The d and f Block Elements

The d-block of the periodic table contains the elements of the groups 3-12 in which the d orbitals are progressively filled in each of the four long periods. The f-block consists of elements in which 4 f and 5 f orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table. The names transition metals and inner transition metals are often used to refer to the elements of d-and f-blocks respectively. There are mainly four series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd), 5d series (La and Hf to Hg) and 6d series which has Ac and elements from Rf to Cn. The two series of the inner transition metals; 4f (Ce to Lu) and 5f (Th to Lr) are known as lanthanoids and actinoids respectively. Originally the name transition metals was derived from the fact that their chemical properties were transitional between those of s and p-block elements. Now according to IUPAC, transition metals are defined as metals which have incomplete d subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full d<sup>10</sup> configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the 3d, 4d and 5d transition series, respectively, their chemistry is studied along with the chemistry of the transition metals. The presence of partly filled d or f orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non-transition elements can be applied successfully to the transition elements also. Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series. In this Unit, we shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3d) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals. THE TRANSITION ELEMENTS (d-BLOCK)

Position in the Periodic Table: The d-block occupies the large middle section of the periodic table flanked between s- and p- blocks in the periodic table. The d-orbitals of the

penultimate energy level of atoms receive electrons giving rise to four rows of the transition metals, i.e., 3d, 4d, 5d and 6d. Electronic Configurations of the d-Block Elements: In general the electronic configuration of outer orbitals of these elements is (n-1)d<sup>1-10</sup>ns<sup>1-2</sup> except for Pd where its electronic configuration is  $4d^{10}5s^2$ . The (n-1) stands for the inner d orbitals which may have one to ten electrons and the outermost ns orbital may have one or two electrons. However, this generalisation has several exceptions because of very little energy difference between (n-1)d and ns orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3d series. For example, consider the case of Cr, which has 3d<sup>5</sup>4s<sup>1</sup> configuration instead of 3d<sup>4</sup>4s<sup>2</sup>; the energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d orbitals. Similarly in case of Cu, the configuration is  $3d^{10}4s^{1}$  and not  $3d^{9}4s^{2}$ . The ground state electronic configurations of the outer orbitals of transition elements are given below: VSc  $\operatorname{Cr}$ Со Τi Mn Fe Ni CuZn 2122 23 24 25 26 27 28 29 30 Z2 2 2 2 2 2 2 2 1 1 3d2 3 5 5 6 7 8 10 10

2nd Series Y Tc Rh Cd Zr Nb Mo Ru Ρd Ag Z39 40 41 42 43 44 45 46 47 48 2 2  $^{2}$ 1 1 1 1 1 0 1 5s8 4d 2 5 6 10 10 10 3rd Series W La Ηſ Та Re Os Ir Ρt Au Hg 57 72 73 74 75 76 77 78 79 80 Z2 2 2 2 2 2 2 2 1 1 6s2 3 5 5d10 10 4th Series Cn Rf Db Вh Hs Μt DsAc Sg Rg 89 104 105 106 107 108 109 110 111 112 Z7s $^{2}$  $^{2}$ 2 2 2 2 2 2 2 1 2 3 5 7 8 10 10 6d 1 4 6 the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements. been discussed in detail later in this Unit. **General Properties of the Transition Elements(d-Block)** 

The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula (n-1)d<sup>10</sup>ns<sup>2</sup>. The orbitals in these elements are completely filled in The d orbitals of the transition elements protrude to the periphery of an atom more than the other orbitals (i.e., s and p), hence, they are more influenced by the surroundings as well as affect the atoms or molecules surrounding them. In some respects, ions of a given  $d^n$  configuration (n = 1 - 9) have similar magnetic and electronic properties. With partly filled d orbitals these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. All these characteristics have There are greater similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3d row) and then consider some group similarities.

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

Co

ccp

(hcp)

сср

 $z_n$ 

Χ

(hcp)

сср

Ru Rh Nb Mo Tc Cd Х hep bec bee hep hep hcp ccp сср ccp (bcc) (bcc) (hcp) Hf Re Hg hep Х hep bec bcc hcp hcp сср сср сср (ccp, bcc) (bcc) Atomic number

Mn

Х

(bcc, ccp)

hcp

(bcc)

metals.

hep

(bcc)

bee

Fe

bec

(hcp)

The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. Their melting and boiling points are high. Figure on the left depicts the melting points of transition metals belonging to 3d, 4d and 5d series. The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding. In any row the melting points of these metals rise to a maximum at d<sup>5</sup> except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. 900 800-Series 1 700-600-∆H°/kJ mol' 500-400

300-200-100-Atomic number ---> They have high enthalpies of atomisation which are shown in the left figure. The maxima at about the middle of each series indicate that one unpaired electron per d orbital is

particularly favourable for strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in

Another generalisation that may be drawn from the same figure is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding

Variation in Atomic and Ionic Sizes of Transition Metals: In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a d orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a d electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. An interesting point emerges when atomic sizes of one series are compared with those of the

The curves in the given figure show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm)

and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship. Cr Mn Fe Co Ni Cu Zn Y Zr Nb Mo Tc Ru Rh Pd Ag Cd ---- La Hf Ta W Re Os Ir Pt Au Hg Trends in atomic radii of transttton elements The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one 4f electron by another is less than that of one d electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire 4f n orbitals. The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (Z = 22) to copper (Z = 29) the significant increase in the density may be noted **Ionisation Enthalpies:** There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the

corresponding elements in the other series.

Exchange energy is responsible for the stabilisation of energy state. Exchange energy is approximately proportional to the total number of possible pairs of parallel spins in the degenerate orbitals. When several electrons occupy a set of degenerate orbitals, the lowest energy state corresponds to the maximum possible extent of single occupation of orbital and parallel spins (Hunds rule). The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult. There is no loss of exchange energy at d6 configuration. Mn<sup>+</sup> has 3d<sup>5</sup>4s<sup>1</sup> configuration and configuration of Cr<sup>+</sup> is d<sup>5</sup>, therefore, ionisation enthalpy of Mn<sup>+</sup> is lower than Cr<sup>+</sup>. In the same way, Fe2+ has d6 configuration and  $Mn^{+2}$  has  $3d^5$  configuration. Hence, ionisation enthalpy of Fe<sup>+2</sup> is lower than the  $Mn^{+2}$ . In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn. The lowest common oxidation state of these metals is  $\pm 2$ . To form the  $M^{+2}$  ions from the gaseous atoms, the sum of the first and second ionisation enthalpy is required in addition to the enthalpy of atomisation. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where M<sup>+</sup> ions have the d<sup>5</sup> and d<sup>10</sup> configurations respectively. The value for Zn is correspondingly low as the ionisation causes the removal of one 4s electron which results in

the formation of stable d<sup>10</sup> configuration. The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the d5 (Mn<sup>+2</sup>) and d<sup>10</sup> (Zn<sup>+2</sup>) ions. In general, the third ionisation enthalpies are quite high. Also the high values for third ionisation enthalpies of copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements. Although ionisation enthalpies give some guidance concerning the relative

Oxidation States: One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds. Table lists the common oxidation states of the first row transition elements. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or

too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese (Ti<sup>IV</sup>O<sub>2</sub>, V<sup>V</sup>O<sub>2</sub><sup>+</sup>, Cr<sup>VI</sup>O<sub>2</sub><sup>2-</sup>, Mn<sup>VII</sup>O<sub>4</sub><sup>-</sup>) followed by a rather abrupt decrease

+2

incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g., VII, VIII, VIV, VV. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two. An interesting feature in the variability of oxidation states of the d- block elements is noticed among the groups (groups 4 through 10). Although in the p—block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of d-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO<sub>3</sub> and WO<sub>3</sub> are not. Low oxidation states are found when a complex compound has ligands capable of p-acceptor

Trends in the M<sup>2+</sup>/M Standard Electrode Potentials: Following Table contains the thermochemical parameters related to the transformation of the solid metal atoms to M<sup>2+</sup> ions in solution and their standard electrode potentials. The observed values of E<sup>0</sup> and those calculated using the data of Table are compared in Figure. The unique behaviour of Cu, having a positive E<sup>0</sup>, accounts for its inability to liberate H<sub>2</sub> from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced.

The variability of oxidation states, a characteristic of transition elements, arises out of

Cu

+1

+2

inner d orbitals, the successive enthalpies of these elements do not increase as steeply as in the case of non-transition elements for a particular series. The variation in ionisation enthalpy along a series of transition elements is much less in comparison to the variation along a period of non-transition elements. The first ionisation enthalpy, in general,

increases, but the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, is much higher along a series. The irregular trend in the first

ionisation enthalpy of the metals of 3d series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. You have learnt that when d-block elements form ions, ns electrons are lost before (n-1) d electrons. As we move along the period in 3d series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of inner subshell, i.e., 3d orbitals. These 3d electrons shield the 4s electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the 3d series. The doubly or more highly charged ions have dn configurations with no 4s electrons. A general trend of increasing values of second ionisation enthalpy is expected as the effective nuclear charge increases because one d electron does not shield another electron from the influence of nuclear

charge because d-orbitals differ in direction. However, the trend of steady increase in second and third ionisation enthalpy breaks for the formation of Mn<sup>+2</sup> and Fe<sup>+3</sup>

The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy.

respectively. In both the cases, ions have d5 configuration. Similar breaks occur at corresponding elements in the later transition series.

The interpretation of variation in ionisation enthalpy for an electronic configuration dn is as follows:

stabilities of oxidation states, this problem is very complex and not amenable to ready generalisation.

in stability of higher oxidation states, so that the typical species to follow are Fe<sup>II,III</sup>, Co<sup>II,III</sup>, Ni<sup>II</sup>, Cu<sup>I,II</sup>, Zn<sup>II</sup>.

+2

+3

+4

+2

+3

+4

character in addition to the s-bonding. For example, in  $Ni(CO)_4$  and  $Fe(CO)_5$ , the oxidation state of nickel and iron is zero.

Thermochemical data (kJ mol-1) for the first row Transition

1734

Oxidation States of the first row Transition Metals

(the most common ones are in bold types)

+2

+3

+4

+6

The high energy to transform Cu(s) to  $Cu^{2+}(aq)$  is not balanced by its hydration enthalpy.

130

906

Calculated values

configuration in  $Zn^{2+}$  are related to their  $E^0$  values, whereas  $E^0$  for Ni is related to the highest negative  $\Delta H^0$ .

Observed and calculated values for the standard

 $VF_5$ 

 $VX_2$ 

 $TiX_4$ 

TiX<sub>3</sub>

 $TiX_2^{III}$ 

Key:  $X = F \rightarrow I$ ;  $X^{I} = F \rightarrow Br$ ;  $X^{II} = F$ , CI;  $X^{III} = CI \rightarrow I$ 

 $CrF_5$ 

 $CrX_4$ 

 $CrX_3$ 

 $CrX_2$   $MnX_2$ 

However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.

Calculated and Observed Magnetic Moments (BM)

Unpaired electron(s)

0

1

2

3

4

5

4

3

2

1

0

Transition Metal Ions

Colours of Some of the First Row (aquated)

Example

Sc3+

 $T1^{4+}$ 

 $T1^{3+}$ 

For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

Magnetic moment

Observed

0

1.75

2.76

3.86

4.80

5.96

5.3 - 5.5

4.4 - 5.2

2.9 - 3, 4

1.8 - 2.2

Colour

colourless

colourless

purple

Formation of Coloured Ions: When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in the Table given

Formation of Interstitial Compounds: Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn<sub>4</sub>N, Fe<sub>3</sub>H, VH<sub>0.56</sub> and TiH<sub>1.7</sub>, etc. The formulas quoted do not, of course,

correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal

Alloy Formation: An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non

Oxides and Oxoanions of Metals: These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in  $Sc_2O_3$  to  $Mn_2O_7$ . Beyond group 7, no higher oxides of iron above  $Fe_2O_3$  are known. Besides the oxides, the oxocations stabilise  $V^V$  as  $VO_2^+$ ,  $V^{IV}$  as  $VO_2^{2+}$  and  $Ti^{IV}$  as  $TiO_2^+$ . As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn<sub>2</sub>O<sub>7</sub> is a covalent green oil. Even CrO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> have low melting points. In these higher oxides, the acidic character is predominant.

Thus, Mn<sub>2</sub>O<sub>7</sub> gives HMnO<sub>4</sub> and CrO<sub>3</sub> gives H<sub>2</sub>CrO<sub>4</sub> and H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. V<sub>2</sub>O<sub>5</sub> is, however, amphoteric though mainly acidic and it gives VO<sub>4</sub><sup>3-</sup> as well as VO<sub>2</sub><sup>+</sup> salts. In vanadium there is gradual change from the basic  $V_2O_3$  to less basic  $V_2O_4$  and to amphoteric  $V_2O_5$ .  $V_2O_4$  dissolves in acids to give  $VO^{2+}$  salts. Similarly,  $V_2O_5$  reacts with alkalies as well

The structures

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

Potassium permanganate is prepared by fusion of MnO<sub>2</sub> with an alkali metal hydroxide and an oxidising agent like KNO3. This produces the dark green K<sub>2</sub>MnO<sub>4</sub> which

permanganate ion

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of KClO<sub>4</sub>. The salt is not very soluble in water (6.4 g/100 g of water at 293

It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained

The manganate and permanganate ions are tetrahedral; the  $\pi$ - bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese. The green manganate is

 $3~\text{Sn}^{2^{\text{+}}} \rightarrow 3\text{Sn}^{4^{\text{+}}}$  + 6  $e^{\text{-}}$ 

 $6~Fe^{2^{+}} \rightarrow 6Fe^{3^{+}}$  +  $6~e^{-}$ 

Commercially it is prepared by the alkaline oxidative fusion of MnO<sub>2</sub> followed by the electrolytic oxidation of manganate (VI).

paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.

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

transition elements are given in Table. The experimental data are mainly for hydrated ions in solution or in the solid state.

Calculated

0

1.73

2.84

3.87

4.90

5.92

4.90

3.87

2.84

1.73

0

 $MnF_3$ 

 $(M^{2+} \rightarrow M^{\circ})$  of the elements Tt to Zn

Mn

+2

+3

+4

+5

+6

+7

Sc

+3

+2

+3

+4

Zn

0.5

0

-0.5

-1

-1.5

-2

+5

+4

+3

+2

 $2Cu^{2+} + 4I^{-} \rightarrow Cu_{2}I_{2} + I_{2}$ 

 $2Cu^+ \rightarrow Cu^{2+} + Cu$ 

Mn<sup>V</sup>, Mn<sup>VI</sup> and Mn<sup>VII</sup>.

 $2Cr^{2+}(aq) + 2H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + H_{2}(g)$ 

Configuration

 $3d^{\circ}$ 

 $3d^1$ 

3æ

 $3d^3$ 

 $3d^4$ 

3₫

 $3d^6$ 

 $3d^7$ 

3ď

3₫

 $3d^{10}$ 

Configuration

 $3d^{\circ}$ 

 $3d^{\circ}$ 

 $3d^1$ 

 $2~\text{I}^{\scriptscriptstyle{-}} + ~\text{S}_2{\text{O}_8}^{^{2\scriptscriptstyle{-}}} \rightarrow \text{I}_2 + 2~\text{SO}_4^{^{2\scriptscriptstyle{-}}}$ 

2 Fe<sup>3+</sup> + 2  $\Gamma \rightarrow 2$  Fe<sup>2+</sup> +  $I_2$ 

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

 $2 \text{ Fe}^{2+} + \text{S}_2 \text{O}_8^{2-} \rightarrow 2 \text{ Fe}^{3+} + 2 \text{SO}_4^{2-}$ 

An explanation of this catalytic action can be given as:

**Some Important Compounds of Transition Elements:** 

physical and chemical characteristics of these compounds are as follows: (i) They have high melting points, higher than those of pure metals. (ii) They are very hard, some borides approach diamond in hardness.

 $\mu = \sqrt{n(n+2)}$ 

Ion

Sc<sup>3+</sup>

 $T1^{3+}$ 

 $T1^{2+}$ 

 $V^{2+}$ 

 $Cr^{2+}$ 

Mn<sup>24</sup>

Fe2+

Co<sup>24</sup>

 $N1^{2+}$ 

Cu2+

Zn24

below.

of Cu.

Observed values

electrode potentials

Standard electrode potential/V

+2

+3

+4

+5

+2

+3

+4

+5

+6

Elements and the Standard Electrode Potentials for the Reduction of MI to M. Element (M)  $\Delta_{\mathbf{x}}H^{\circ}$  (M)  $\Delta_{\text{hwd}} \mathbf{H}^{\Theta}(\mathbf{M}^{2+})$  $\Delta_1 \mathbf{H}_1^{\Theta}$  $\Delta_1 \mathbf{H}_2^{\Theta}$ E<sub>e</sub>/V T1 469 656 1309 -1866 -1.63V 515 650 1414 -1895-1.18398 653 1592 -1925 -0.90 $\operatorname{cr}$ 279 717 1509 -1862 -1.18Mn 762 Fe 418 1561 -1998 -0.44 Co 427 758 1644 -2079-0.28431 736 1752 -2121 -0.25N1Cu 339 745 1958 -2121 0.34

-0.76

-2059

Trends in the M<sup>3+</sup>/M<sup>2+</sup> Standard Electrode Potentials: An examination of the E<sup>0</sup> (M<sup>3+</sup>/M<sup>2+</sup>) values shows the varying trends. The low value for Sc reflects the stability of  $Sc^{3+}$  which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable  $d^{10}$  configuration of  $Zn^{2+}$ . The comparatively high value for Mn shows that  $Mn^{2+}(d^5)$  is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $Fe^{3+}(d^5)$ . The comparatively low value for V is related to the stability of  $V^{2+}$  (half-filled  $t_{2g}$  level). Trends in Stability of Higher Oxidation States: Following Table shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in TiX<sub>4</sub> (tetrahalides), VF<sub>5</sub> and CrF<sub>6</sub>. The +7 state for Mn is not represented in simple halides but MnO3F is known, and beyond Mn no metal has a trihalide except FeX<sub>3</sub> and CoF<sub>3</sub>. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF<sub>3</sub>, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF<sub>5</sub> and CrF<sub>6</sub>. Formulas of Halides of 3d Metals **Oxidation Number** CrF<sub>6</sub> +6

CoF<sub>3</sub>

 $CoX_2$ 

 $NiX_2$ 

Although  $V^{+5}$  is represented only by  $VF_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $VOX_3$ . Another feature of fluorides is their instability in the low oxidation states e.g.,  $VX_2$  (X = CI, Br or I) and the same applies to CuX. On the other hand, all Cu<sup>II</sup> halides are known except the iodide. In this case, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>:

The stability of  $Cu^{2+}(aq)$  rather than  $Cu^{+}(aq)$  is due to the much more negative  $\Delta_{hvd}H^{o}$  of  $Cu^{2+}(aq)$  than  $Cu^{+}$ , which more than compensates for the second ionisation enthalpy

The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides coincides with the group number and is attained in Sc<sub>2</sub>O<sub>3</sub> to Mn<sub>2</sub>O<sub>7</sub>. Beyond Group 7, no higher oxides of Fe above Fe<sub>2</sub>O<sub>3</sub>, are known, although ferrates(VI)(FeO<sub>4</sub>)<sup>2-</sup>, are formed in alkaline media but they readily

decompose to  $Fe_2O_3$  and  $O_2$ . Besides the oxides, oxocations stabilise  $V^V$  as  $VO_2^+$ ,  $V^{IV}$  as  $VO_2^{++}$  and  $Ti^{IV}$  as  $TiO_2^{-+}$ . The ability of oxygen to stabilise these high oxidation states

exceeds that of fluorine. Thus the highest Mn fluoride is MnF<sub>4</sub> whereas the highest oxide is Mn<sub>2</sub>O<sub>7</sub>. The ability of oxygen to form multiple bonds to metals explains its

superiority. In the covalent oxide  $Mn_2O_7$ , each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral  $[MO_4]^{n-1}$  ions are known for  $V^V$ ,  $Cr^{VI}$ ,

 $CuX_2^{II}$ 

CuX<sup>III</sup>

FeX<sub>3</sub><sup>I</sup>

 $FeX_2$ 

Oxides of 3d Metals

The general trend towards less negative  $E^0$  values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of  $E^0$  for Mn,Ni and Zn are more negative than expected from the trend. The stability of the half-filled d sub-shell in Mn<sup>2+</sup> and the completely filled d<sup>10</sup>

Oxidation Number 10 + 7  $Mn_2O_7$ + 6 + 5 + 4  $T1O_2$ + 3  $Sc_2O_3$  $Mn_2O_3$  $Fe_2O_3$  $Mn_3O_4$ Fe<sub>3</sub>O<sub>4</sub> Co<sub>3</sub>O<sub>4</sub> + 2 OfT VO (CrO) MnO FeO CoO NiO CuO ZnO + 1 Cu<sub>2</sub>O mixed oxides Chemical Reactivity and E<sup>0</sup> Values: Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids. although a few are 'noble'—that is, they are unaffected by single acids. The metals of the first series with the exception of copper are relatively more reactive and are oxidised

by 1M H<sup>+</sup>, though the actual rate at which these metals react with oxidising agents like hydrogen ion (H<sup>+</sup>) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature. The E<sup>o</sup> values for M<sup>2+</sup>/M indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative E<sup>o</sup> values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the E<sup>o</sup> values for Mn,Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled d subshell ( $d^5$ ) in Mn<sup>2+</sup> and completely filled d subshell ( $d^{10}$ ) in zinc are related to their  $E^{o}$  values; for nickel,  $E^{o}$  value is related to the highest negative enthalpy of hydration. An examination of the  $E^{o}$  values for the redox couple  $M^{3+}/M^{2+}$  shows that  $Mn^{3+}$  and

 $Co^{3+}$  ions are the strongest oxidising agents in aqueous solutions. The ions  $Ti^{2+}$ ,  $V^{2+}$  and  $Cr^{2+}$  are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.,

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

Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance.

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row

 $3d^1$ blue  $V^{3+}$  $3d^2$ green  $V^{2+}$  $3d^3$ violet  $\mathrm{Cr}^{^{3+}}$ 3d<sup>3</sup> violet  $3d^4$  $Mn^{3+}$ violet  $\operatorname{Cr}^{2+}$  $3d^4$ blue  $\mathrm{Mn}^{2+}$  $3d^5$ pink  $3d^5$ Fe<sup>3+</sup> yellow  $3d^6$ Fe<sup>2+</sup> green  $3d^63d^7$ Co3+Co2+ bluepink  $N1^{2+}$ 3d<sup>8</sup> green  $3d^9$  $Cu^{2+}$ blue  $3d^{10}$  $Zn^{2+}$ colourless Formation of Complex Compounds: Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are:  $[Fe(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{4-}$ ,  $[Cu(NH_3)_4]^{2+}$  and  $[PtCl_4]^{2-}$ . The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation. Catalytic Properties: The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

as acids to give VO<sub>4</sub><sup>3</sup>-and VO<sub>4</sub><sup>+</sup> respectively. The well characterised CrO is basic but Cr<sub>2</sub>O<sub>3</sub> is amphoteric.

Potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>: Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr<sub>2</sub>O<sub>4</sub>) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows: 4  $FeCr_2O_4 + 8 Na_2CO_3 + 7 O_2 \rightarrow 8 Na_2CrO_4 + 2 Fe_2O_3 + 8 CO_2$ The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. 2H<sub>2</sub>O can be crystallised.  $2Na_2CrO_4 + 2 H^{\dagger} \rightarrow Na_2Cr_2O_7 + 2 Na^{\dagger} + H_2O$ Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.  $Na_2Cr_2O_7 + 2 KCl \rightarrow K_2Cr_2O_7 + 2 NaCl$ Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.  $2~\mathrm{CrO_4}^{2\text{-}} + 2\mathrm{H}^{^{\dagger}} \rightarrow \mathrm{Cr_2O_7}^{2\text{-}} + \mathrm{H_2O}$  $Cr_{9}O_{7}^{2-} + 2 OH^{-} \rightarrow 2 CrO_{4}^{2-} + H_{9}O$ chromate ion, CrO42- and the dichromate ion, Cr<sub>2</sub>O<sub>7</sub><sup>2</sup> are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Dichromate ion Chromate ion Cr-O-Cr bond angle of 126°. Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

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

 $\text{Cr}_2\text{O}_7^{2-}$  + 14 H<sup>+</sup> + 6 Fe<sup>2+</sup>  $\rightarrow$  2 Cr<sup>3+</sup> + 6 Fe<sup>3+</sup> + 7 H<sub>2</sub>O

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

Fused with KOH, oxidised

K), but when heated it decomposes at 513 K.  $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ 

by the use of molecular orbital theory.

Tetrahedral manganate ion (green)

Tetrahedral permanganate ion (purple)

 $10I^{-} + 2MnO_{4}^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_{2}O + 5I_{2}$ 

 $5S^{2-} + 2MnO_4^- + 16H_4^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$ 

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

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

(a) A notable reaction is the oxidation of iodide to iodate:  $2MnO_4^- + H_2O + \Gamma \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$ 

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

The Inner Transition Elements(f-Block)

general symbol Ln is used) are given in the following table:

Lanthanum

Neodymium

Promethium

Samarium

Europium

Terbium

Holmium

Erbium

Thulium

Ytterbium

Lutetium

 $Sm^{2}$ 

 $Eu^{z_{\dagger}}$ 

Gadolinium

Dysprosium

Praseodymium

Certum

Symbol

La

Се

Ρr

Nd

Рm

sm

Εu

Gd

Tb

Dy

Но

 $\operatorname{Er}$ 

Tm

Υb

Lu

 $5d^{1}6s^{2}$ 

 $4f^{3}6s^{2}$ 

 $4f^46s^2$ 

 $4f^{5}6s^{2}$ 

 $4f^{6}6s^{2}$ 

 $4f^{7}6s^{2}$ 

 $4f^{9}6s^{2}$ 

 $4f^{10}6s^{2}$ 

 $4f^{11}6s^2$ 

 $4f^{12}6s^2$ 

 $4f^{13}6s^2$ 

 $4f^{14}6s^2$ 

 $4f^{14}5d^{1}6s^{2}$ 

 $4f^75d^16s^2$ 

 $4f^{1}5d^{1}6s^{2}$ 

(b) Thiosulphate is oxidised almost quantitatively to sulphate:  $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$ 

 $5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ (d) Hydrogen sulphide is oxidised, sulphur being precipitated:

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

(c) Manganous salt is oxidised to MnO<sub>2</sub>; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

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

Electronic Configurations and Radii of Lanthanum and Lanthanoids

Electronic configurations\*

 $5d^1$ 

 $4f^2$ 

 $4f^{3}$ 

 $4f^4$ 

 $4f^{5}$ 

 $4f^6$ 

 $4f^7$ 

 $4f^9$ 

 $4f^{10}$ 

 $4f^{11}$ 

 $4f^{12}$ 

 $4f^{13}$ 

 $4f^{14}$ 

 $4f^{14}5d^{1}$ 

 $4f^{7}5d^{1}$ 

(b) Fe<sup>2+</sup> ion (green) is converted to Fe<sup>3+</sup> (yellow):  $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ (c) Oxalate ion or oxalic acid is oxidised at 333 K:

 $H_2S \longrightarrow 2H^+ + S^2$ 

separately here.

Atomic

Number

57

58

59

60

61

62

63

64

65

66

67

68

69

70

71

lanthanoids.

110

lutetium

 $Ln^{3+}(aq) + 3e^- \rightarrow Ln(s)$ 

aluminium. Values for E<sup>o</sup> for the half-reaction:

heated with S

participate in bonding to a far greater extent.

Mendelevium

Lawrencium

Nobelium

electrons.

101

102

103

**Oxidation States:** 

are listed in Table.

known at the present time.

 $N_2/H_2$  mixtures.

(f) Nitrite is oxidised to nitrate:

2. In neutral or faintly alkaline solutions:

disproportionates in a neutral or acidic solution to give permanganate.

 $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H_2^{+}$ 

 $\rightarrow$  MnO<sub>4</sub><sup>2-</sup> ; MnO<sub>4</sub><sup>2-</sup>

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

manganate ion manganate

 $6 \text{ I}^{\scriptscriptstyle{-}} \rightarrow 3 \text{I}_2 + 6 \text{ e}^{\scriptscriptstyle{-}};$ 

 $MnO_2$ 

 $3 \text{ H}_2\text{S} \rightarrow 6\text{H}^+ + 3\text{S} + 6\text{e}^-;$ 

Potassium permanganate KMnO<sub>4</sub>:

Chemical properties: Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:  $5 \stackrel{\smile}{\text{10}} \longrightarrow 10 \text{CO}_2 + 10 \text{e}^{-1}$  $5~Fe^{2+} \rightarrow 5~Fe^{3+} + 5e^{-}$  $5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^ 10I^- \rightarrow 5I_2 + 10e^-$ The full reaction can be written by adding the half-reaction for KMnO<sub>4</sub> to the half-reaction of the reducing agent, balancing wherever necessary.  $MnO_4^- + e^- \rightarrow MnO_4^{2-}$  $(E^{\circ} = + 0.56 \text{ V})$  $\mathrm{MnO_4}^-$  +  $4\mathrm{H}^+$  +  $3\mathrm{e}^- o \mathrm{MnO_2}$  +  $2\mathrm{H_2O}$  $(E^{\circ} = + 1.69 \text{ V})$  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$  $(E^{\circ} = + 1.52 \text{ V})$ We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at  $[H^+] = 1$  should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised. A few important oxidising reactions of KMnO<sub>4</sub> are given below: 1. In acid solutions: (a) Iodine is liberated from potassium iodide:

Uses: Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton,

The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the

The Lanthanoids: The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the

4f°

 $4f^{-1}$ 

 $4f^{2}$ 

 $4f^3$ 

 $4f^{4}$ 

4f 5

4f 6

 $4f^{7}$ 

 $4f^8$ 

4f 9

 $4f^{10}$ 

4f 11

 $4f^{12}$ 

 $4f^{13}$ 

 $4f^{14}$ 

Radii/pm

187

183

182

181

181

180

199

180

178

177

176

175

174

173

 $4f^{0}$ 

 $4f^{-1}$ 

 $4f^7$ 

Electronic Configurations: It may be noted that atoms of these elements have electronic configuration with 6s<sup>2</sup> common but with variable occupancy of 4f level. However, the

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

Atomic and Ionic Sizes: The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol<sup>-1</sup>, the second about 1200 kJ mol<sup>-1</sup> comparable with those of calcium. A detailed discussion of the

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

The metals combine with hydrogen when gently heated in the gas. The carbides, Ln<sub>2</sub>C<sub>3</sub> and LnC<sub>2</sub> are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides M<sub>2</sub>O<sub>3</sub> and hydroxides M(OH)<sub>3</sub>. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in the adjacent figure. The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is mischmetall which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some

The Actinoids: The actinoids include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table below. The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z = 103).

Electronic Configurations: All the actinoids are believed to have the electronic configuration of 7s<sup>2</sup> and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the  $f^0$ ,  $f^7$  and  $f^{14}$  occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn]5 $f^7$ 7s<sup>2</sup> and [Rn]5f<sup>7</sup>6d<sup>1</sup>7s<sup>2</sup>. Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can

**Ionic Sizes:** The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or  $M^{3+}$  ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f

 $5f^{12}$ 

 $5f^{13}$ 

There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The known oxidation states of actinoids

variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less

Some Applications of d- and f-Block Elements: Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO<sub>2</sub> for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of

Al(CH<sub>3</sub>)<sub>3</sub> forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from

Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by PdCl<sub>2</sub>. Nickel complexes are useful in the

the metals and/or their compounds are essential catalysts in the chemical industry. V<sub>2</sub>O<sub>5</sub> catalyses the oxidation of SO<sub>2</sub> in the manufacture of sulphuric acid. TiCl<sub>4</sub> with

polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation

 $5f^{13}$ 

 $5f^{14}$ 

variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and

106

103

101

99

98

96

95

94

92

91

89

88

87

86

actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered

100 Ionic radii/pm \_ Tm²⁺ 57 59 61 63 65 67 71 Atomic number Trends in tonic radii of lanthanoids It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M<sup>3+</sup> ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number. The cumulative effect of the contraction of the lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation. Oxidation States: In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce<sup>IV</sup>> is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The Eo value for  $Ce^{4+}$   $Ce^{3+}$  is +1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO<sub>2</sub>. Eu<sup>2+</sup> is formed by losing the two s electrons and its f<sup>7</sup> configuration accounts for the formation of this ion. However, Eu<sup>2+</sup> is a strong reducing agent changing to the common +3 state. Similarly Yb<sup>2+</sup> which has  $f^{14}$  configuration is a reductant. Tb<sup>IV</sup> has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states. General Characteristics: All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm. Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f-electrons. Neither La<sup>3+</sup> nor Lu<sup>3+</sup> ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f-level. The lanthanoid ions other than the f<sup>0</sup> type (La<sup>3+</sup> and Ce<sup>4+</sup>) and the f<sup>14</sup> type (Yb<sup>2+</sup> and Lu<sup>3+</sup>) are all paramagnetic.

are in the range of -2.2 to -2.4 V except for Eu for which the value is -2.0 V. This is, of course, a small variation.

with halogens

 $Ln(OH)_3 + H_2$ 

individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

Some Properties of Actinium and Actinoids

Electronic conifigurations\*

ĽnC,

Chemical reactions of the lanthanoids.

Name Symbol Atomic  $5f^{\circ}$ Actinium  $6d^{1}7s^{2}$ 89 111 Αc  $5f^{-1}$  $5f^{\circ}$ 90 Thorium Τh 99 6d"7s" 5f <sup>2</sup>  $5f^{-1}$  $5f^{2}6d^{1}7s^{2}$ 91 Protactinium Ра 96 5*f* <sup>3</sup>  $5f^2$  $5f^{3}6d^{1}7s^{2}$ Uranium U 103 93 92  $5f^4$  $5f^{3}$  $5f^46d^17s^2$ 101 93 Neptunium Np 92  $5f^{4}$ 5f 5  $5f^{6}7s^{2}$ 94 Plutonium 100 90 Pu  $5f^6$  $5f^5$  $5f^{7}7s^{2}$ 95 Americium 99 89 Am  $5f^7$ 5f 6  $5f^{7}6d^{1}7s^{2}$ 96 Curium cm99 88 5f <sup>8</sup>  $5f^7$  $5f^{9}7s^{2}$ 97 Berkelium 98 87 Bk5f 9  $5f^{10}7s^2$  $5f^{-8}$ 98 Californium 98 86 Cf  $5f^{10}$  $5f^9$  $5f^{11}7s^2$ 99 Einstenium Es $5f^{11}$  $5f^{12}7s^2$  $5f^{10}$ Fermium 100 Fm  $5f^{12}$  $5f^{11}$ 

 $5f^{13}7s^2$ 

 $5f^{14}7s^2$ 

 $5f^{14}6d^{1}7s^{2}$ 

Md

No

Lr

state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states. Table 8.11: Oxidation States of Actinium and Actinoids Th Bk 3 3 3 3 3 3 3 3 3 3 3 3 4 4 4 4 4 4 4 4 5 5 5 5 5 6 6 6 6 7 General Characteristics and Comparison with Lanthanoids: The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids. The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action. The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 f electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values. It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids. A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual