a) It is due to formation of  $Mn_2O_7$ .
- S16. (d) Cromium(Cr) and copper(Cu) are the exceptions of 3-d transition series which show anomalous electonic configuration.Cr and Cu attain extra stability of half-filled and full-filled electronic configuration by changing the expected pattern of electronic configuration.

The electronic configuration of Cr and Cu is  $[Ar]3d^5 4s^1$  and  $[Ar]3d^{10} 4s^1$  respectively.

In both cases, an electron from the 4s orbital jumps to 3d subshell as it is more stable due to half-filled and full-filled stable configuration.

**S17. (b)** Transition elements are characterized by partially filled(n-1) d subshells.

Zn, Cd and Hg are not regarded as transition elements as they have completely filled(n-1)d subshell.

The electronic configuration of zinc is [Ar]  $3d^{10}$   $4s^2$ .

The electronic configuration of cadmium is [Kr]  $4d^{10}5s^2$ .

The electronic configuration of mercury is [Xe]  $5d^{10} 6s^2$ .

S18. (a) Anhydrous CuSO<sub>4</sub> is white in colour due to the absence of water molecules. When we make the solution of CuSO<sub>4</sub> water molecules will attach to CuSO<sub>4</sub> molecule making CuSO<sub>4</sub>.Two of the orbitals interact with the water molecules and raises in energy. The energy difference is equivalent of the wavelength of blue light.

The blue colour of the  $CuSO_4$  is because of Cu(II), which means it had lost two electrons; it gives the copper a 2+ charge.

Due to the arrangement of d-orbitals, there is a splitting effect. There are 5 d orbitals that can interact with other orbitals. Two of the orbitals interact with the water molecules and raises in energy. The energy difference is equivalent of the wavelength of blue light. When the copper absorbs photons, it releases energy from the upper-level energy orbitals back to the lower orbitals, giving blue light.

- S19. (c)
- **S20. (d)** Due to large surface area and variable oxidation state, d-block element shows catalytic activities.
- S21. (d)
- S22. (c),(d) Statement(a) HCl cannot be used because some KMnO<sub>4</sub> is consumed in the reaction. Is Correct as it reacts with KMnO<sub>4</sub> to get oxidized and follows up with the liberation of Cl<sub>2</sub> gas. Statement(b) Nitric acid is not used for the above purpose because it itself acts as a self-oxidizing agent and will react with the reducing agent. Is Correct as it is a very strong oxidizing agent which reduces the KMnO<sub>4</sub>.

 $\mu = \sqrt{n(n+2)} = 5.9$  B.M.

Statement(c) The equivalent weight of  $KMnO_4$  in the basic medium is 158. This is Incorrect as the equivalent weight of  $KMnO_4$  in the basic medium is 52.66gm/equivalent.

statement(d) The number of electrons involved in the oxidation of  $KMnO_4$  in an acidic medium is 3. This is Incorrect as the number of electrons involved in the oxidation of  $KMnO_4$  in an acidic medium is 5.

S23. (d)

$$n(n + 2) = 5.9 \times 5.9 = 34.8$$
  
 $n^2 + 2n = 34.8$ 

$$\mathbf{n} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

After solving, n = -2 + 12/2 or n = -2 - 12/2n = 10/2 or n = -14/2n = 5 or n = -7The negative value is discarded as the number of

electrons cannot be negative.

∴n=5

Fe<sup>3+</sup> ion(with valence shell electronic configuration 3d<sup>5</sup> 4s<sup>0</sup> has magnetic moment 5.90 B.M. It has 5 unpaired electrons.

- S25. (b),(d) As we move from left to right in a row of actinoid, oxidation state first increases than reaches maximum(in middle of row) and then decreases so Np, Pu will show +7 oxidation state.
- S26. (a),(b) Actinoids are element 89 to 103 and fill their 5f shell. They are typical metals and radioactive also. Eg-Th,U,Pu.

$$U(z = 92) \rightarrow 5f^{3}6d^{1}7s^{2}$$

$$Np(z = 93) \rightarrow 5f^{4}6d^{1}7s^{2}$$

$$Pu(z = 94) \rightarrow 5f^{6}6d^{0}7s^{2}$$

$$Am(z = 95) \rightarrow 5f^{7}6d^{0}7s^{2}$$

So, U and Np have one electron in 6d orbital.

- S27. (b),(c) Europium and Ytterbium have this characteristic oxidation which is an exception from the characteristic +3 oxidation exhibited in general by the Lanthanoids.
- S28. (a)
- Melting points of metals are attributed to the S29. (c) involvement of number of electrons from(n-1) d in addition to the ns electrons in the interatomic metallic bonding. Unpaired electron per d orbital is particularly favourable for strong interatomic interaction. Zn has no unpaired electron hence it has lowest melting and boiling point.
- S30. (d) Zinc(Zn) has the minimum melting point among 3d-series of transition metals. Vanadium(V) has the maximum melting point. The reason for least melting point for zinc is absence of unpaired delectrons.
- S31. (c) (a)=8.95,(b)=8.95,(C)=3.0,(d)=7.14 Across the period atomic volume decrease upto copper due poor shielding of d-orbital electrons

and addition of extra electrons in inner orbital and then increase in Zinc due to interelectronic repulsion in completely filled d-and s-orbitals. Consequently densities increase from Sc to Cu and then decreases in Zn.

- S32. (d) The catalyst used in Haber's process in a metal catalyst. Usually, iron is widely used as a catalyst in this process. Iron has been preferred because it helps to achieve an acceptable yield of a product in a much faster time.
- S33. (b) When blackish coloured compound MnO<sub>2</sub> is fused with KOH in presence of air, produces a dark green coloured compound potassium manganate.

 $MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + H_2O$ 

- S34. (c) The melting points of the alkali metals as a group are lower than those of any other non-gaseous group of the periodic table, ranging between 179 °C(354 °F) for lithium and 28.5 °C(83.3 °F) for cesium. Among the metallic elements, only mercury has a lower melting point(-38.9 °C, or -38.02 °F) than cesium.
- S35. (c) Generally man-made elements are radioactive in nature and to gain stability they emit radiation to get a stable nucleus. The emitted radiation may contain alpha, beta and gamma particles. Technetium is the first man-made element.
- S36. (c) Highest oxidation state (+8) is shown by Os.
- KMnO4 dissociates as K+ and MnO4<sup>-</sup>. Thus we S37. (d) will now calculate the oxidation number of Mn Let us suppose it has an oxidation state of X. Thus the equation is-0

Thus the value of X is +7

The equation has been written in that manner because KMnO<sub>4</sub> has an overall oxidation number of 0. K has an oxidation number of +1 and 0 has an oxidation number of -2. Thus four oxygen atoms will have an oxidation number of -8Oxidation numbers on both the sides should be balanced and hence we get the value to be +7.

- S38. (d) When KMnO<sub>4</sub> acts as oxidizing agent in acidic medium, the oxidation number of manganese decreases from +7 to +2. Thus, the oxidation number decreases by 5.
- S39. (b) The species which contain the same number of electrons are called isoelectronic species. The number of electrons in  $Ag^+$  is 47-1 = 46The number of electrons in  $Au^{+3}$  is 79-3 = 76 The number of electrons in  $Zn^{+2}$  is 30-2 = 28

The number of electrons in  $Cd^{+2}$  is 48-2 = 46. Hence  $Cd^{+2}$  is isoelectronic with  $Ag^+$  as they contain the same number of electrons.

- **S40. (a)** Scandium is the first transition metal.
- **S41.** (d) CaO is basic, CO<sub>2</sub> is acidic, SiO<sub>2</sub> is weakly acidic. SnO<sub>2</sub> is amphoteric.
- An equivalent weight of a solution is defined as S42. (c) the molecular weight of the solute divided by the valence of the solute. Equivalent weight is used for predicting the mass of a substance that reacts with one atom of hydrogen in an acid-base analysis like in titration. The equivalent weight of  $K_2Cr_2O_7 = 49 \text{ g/mol}$ In the solution, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives the following ions,  $K_2Cr_2O_7 + 14H^+ + 6e^- \rightarrow 2K_+ + 2Cr^{3+} + 7H_2O$ The chemical equivalent is 6 because six electrons participate in the chemical reaction. Formula to calculate equivalent weight is Equivalent weight(Z) = molecular weight / chemical equivalent Z = M/6
- **S43. (b)** Rutile is a mineral compared primarily of titanium dioxide, TiO<sub>2</sub>.
- **S44. (d)** Compounds with identical crystal structures and analogous chemical formula are called isomorphous.
- S45. (c)
- S46. (d) Zn<sup>2+</sup>: [Ar]<sup>18</sup> 3d<sup>10</sup>, Ag<sup>+</sup>: [Kr]<sup>36</sup> 4d<sup>10</sup> Cu<sup>+</sup>: [Ar]<sup>18</sup> 3d<sup>10</sup>, Ni<sup>2+</sup>: [Ar]<sup>18</sup> 3d<sup>8</sup> As such Ni<sup>2+</sup> has two unpaired electrons and is paramagnetic.
- **S47. (d)** The valence electrons of the terbium element enter into 4f-orbital so the terbium is not an actinide. It is a lanthanide.
- **S48. (d)** Paramagnetic property is dependent on the number of unpaired electron. Element which has least number of unpaired electron will be less paramagnetic. Electronic configuration of given elements is as follows:  $Fe = [Ar] 3d^6 4s^2$  $Mn = [Ar] 3d^5 4s^2$ 
  - Ni =  $[Ar] 3d^8 4s^2$
  - $Cu = [Ar] 3d^{10} 4s^1$

Number of unpaired electrons in Fe, Mn, Ni, Cu is 4, 5, 2, 1. Therefore, Cu shows least paramagnetic property.

**S49.** (c) Vanadium(III) oxide is a strong reducing agent because vanadium is electropositive metal and

have high reduction potential. It has a low heat of sublimation and low ionisation potential.

**S50.** (a) Spin magnetic moment =  $\sqrt{n(n+2)}$ B.M. Where, n = number of unpaired electrons. Given,  $\sqrt{n(n+2)} = 2.84$ or, n(n + 2) = 8.0656 or, n = 2 In an octahedral complex, for a d4 configuration in a strong filed ligand, number of unpaired electrons = 2



# ASSERTION AND REASONING

S1. (b) The magnetic moments are lesser than the fact that 5f electrons of actinides are less effectively shielded which results in quenching of orbitals contribution.

Actinide elements are strongly paramagnetic due to the presence of unpaired electrons.

- **S2.** (d)  $Cu^+ \rightarrow [Ar]3d^{10}$  is diamagnetic because it has no unpaired electrons and is colourless.  $Cu^{2+} \rightarrow [Ar]3d^9$  is paramagnetic because it has one unpaired electron and is coloured.
- S3. (c) The assertion is correct but the reason is false. Transition metals show variable valency due to very small difference between the ns and(n-1)d electrons.

# TRUE/FALSE

- **S1.** (a) Interstitial compounds have high melting points, higher than those of pure metals due to strong interatomic forces.
- **S2.** (a) Permangnate titrations in presence of hydrochloric acid are unsatisfactory because in that case hydrochloric acid is oxidised to chlorine.
- **S3.** (b) In strong alkaline medium, it act as oxidising agent. The reaction occurs as:  $MnO_{4}$ <sup>-</sup> + e<sup>-</sup>  $\rightarrow MnO_{4}^{2-}$

# SOLUTION FOR PRACTICE QUESTIONS

- S1. (c) Coloured compound of transition elements is associated with partially filled(n-1)d orbitals. The transition metal ions containing unpaired d-electrons undergoes electronic transition from one d-orbital to another. During this d-d transition process the electrons absorb certain energy from the radiation and emit the remainder of energy as coloured light. The colour of ion is complementary of the colour absorbed by it. Hence, coloured ion is formed due to d-d transition which falls in visible region for all transition elements.
- **S2.** (c) d-block elements are often paramagnetic owing to the presence of unpaired d-electrons.
- S3. (d) The ability of the transition metals to exhibit variable valency is generally attributed to the availability of more electrons in the(n-1)d orbitals which are closer to the outermost ns orbital in energy levels.
- **S4.** (c) Transition metals have variable oxidation states as they have high number of unpaired valence electrons. This property is used as catalysing the reactions
- S5. (b) Because they are all metals, the transition elements are often called the transition metals. As a group, they display typical metallic properties and are less reactive than the metals in group 1 and group 2 of the periodic table.
- S6. (d) Unlike s or p block elements which are usually discussed as columns or groups, d-block elements are better discussed by classifying them into horizontal series. In the periodic table, there are four main transition series of elements corresponding to filling of 3d, 4d, 5d and 6d sublevels in the 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> periods.
- S7. (a) The second transition series or 4d series corresponding to the filling of 4d sublevel consists of the following 10 elements of the 5<sup>th</sup> period: Y(Atomic No. = 39), Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag and Cd(Atomic No. = 48).
- S8. (c) The third transition series or 5d series corresponding to the filling of 5d sublevel consists of the following 10 elements of the 6<sup>th</sup> period: La(Atomic No. = 57); Hf(Atomic No. = 72), Ta, W, Re, Os, Ir, Pt, Au and Hg(Atomic No. = 80).
- S9. (c) All transition elements are d-block elements, but all d-block elements are not transition elements. Zinc has the electronic configuration [Ar] 3d<sup>10</sup>4s<sup>2</sup>, and the configuration of the Zn<sup>2+</sup> ion is

[Ar] 3d^10. Thus, both the element and its only known stable ion have completely filled dorbitals. Also, the metal does not exhibit any variable valency or multiple oxidation states in compound formation.

- S10. (a) Uranium(atomic no. 92, symbol-U) is used as nuclear fuel. Its salts are used in the glass industry(for imparting green colour), textile industry, ceramic industry and in medicines. Natural uranium has three major isotopes.
- S11. (d) Potassium permanganate(KMnO<sub>4</sub>) reacts with hydrochloric acid(HCl) to form potassium chloride, manganese chloride, chlorine and water. Here, one of the products formed, chlorine, is a greenish yellow gas. It has a pungent smell and is toxic.
- S12. (a) The physical state of potassium permanganate(KMnO<sub>4</sub>) is an odourless solid, and they look like dark purple or bronze-coloured crystals. If we dissolve these crystals in water, then the solution becomes purple in colour.
- S13. (d) Their magnetic properties cannot be explained easily, as they are more complex. The 5f bands formed due to 5f-5f wave function overlap or to hybridisation with s, p or d electrons. As a result of the band formation, a wide variety of magnetic phenomena may occur.
- S14. (a) Actinoids are highly reactive metals especially in the finely divided state. All these metals are attacked by hydrochloric acid but the effect of nitric acid is very small due to the formation of a protective oxide layer on their surface.
- S15. (b) Chromium(atomic no.24, symbol-Cr) forms many oxides. Some of its common oxidation states are +2, +3 and +6. Chromium(III) oxide(green in colour) is amphoteric, i.e., it can react as both acid and base. Its formula is Cr<sub>2</sub>O<sub>3</sub>.
- S16. (b) The gradual decrease in the atomic and ionic radii of the lanthanides with an increase in atomic number is called lanthanide contraction. It occurs due to the poor shielding effect of the 4f electrons.
- **S17. (c)** The small average decreases in the atomic size is responsible for a small decrease in electronegativity and S.O.P of lanthanides. As the size of the lanthanide ions decreases the covalent character of M—OH bond increases and hence basic strength decreases.
- **S18. (a)** All lanthanides are soft metals with silvery white colour. They tarnish rapidly by air. With increase

in atomic number, the harness of these metals also increases. The melting points of the lanthanides ranges from 1000 to 1200K but samarium melts at 1623K.

- S19. (b) The first five elements of Lanthanides are: Lanthanum(La) – 57 Cerium(Ce) – 58 Praseodymium(Pr) – 59 Neodymium(Nd) – 60 Promethium(Pm) – 61
- S20. (b) The atomic numbers of Erbium, Thulium, Ytterbium and Lutetium is 68, 69, 70 and 71 respectfully. So the last element of lanthanide series is Lutetium with electronic configuration [Xe]4f<sup>14</sup>5d<sup>16</sup>s<sup>2</sup>.
- S21. (b) Because they are all metals, the transition elements are often called the transition metals. As a group, they display typical metallic properties and are less reactive than the metals in group 1 and group 2 of the periodic table.
- S22. (a) Near the end of the period, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to increased nuclear charge. This result in the expansion of the electron cloud and therefore, increases the atomic size.
- **S23.** (c) In the atoms of the second transition series, the number of shells increases and so, their atomic radii is greater than that of the first transition series. The atomic radii of the second and third transition series are almost same due to lanthanoid contraction.
- S24. (c)
- S25. (c)
- S26. (b) Alkaline KMnO<sub>4</sub> is called Baeyer's reagent. Baeyer's reagent is an alkaline solution of cold potassium permanganate, which is a powerful oxidant making this a redox reaction. Reaction with double or triple bond in an organic material causes the colour to fade from purplish-pink to brown. It is a syn addition reaction.
- **S27. (c)** Mercury is the only liquid metal at room temperature. It has a high coefficient of expansion and boiling point. This helps use to identify even the slightest change in temperature of the surroundings.
- S28. (a)
- S29. (d)

S30. (c)

# ASSERTION AND REASONING

S1. (a) A Catalyst is a substance which accelerates the rate of a chemical reaction without undergoing any change in its chemical composition or mass during the reaction. A catalyst accelerates the rate of a reaction by lowering the activation energy. Transition metals are efficient catalysts. For example, Ni, Pd and Pt are used for the hydrogenation of alkenes. Transition metals usually contain incomplete d-orbitale (so that they can show variable valency)

orbitals(so that they can show variable valency) and provide a larger surface area for adsorption. Hence, both Assertion and Reason are correct and Reason is the correct explanation for Assertion.

- S2. (a)
- S3. (a)
- S4. (d) Copper corrodes at negligible rate in unpolluted air, water and non-oxidising acids. Pure copper and the high copper alloys can be considered to exhibit similar resistance to most Corrosive environments. They possess excellent resistance to atmospheric environments.(corrosion is a spontaneous process for which free energy change must be negative.
- **S5.** (a) Promethium is a man-made element because it has been prepared by artificial me

### TRUE/FALSE

- **S1.** (a) It is because Mn<sup>2+</sup> has 3d<sup>5</sup> configuration which has extra stability.
- S2. (b) Not Titanium but copper, because with +1 oxidation state an extra stable configuration 3d<sup>10</sup> results.
- S3. (a) Elements belonging to the d-block of the periodic table are transition elements. The d-block of the periodic table, includes groups 3 to 12. The boiling points and the melting points of transition elements are high, due to the delocalized d-electrons in metallic bonding and these elements form coloured compounds and ions due to the d-d transition of metals.
- S4. (b) The second transition series involves the filling of 4d- subshell not the 3d- subshell. This series contains the elements which have an atomic number from 39 to 48 and Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd. All of these elements involve the filling of the 4d subshell.