Indira Gandhi National Open University
School of Sciences

BCHCT-137

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

VOL.

1

COORDINATION CHEMISTRY

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

This is the core course of Chemistry in the B.Sc. General programme being offered under CBCS Scheme at the fourth semester. The theory course (BCHCT-137) has a credit-weightage worth 4 credits. This course contains two parts, i.e., Part A and Part B. Both of them have a weightage of two credits each. Part A is devoted to the content related to *d* and *f*-block elements and coordination chemistry. Part B contains the content related to states of matter and chemical kinetics. These sections have seven Units each and you are expected to devote equal time to both these parts.

The first two blocks of Part A deal with *d* and *f*-block elements and coordination chemistry.

Block 1 on '*d* and *f*-block elements' has three units. In this block you will study the general features of the chemistry of the *d* and *f*-block elements which are also referred to as transition and inner-transition elements. Block 2 on 'Coordination Chemistry' has four units. In this block you will study about the coordination compounds and the crystal field theory. Block 3 on 'States of Matter' has five units. It deals with details of gases, liquids and solids. Block 4 on 'Chemical Kinetics' has two units and deals with rate laws, its theories and order of reactions.

This course is being offered at the fourth Semester and will build up foundation for the other courses which you will study in the other semesters.

You are expected to spend a total of about 120 hours for completing this course. This is the average time which is to be spent by a learner on studying the course material, doing self-assessment questions as well as terminal questions given in the blocks and the assignment, attending counseling sessions, watching the audio-video programmes and participating in IRC/ teleconferencing sessions related to this course.

We hope you will find this course quite interesting to study. Our best wishes.

Expected Learning Outcomes

After studying this course, you should be able to

- understand the main features of transition elements and the inner-transition elements;
- understand coordination chemistry with details of nomenclature and types of isomerism in coordination compounds;
- discuss the details of crystal field theory in octahedral and tetrahedral complexes along with square planar complexes;
- state the postulates of kinetic theory of gases and derive an expression for the pressure of a gas;
- derive expressions for the collision number between gas molecules; and the mean free path of molecules;
- state and explain the deviation from ideal behaviour, critical phenomenon and viscosity of gases;
- explain the main features of liquid and solid states;
- define rate and order of reaction and describe the methods of their determination; and
- explain the temperature dependence of rate and theories of reaction rate

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Block

1

d AND *f*-BLOCK ELEMENTS

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BLOCK 1: *d* AND *f*-BLOCK ELEMENTS

In your previous courses you have studied about the structures of the atom and the theories of chemical bonding.

In this block you will study the general features of the chemistry of the *d* and *f*-block elements which are also referred to as transition and inner-transition elements. After studying this course, you will be knowing the details of the these elements and their position in the periodic table.

Unit 1 deals with the *d*-block elements which constitute three series of elements belonging to the fourth, fifth and sixth rows of the periodic table. The general characteristics including the electronic configuration have been highlighted. Thereafter, the periodic trends of many properties, stability of various oxidation states including Latimer diagrams have also been discussed.

In Unit 2 the discussion on transition elements has been continued and features like formation of complexes, colour, magnetic and catalytic properties, alloys and interstitial compounds have been discussed briefly.

Unit 3 deals with the inner-transition elements that is, the chemistry of *f*-block elements comprising the lanthanoids and the actinoids. These two series of elements, each consisting of fourteen closely similar elements and their important properties have been discussed.

We expect that after studying this block, you should be able to:

- describe the electronic configuration of transition elements and their ions;
- outline the general characterisitics of transition elements and describe the periodic trends in the properties of transition elements ;
- discuss the stability of various oxidation states for Mn, Fe and Cu along with Latimer diagrams.
- understand why transition metals form coloured compounds and complexes;
- discuss their magnetic and catalytic properties;
- understand the electronic configuration and position in periodic table of the inner-transition elements;
- understand lanthanoid contraction and its consequences;
- follow the trends in general characteristics of the inner-transition elements and get an idea about their various oxidation states and their magnetic properties; and
- discuss the separation of lanthanoids by Ion-Exchange method.

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UNIT 1

TRANSITION ELEMENTS-I

Structure

1.1 INTRODUCTION

Transition elements are important in our daily lives. Iron, an element of this series is a very common metal and is present in nails, kitchenware, automobiles, buildings and even in the hemoglobin in blood. Titanium is present in lightweight, durable products like bicycle frames, artificial limbs. Chromium is used as protective plating on plumbing fixtures and so on. Emerging areas of modern inorganic chemistry like coordination chemistry, organometallic chemistry, catalysis etc. focus on the chemistry of transition metals. Transition metals often form coloured compounds. Some minerals of transition metals are depicted in Fig. 1.1 below:

Fig. 1.1 Malachite (green), azurite (blue), and proustite (red).

In previous classes, you have studied the periodic table and must have noticed that the majority of elements listed there are metals of which the larger fraction are the transition elements. In fact, they are the most prominent in occurrence and importance among other metals.The term transition elements or transition metals probably was first used during Mendeleev's early classification of elements. It was observed that the elements like Ti, V, Cr etc. required a separate subgroup to maintain the vertical similarity of properties among the elements in Mendeleev's 8-group periodic table. Also the triad of elements in Group VIII (Fe, Co, Ni) had some similarities to some of the elements in Group VII (here Mn) as well as to some elements in the beginning of the next row in Group I (Cu). Thus, the properties of the elements showed a transitional character from one row to the next in the periodic table. They are called the transition metals because their position in the periodic table is between the *s* and *p*-block elements and their properties are transitional between the *s*-block elements which form ionic compounds and the *p*-block elements which form typically covalent compounds.

In this unit, you will study about the electronic configuration of the transition elements and their ions and their general characteristics. Thereafter, you will be understanding the periodic trends in the properties of transition elements. Finally you will understand the stability of various oxidation states for metals like Mn, Fe and Cu along with Latimer diagrams (which are diagrammatic representatives of the relaive stabilities of different oxidation states).

Expected Learning Outcomes

After studying this unit you should be able to:

- describe the electronic configuration of transition elements and their ions;
- outline the general characterisitics of transition elements;
- describe the periodic trends in the properties of transition elements;
- discuss the stability of various oxidation states for Mn, Fe and Cu along with Latimer diagrams.

1.2 ELECTRONIC CONFIGURATION

In the previous courses (BCHCT-131, Unit-5), you have learnt in detail about the electronic configuration of multi electron atoms. Before going through this section you can revisit that unit for recapitulation. In this section we are going to deal with the electronic configuration of the transition elements.

Transition elements (also known as *d*-block elements) constitute a major part of modern inorganic chemistry especially in fields like coordination chemistry. Now, transition elements have properties which are transitional between the *s* and *p* blocks. In the *s* and *p*-blocks, electrons are added to the outer shell of the atoms. In the *d*-block, electrons are added to the penultimate shell, expanding it from 8 to 18 electrons. Typically the transition elements have incompletely filled *d* level.

In this unit, transition elements and the periodic trends in their properties, along with the stability of various oxidation states including Latimer diagrams for some of them will be discussed. The two terms *d*-block metal and transition metal are often used interchangeably; however, they do not mean the same thing. The name 'transition metal' originally derived from the fact that their chemical properties were transitional between those of the *s* and *p* blocks. Now, however, the IUPAC definition of a transition element is an element that has an incomplete *d* subshell in either the neutral atom or its ions. The latest periodic table by the International Union of Pure and Applied Chemistry (IUPAC Periodic Table of the Elements) is given below. Here you can see that, the transition elements are placed in between the *s*-block and *p*-block elements. That is they are in between highly electropositive elements on the left and the electronegative elements on the right. The 3*d*, 4*d*, 5*d* and 6*d* shells of electrons get filled up in the four series of elements and they are thus called the *d*-block elements.

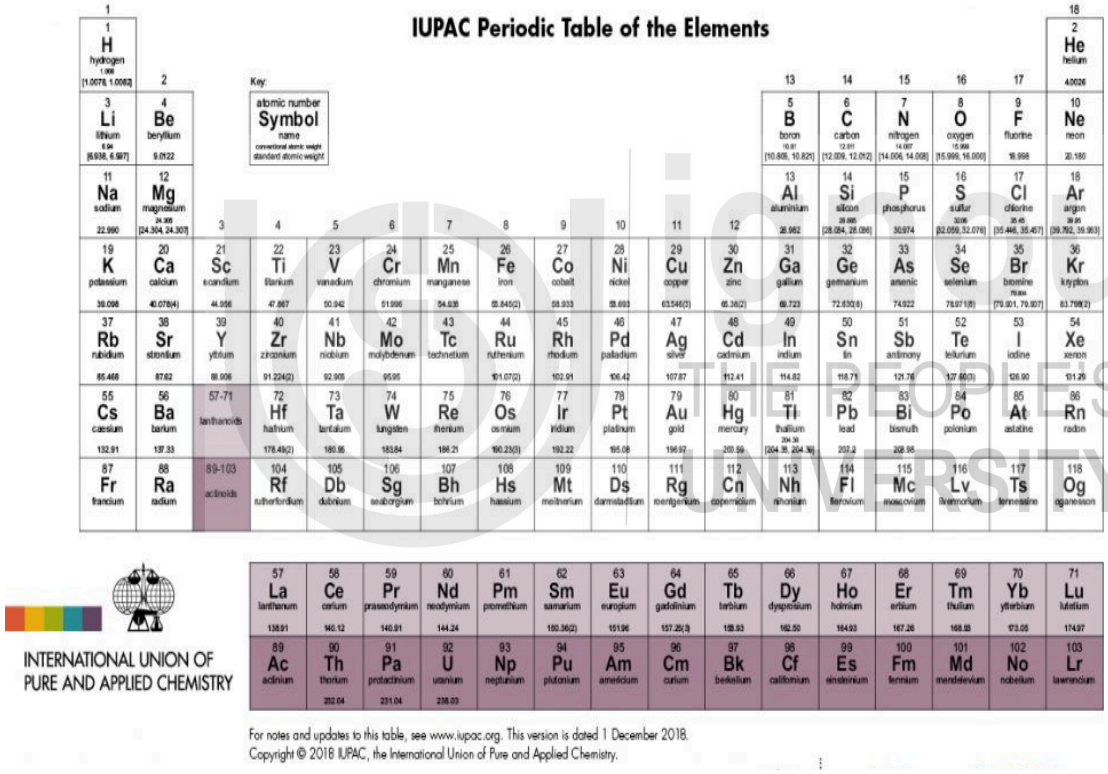


Fig. 1.2: IUPAC PeriodicTable of the Elements.

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. Inorganic chemists generally restrict the term transition metal to an element that has at least one simple ion with an incomplete outer set of *d* electrons. Some examples listed below will enable you to follow this better.

EXAMPLE 1.1: Can you examine the electronic configuration of chromium and say why it is considered as a transition element?

SOLUTION: Chromium has two common oxidation states (apart from less common ones). The +3 oxidation state has a partially filled *d* set even though the +6 state has an empty *d* set. Thus, chromium is considered to be a transition metal.

Atom	Electronic configuration	Ion	Electronic configuration
Cr	$[Ar]4s^1 3d^5$	Cr^{3+}	$[Ar]3d^3$
		Cr^{6+}	[Ar]

EXAMPLE 1.2: At the other end that is the extreme right of the *d* block, look at the elements that retain a full *d* set in their oxidation states. Can you say which are those?

SOLUTION: Well, they are the Group 12 elements- zinc, cadmium, and mercury. Their common oxidation state is +2. Thus, these elements are not considered as transition metals.

Atom	Electronic configuration	Ion	Electronic configuration
Zn	$[Ar]4s^2\ 3d^{10}$	Zn^{2+}	$[Ar]3d^{10}$

So you see, transition elements by definition should contain an incomplete *d* shell in the ground states of their atoms, or in any of their principal oxidation states. However, the last member ($d^{10}s^2$) like Zn do not have incomplete *d*-levels in their Zn^{2+} state. So they are often excluded from the category of the first transition series.

Previously, you must have been acquainted with the electronic configuration of the elements. The electronic configuration of argon atom is $1s^2 2s^2 2p^6 3s^2 3p^6$. If you refer to the periodic table in Fig. 1.2 then you will see that the element following argon is potassium. If you check the electronic configurations of the elements from potassium to zinc, it can be seen that electrons may enter a 3*d* or a 4*s* level. These are illustrated in Table 1.1.

Note: Using the IUPAC definition of transition elements, the elements of Group 12 would not be called transition elements as they do not have incompletely filled *d* shells even in any of their compounds. Thus, two of the Group 12 elements (Zn, Cd) are members of the *d*-block but are not transition elements as they do not have any compounds with an incomplete *d* subshell. The situation for the third Group 12 element, mercury, is different: very recently it has been reported that mercury forms a compound in the mercury (IV) state (HgF_4), which has the d^8 electron configuration. This qualifies mercury as a transition metal.

Using the IUPAC definition there are four series of transition elements and they are discussed below.

The first series of transition elements: Sc(21) to Zn (30), here 3*d* orbitals are filled.

Table 1.1: Electronic configuration of the free atoms and dispositive ions of the first transition series

Element	Name	Free atom	Free M^{2+} ion	Element	Name	Free atom	Free M^{2+} ion
Sc	Scandium	$[Ar]3d^14s^2$	$[Ar]3d^1$	Fe	Iron	$[Ar]3d^64s^2$	$[Ar]3d^6$
Ti	Titanium	$[Ar]3d^24s^2$	$[Ar]3d^2$	Co	Cobalt	$[Ar]3d^74s^2$	$[Ar]3d^7$
V	Vanadium	$[Ar]3d^34s^2$	$[Ar]3d^3$	Ni	Nickel	$[Ar]3d^84s^2$	$[Ar]3d^8$
Cr	Chromium	$[Ar]3d^54s^1$	$[Ar]3d^4$	Cu	Copper	$[Ar]3d^{10}4s^1$	$[Ar]3d^9$
Mn	Manganese	$[Ar]3d^54s^2$	$[Ar]3d^5$	Zn	Zinc	$[Ar]3d^{10}4s^2$	$[Ar]3d^{10}$

The second series of transition elements:Y(39) to Cd (48), here 4*d* orbitals are filled .

Table 1.2: Electronic configurations of elements of the second transition series.

Element	Name	Free atom
Y	Yttrium	$[Kr]4d^15s^2$
Zr	Zirconium	$[Kr]4d^25s^2$
Nb	Niobium	$[Kr]4d^45s^1$
Mo	Molybdenum	$[Kr]4d^55s^1$
Tc	Technetium	$[Kr]4d^55s^2$
Ru	Ruthenium	$[Kr]4d^75s^1$
Rh	Rhodium	$[Kr]4d^85s^1$
Pd	Palladium	$[Kr]4d^{10}5s^0$
Ag	Silver	$[Kr]4d^{10}5s^1$
Cd	Cadmium	$[Kr]4d^{10}5s^2$

The third series of transition elements La(57) and then Hf(72) to Hg(80), here 5*d* orbitals are filled.

Table 1.3: Electronic configurations of elements of the third transition series.

Element	Name	Free atom
La	Lanthanum	$[Xe]5d^16s^2$
Hf	Hafnium	$[Xe]4f^{14}5d^26s^2$
Ta	Tantalum	$[Xe]4f^{14}5d^36s^2$
W	Tungsten	$[Xe]4f^{14}5d^46s^2$
Re	Rhenium	$[Xe]4f^{14}5d^56s^2$
Os	Osmium	$[Xe]4f^{14}5d^66s^2$
Ir	Iridium	$[Xe]4f^{14}5d^76s^2$
Pt	Platinum	$[Xe]4f^{14}5d^96s^1$
Au	Gold	$[Xe]4f^{14}5d^{10}6s^1$
Hg	Mercury	$[Xe]4f^{14}5d^{10}6s^2$

The fourth series of transition elements Ac(89) and then Rf(104) to Cn (112), here 6*d* orbitals are filled.

Table 1.4: Electronic configurations of elements of the fourth transition series

	Elements of fourth transition series	
Element	Name	Free atom
Ac	Actinium	[Rn]6$d^1$7s^2
Rf	Rutherfordium	[Rn]5f^{14}6$d^2$7s^2
Db	Dubnium	[Rn]5f^{14}6$d^3$7s^2
Sg	Seaborgium	[Rn]5f^{14}6$d^4$7s^2
Bh	Bohrium	[Rn]5f^{14}6$d^5$7s^2
Hs	Hassium	[Rn]5f^{14}6$d^6$7s^2
Mt	Meitnerium	[Rn]5f^{14}6$d^7$7s^2
Ds	Darmstadtium	[Rn]5f^{14}6$d^8$7s^2
Rg	Roentgenium	[Rn]5f^{14}6d^{10}7s^1
Cn	Copernicium	[Rn]5f^{14}6d^{10}7s^2

Although lanthanoid means 'like lanthanum' and so should not include lanthanum, lanthanum has become included by common usage. Similarly, actinoid. The ending 'ide' normally indicates a negative ion, and therefore lanthanoid and actinoid are preferred to lanthanide and actinide. However, lanthanide and actinide are still allowed owing to wide current use. This is as per the IUPAC recommendations.

Zn, Cd, Hg and Cn have their electronic configurations of outer orbitals represented by the general formula (n-1)d^{10}ns^2. The *d* orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. The recent (though disputed and so far not reproduced independently) synthesis of mercury(+4) fluoride (HgF_4) has led to the conclusion that the group 12 elements should be considered as transition metals. Cn (Copernicium) is expected to be able to use its *d* electrons for formation of compounds. A plausible reason could be attributed to the fact that the high atomic number destabilizes the 6*d* subshell by strong relativistic effects. Thus Cn in oxidation states higher than +2 (which are not definitely known for the lighter group 12 elements) shows a transition-metal-like behavior.

In the later unit of “Inner-transition elements ” you will learn about the following 30 elements of Lanthanoids and Actinoids:

The first series of inner-transition elements or lanthanoids: La (57) to Lu (71)

The second series of inner-transition elements or actinoids: Ac(89) to Lr (103)

You have learnt earlier how the penetration of inner electron core influences the radial distribution functions of various orbitals. It was discussed that the extent of penetration decreases as

$$s > p > d > f$$

The way in which the energy–levels of different individual orbitals change in multi-electron atoms, depends a lot on the population of other levels.This is qualitatively shown in Fig. 1.3.

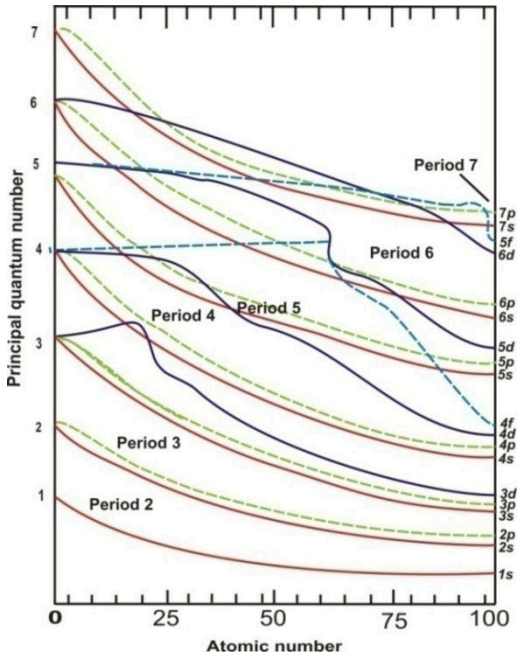


Fig. 1.3: The variation of the energies of atomic orbitals with increasing atomic number in neutral atoms.

You have studied previously that all the subshells of a principal shell (like those of 3*s*, 3*p*, 3*d*) of a hydrogen atom have the same energy.The same is not true for complex atoms, where the n*s* orbitals, which penetrates most, have the highest increase in effective nuclear charge. So,the energy of n*s* orbitals drops much below the corresponding energies of the n*p* or the n*d* atomic orbital. In multielectron system the 4*s* orbital lies a little lower in energy than the 3*d* orbital. But, the situation changes when the 3*d* orbitals get filled up with some electrons. If you follow the Fig 1.4 you will understand the radial distribution curves of the 3*d* and 4*s* orbitals. From Fig. 1.4 you can see that the 4*s* orbital occupies much space so it is far more penetrating than the 3*d* orbital. Thus after argon, in potassium and calcium the electrons enter the 4*s* orbital rather than 3*d*. The radial distribution functions for the two orbitals is shown in Fig. 1.4. If you look at this you can see that the radial distribution curve of the 4*s* orbital has (4-1) i.e. 3 small concentric spheres just below the main 4*s* shell. But these inner spheres have a small probability of finding the electron. Also, refer to Fig. 1.4 again and you will see that the 4*s* orbital occupies much more space than the 3*d* orbitals. So you can say that 4*s* orbital is much more penetrating than the 3*d* orbital. Thus the effect of the positive nuclear charge is much more in 4*s* than that of 3*d* and the energy of 4*s* orbital falls and it becomes more stable than that of 3*d*.

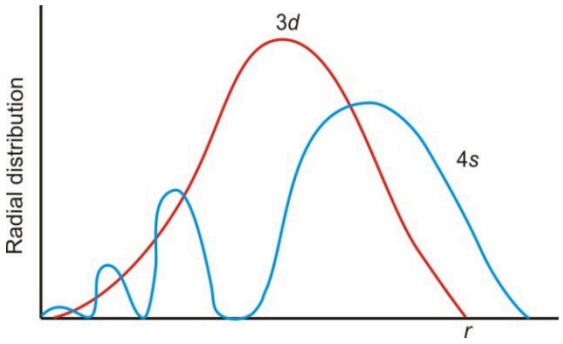


Fig. 1.4: Radial distributions of 3*d* and 4*s* atomic orbitals in H-atom (qualitatively).

After the addition of a few 3*d* electrons, the energy of the 3*d* orbitals fall below the 4*s* level quite fast because the 3*d* electrons experience more effective nuclear charge. So, at the beginning you will see 4*s* orbital has lower energy. But if you look at Fig. 1.3, you will see that, on addition of some electrons in 3*d* level, the 3*d* orbitals becomes lower in energy than those of 4*s*. Now let us understand this concept clearly with the help of few examples.

EXAMPLE 1.3: Now can you inspect the electronic configuration of K, Ca and Sc? In that process, what can you say about the ground state configuration of Sc^+ ion?

SOLUTION: The last electrons in K and Ca enter the 4*s* orbital after argon core as 4*s* is more stable than 3*d*. But since the 4*s* and 3*d* orbitals are very close to each other in energy, the last electron in Sc has the 3*d* orbital occupied, having the ground state electron configuration as $3d^1 4s^2$. But the relative ordering of the energy levels in scandium changes, as the binding energy of the 3*d* electron rises suddenly. Thus it would require much more energy to remove the electron in 3*d* than that in 4*s*. Hence the ground state configuration of the Sc^+ ion is $[Ar]3d^1 4s^1$ and not $[Ar]3d^0 4s^2$.

EXAMPLE 1.4: In this example we will study the electronic configuration of Zn and thereafter the second transition series.

DISCUSSION: The process of filling up the 3*d* orbital in the first transition series continues till all the 3*d* orbitals are filled which happens with Zn, which has the following configuration:

$[Ar]4s^2 3d^{10}$

After that comes the *p*-block elements as you can see in the periodic table in Fig. 1.2, The next lowest available orbital is 4*p* which has the capacity of taking up a maximum of six electrons. So in the next six elements the 4*p* orbitals are filled in a regular manner. The noble gas Krypton (Kr) has the configuration $[Ar]3d^{10} 4s^2 4p^6$. Thereafter comes the question, which orbital will be filled up first, 4*d* or 5*s* and 5*p*? Well, the 4*d* orbital has higher energy compared to 5*s* and 5*p*. So, the two *s*-block elements come after that followed by the second transition series, with Y as $[Kr]4d^1 5s^2$ and Ag as $[Kr]4d^{10} 5s^1$. Thereafter comes Cd as $[Kr]4d^{10} 5s^2$ and the six *p*-block elements which ends at the noble gas Xe as $[Ar]\ 4d^{10} 5s^2 5p^6$. After this the 4*f*, 5*d* and 6*s* orbitals are available.

Now, if you look at the Fig. 1.3 where the variation of energies of atomic orbitals are shown against the increasing atomic numbers, you can notice that around Z=50, the change in energy of the individual atomic orbitals is very complicated. The 4*f* orbital cannot penetrate much in the xenon core and so has little stability. But, the situation changes when the 6*s* orbital gets filled up with two electrons, into which the 4*f* penetrates much, thus the enhanced nuclear charge sharply lowers the energy of the 4*f* orbital. You can see in the Fig. 1.3 that the lines for 5*d* and 4*f* orbitals merge in this region of atomic number.

In the third transition series, which starts with La, the last electron enters a 5*d* orbital (dealt later in Unit 3).Thus from lanthanum to lutetium, they are classed as lanthanoids. The electronic configurations of transition elements of 4*d*, 5*d* and 6*d* transition series are given in Table 1.2, Table 1.3 and Table 1.4 respectively.

Now after inspecting the electronic configurations of the transition elements do you notice that some elements, prefer half-filled or completely-filled *d* orbitals as the configuration as it gives more stability? We will discuss this with the help of some examples.

EXAMPLE 1.5: Can you find the actual configuration of Cr?

SOLUTION: In the first transition series, V has the configuration $[Ar]3d^3 4s^2$, the next element is Cr which should have another electron entering the *d* orbital thus making it $[Ar]3d^4 4s^2$, whereas the actual configuration is $[Ar]3d^5 4s^1$, which is half-filled and preferred.

EXAMPLE 1.6: Similarly, can you find the electronic configuration of Mo?

SOLUTION: Mo of second transition series is $[Kr]4d^5 5s^1$. So this half-filled configuration is preferred over $[Kr]4d^4 5s^2$.

EXAMPLE 1.7: Next let us look at the configuration of Cu (of first transition series) which follows Ni($[Ar]3d^8 4s^2$).

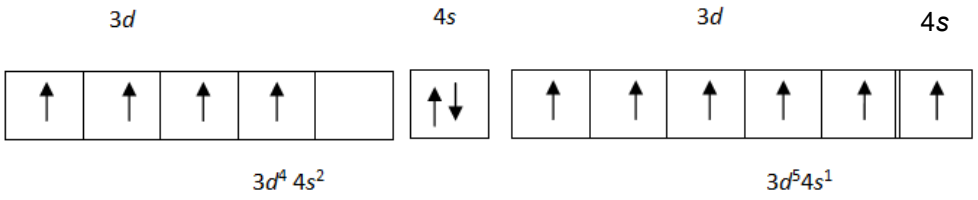
SOLUTION: This is also a very interesting case. It should have been $[Ar]3d^9 4s^2$, but instead it prefers the more stable completely-filled configuration, which is $[Ar]3d^{10} 4s^1$.

EXAMPLE 1.8: What about the electronic configuration of Ag of second transition series?

SOLUTION: It also has the configuration $[Kr]4d^{10} 5s^1$. Whenever transition elements are ionized the n*s* electrons are lost first.Thus it is seen that the stability of the electronic configurations of the transition elements can be explained when various factors like the nuclear-electron attraction, electron-electron repulsion in different orbitals, shielding of one electron by others from the nuclear charge, the magnitude of nuclear charge and many other factors must be considered.

In the above examples (1.5,1.6,1.7& 1.8) you can see that exactly half-filled and (completely) filled orbitals are more stable for both the first and second transition series. This is because half-filled and completely filled orbitals have an exchange energy which is much greater than the exchange energies associated with any other configuration. This exchange energy is the driving force for these configurations to take an electron out of turn in order to achieve or maintain the half-filled or completely-filled configuration. Also these configurations provide the most stable distributions of electrons which suffer the minimum repulsion.

Let us compare the exchange energy for two possible configurations $3d^4 4s^2$ and $3d^5\ 4s^1$ for chromium.



Electrons present in 4*s* orbital in two configurations contribute nothing to exchange energy as they do not constitute any pair with parallel spin. Four unpaired *d* electrons in first configuration can make six pairs of electrons with parallel spin which contribute towards exchange energy (six combinations). Whereas five unpaired *d* electrons in second configuration contribute more towards exchange energy because they can constitute 10 combinations of pairs of electrons with parallel spin. This gain of exchange energy (worth of 4 combinations) would favour the $3d^5 4s^1$ configuration for chromium. But, you should remember that in achieving this configuration, there would be loss of energy in promoting an electron from 4*s* to 3*d* orbital. In case of chromium the gain in exchange energy is more than the loss in energy and therefore, $3d^5 4s^1$ is the favoured configuration.

EXAMPLE 1.9: After the 4*s* orbital is filled, electrons enter the 3*d* level, rather than the 4*p* orbital which, like the 4*s*, has greater penetration into the core than the 3*d* orbital. Why does this happen?

SOLUTION: After argon, the 4*s* orbital is filled in K and Ca while the nuclear charge increases by two units. Now, the 3*d* orbitals appreciably penetrate the electron density in the 4*s* orbitals and hence are not fully screened by the 4*s* electrons from the enhanced nuclear charge. Consequently their energy drops well below the 4*p* orbitals. As electrons start entering the 3*d* orbitals, the 3*d* electrons exert more screening on the 4*p* orbitals than on the remaining 3*d* orbitals. Hence 3*d* remains the lowest available orbital.

SAQ 1

a) Which of the two orbitals, 3*d* and 4*s* has higher energy in potassium and why?

b). Give the name and symbols for the elements that have the following valence configurations.

i) $4s^2 3d^5$ ii) $5s^2 4d^{10}$ iii) $4s^2 3d^{10}$ iv) $5s^1 4d^8$ v) $4s^2 3d^2$ vi) $5s^2 4d^4$

c) Write the valence electron configurations for the following transition metal cations:

i) Mn^{2+} ii) Ir^{3+} iii) Ni^{2+} iv) Mo^{2+} v) Ti^{2+} vi) Fe^{3+} vii) Pt^{2+} viii) Nb^{3+}

1.3 GENERAL CHARACTERISTICS

In the preceding section you have learnt about the electronic configuration of transition elements and their position in the periodic table. Now we will discuss the general characteristics of transition metals which arise basically due to the presence of incompletely filled *d* shells

METALLIC CHARACTER

In the *d*-block elements the penultimate shell of electrons is expanding which leads to similarity in many physical and chemical properties. The transition elements are all metals. They are therefore good conductors of electricity and heat, have a metallic lustre and are hard, strong and ductile. They also form alloys with other metals.

COMPLEXES

The transition elements have great tendency to form coordination compounds with Lewis bases, that is with groups which are able to donate an electron pair. These groups are called ligands. A ligand may be a neutral molecule such as NH_3, or an ion such as Cl^- or CN^-.

This ability to form complexes is in marked contrast to the *s* and *p*-block elements which form only a few complexes. The tendency to form complex ions by transition metals is due to their ability to form small, highly charged ions. These ions act as Lewis acids as they have vacant low energy orbitals which have suitable energy to accept lone pairs of electrons donated by other groups or ligands. Details about the geometry of complexes are discussed in Block 2 of this course.

The nature of coordination complexes and the important crystal field theory of bonding, as well as their magnetic properties are discussed in later units.

1.4 PERIODIC TRENDS IN PROPERTIES

In the previous section you have studied the important properties of transition metals in general. As you know the transition metals are an integral part of the

periodic table, like the main group elements, the transition metals are also expected to exhibit periodicity in their properties. In this section, you will learn about the variation of the properties of the transition elements.

Some of the important properties of the elements of 3*d* series are listed in Table 1.4. If you study the data in the table carefully, you will notice that within a period,the variation in these properties is much less as compared to the main group elements. There are quite well marked similarities between the *d*-block elements, but the chemistry of the elements of the first transition series differs from that of the other series. The difference in the electronic configuration of the transition metals as discussed earlier (electrons are added to inner (n-1)*d* subshell) is responsible for the difference in the trends in their properties

Table 1.5: Some properties of *d*-block elements

Property	Scandium	Titaniuim	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	21	22	23	24`	25	26	27	28	29	30
Atomic weight	44.956	47.90	50.942	51.996	54.938	55.847	58.933	58.710	63.54	65.37
Metallic Radius (pm)	164	147	135	130	135	126	125	125	128	137
*Ionic radius (pm)	81 (3+)	76,68 (3+) (4+)	74,60 (3+) (4+)	84,69 (2+) (3+)	80,66 (2+) (3+)	76,64 (2+) (3+)	74,63 (2+) (3+)	72,62 (2+) (3+)	96,69 (1+) (2+)	74 (2+)
Covalent radius (pm)	144	132	122	118	117	117	116	115	117	125
Boiling point (K)	3000	3533	3673	2753	2370	3273	3173	3005	2868	1180
Melting point (K)	1812	1948	2173	2163	1517	1808	1768	1726	1356	692
Density 10^3 x kg m^{-3}	3.0	4.5	6.11	7.2	7.44	7.86	8.86	8.90	8.92	7.13
Electro-negativity (A/R)	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.65
Ionisation1st	633	659	650	653	717	762	759	736	745	906
Enthalpy 2nd	1235	1309	1414	1591	1509	1561	1644	1751	1958	1732
(kJ mol^{-1}) 3rd	2388	2648	2866	2992	3259	2958	3230	3391	3556	3828
Electrode	(III)	(III) (IV)	(II) (III)	(II)(III)	(II) (III)	(II) (III)	(II) (III)	(II)	(I) (II)	(II)
Potential $(V)^+$	-2.1	-1.2-1.63	-1.2-0.86	-0.91-0.74	-1.18-0.28	-0.44-0.04	-0.28+0.4	-0.25	+0.52+0.34	-0.76

***** Values in parantheses refer to oxidation states of the metal, + (III) refers to couple M^{3+}/M, etc.

1.4.1 Atomic Radii, Atomic Volume and Density

Atomic Radii

Look at Table 1.5 and note that the covalent radii of the elements decrease from left to right across a row in the transition series. This continues near the end of the row when the size increases slightly. On moving from left to right, the nuclear charge increases due to addition of protons in the nucleus and extra orbital electrons are also added. The orbital electrons shield the nuclear charge incompletely (*d* electrons shield less efficiently than *p* electrons, which in turn shield less effectively than *s* electrons). Due to this poor screening by *d* electrons, the electrons experience stronger nuclear charge. Hence a contraction in size occurs.

Atoms of the transition elements are smaller than those of Groups 1 or 2 elements in the same horizontal period.This is partly because of the usual contraction in size across a horizontal period discussed above, and partly because the orbital electrons are added to the penultimate *d* shell rather than to the outer shell of the atom.

Here the point to be emphasized is that the shielding of the outer n*s* electron(*s*) by (n-1)*d* electron(s) is more efficient than the shielding of a n*s* electron by another n*s* electron (or that of a n*p* electron by another n*p* electrons). Let us discuss these with some examples given below. That is why the decrease in atomic radius from sodium to chlorine is greater than that from scandium to copper.

EXAMPLE 1.10: Why the elements which occur immediately after the transition elements are smaller than expected from simple extrapolation from the group elements?

SOLUTION: This is due to the cumulative effect to incomplete shielding provided by (n-1)d^{10} electrons and therefore, the effective nuclear charge felt by the outer electrons of the elements from gallium to krypton is greater than that if the *d* orbitals had not been gradually filled in transition elements.

EXAMPLE 1.11: Why are the atomic radii of the elements of third transition series much smaller than expected ?

SOLUTION:The rate of decrease in size along the lanthanoid series is even less than that in the transition series since in the lanthanoids the electrons are added to the antepenultimate [(n-2)*f*] shell and these shield the outer electrons much more effectively. The presence of 4*f* electrons in the lanthanoids affects the atomic size and therefore, the chemistry of the subsequent elements. This is due to the effect of the greater than expected effective nuclear charge felt by the electrons of the elements of the third row transition series, hafnium to gold, owing to the insertion of lanthanoids.

Table 1.6: Metallic radii (pm) of some elements of Groups 1-13

1	2	3	4	5	6	7	8	9	10	11	12	13
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
235	197	164	147	135	130	135	126	125	125	128	137	141
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
248	215	178	160	146	139	136	134	134	137	144	154	166
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
267	222	188	160	149	141	137	135	136	139	146	157	171

EXAMPLE 1.12: The data in Table 1.5 and Fig. 1.5 show that the general trend of decreasing size is reversed towards the end of the series. Why?

SOLUTION: The trend in the variation of the metallic radii in alkali, alkaline earth and transition metals is shown in Fig. 1.5. You can see in Fig. 1.5 that as we move from alkali metals to alkaline earth metals and from alkaline earth metals to the transition elements, the radii decrease steeply but within transition elements this rate of decrease is less. This could be due to an increase in inter-electronic repulsion after the addition of sufficient number of electrons in the *d* orbitals to the gradual increase in size.

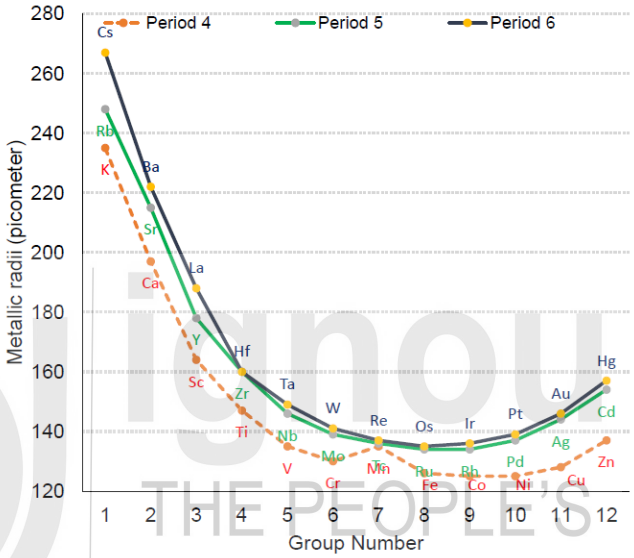


Fig. 1.5: Trends in metallic radii of alkali, alkaline earth and transition metals of fourth, fifth and sixth periods.

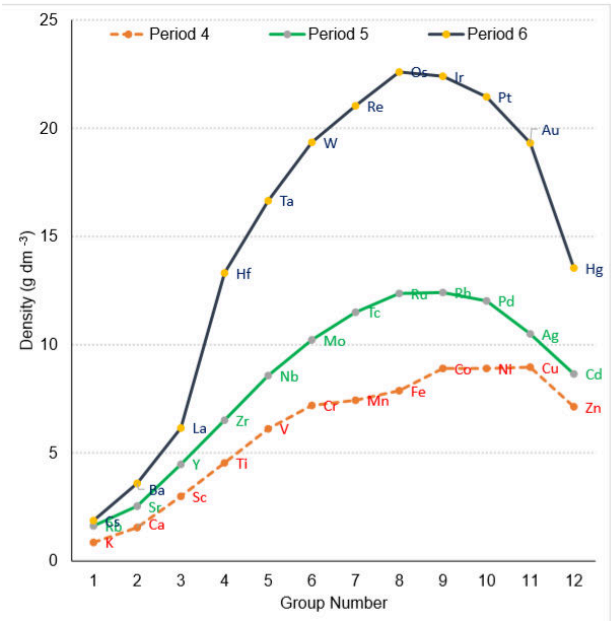


Fig. 1.6: Trend in densities of the alkali, alkaline earth and transition metals of fourth, fifth and sixth periods.

There is a gradual decrease in the size of the 14 lanthanoids from cerium to lutetium. This is called the **lanthanoid contraction** (Details of this are given in section 3.2.2 of Unit 3 of this course). The covalent radius and the ionic radius of Hf are actually smaller than the corresponding values for Zr. The covalent and ionic radii of Nb are similar as those for Ta. Therefore the second and third row transition elements have similar radii. As a result they also have similar lattice energies, solvation energies and ionization energies. Thus the differences in properties between the first row and second row elements are much greater than the differences between the second and third row elements. The effects of the lanthanoid contraction are less seen towards the right of the *d*-block.

SAQ 2

a) Of the following pairs, tick mark the element which is larger in size:

(i) Calcium or scandium

(ii) Vanadium or titanium

(iii) Chromium or molybdenum

(iv) Iron or osmium

b) Why is the size of the elements of third transition series almost similar to that of the elements of second transition series?

Density

The size of an atom of an element is related to its atomic volume. So their trends are the same. Similarly density is also related to the size of the elements. So, across the period, the smaller the size, the higher is the density of the elements. Thus there is a general trend of increasing density across the elements of a transition series. This is well represented in Fig 1.6 which gives the variation of the densities of alkali, alkaline earth and the transition metals of the fourth, fifth and sixth periods. For 4*d* and 5*d* elements, this increase is not that regular as the increase in densities for 3*d* elements. Along the group also, the density increases (Fig. 1.6). The increase in density within the *d* block groups is greater than that within the *s* and *p* block groups.

On descending one of the main groups of elements in the *s* and *p*-blocks, the size of the atoms increases because extra shells of electrons are added. The elements in the first group in the *d*-block (Group 3) show the expected increase in size (Sc→Y→ La). But in the subsequent Groups (4-12), there is an increase in radius of (0.3-13 pm) between the first and second member, but very little increase between the second and third elements. This trend is shown both in the covalent radii (Table 1.4) and in the ionic radii (Table1.5). Between lanthanum and hafnium are the 14 lanthanoids, in which the antepenultimate shell of electrons is filled.

The atomic volumes of the transition elements are low as compared with elements in neighbouring Groups 1 and 2. Can you say why is it so? Well, it is

because the increased nuclear charge is poorly screened and so the electrons are attracted more strongly by the nucleus. Again, the extra electrons added occupy inner orbitals. As a result the densities of the transition metals are high and are greater than 5 gcm^{-3}. (The only exceptions are Sc 3.0 gcm^{-3} and Y and Ti 4.5 gcm^{-3}.) The densities of the second row are high and third row values are even higher. The two elements with the highest densities are osmium 22.57 gcm^{-3} and iridium 22.61 gcm^{-3}.

1.4.2 Melting and Boiling Points

The melting and boiling points of the transition elements are generally very high. Transition elements typically melt above 1000°C. There are a few exceptions. The melting points of La and Ag are just under 1000°C (920°C and 961°C respectively). Other notable exceptions are Zn (420°C), Cd (321°C) and Hg which is liquid at room temperature and melts at –38°C. The last three behave atypically because the *d* shell is complete, and *d* electrons do not participate in metallic bonding. The high melting points are in marked contrast to the low melting points for the *s*-block metals Li (181°C) and Cs (29°C).

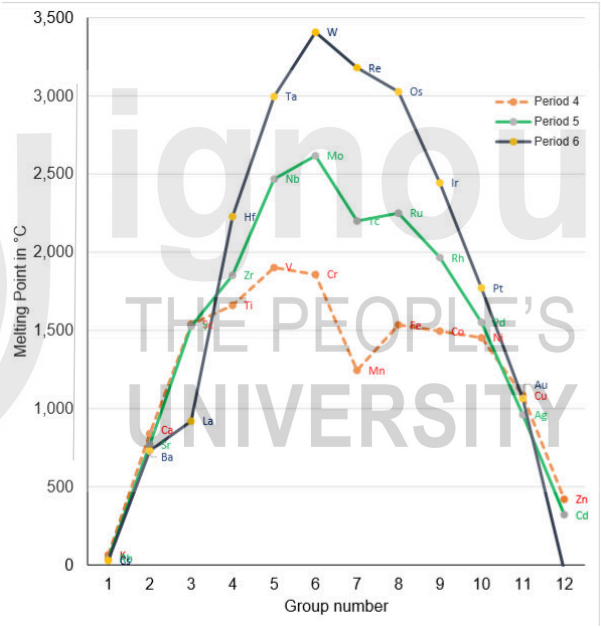


Fig. 1.7: Trends in melting points of alkali, alkaline earth and transition metals of fourth, fifth and sixth periods.

The melting points of the transition elements depend upon the strength of the metallic bond which increases with the availability of the electrons to participate in bonding. If you look at Fig. 1.7 then you can see that between calcium and scandium (where *d* electron first appears), there is a jump of nearly 700 degrees (in Centigrade scale) in the melting point. The unpaired *d* electron leads to higher interatomic forces and therefore the increase in strength of the metallic bond which is reflected in high melting and boiling points. But, this cannot be generalized and there are anomalies. Now let us inspect the values of the melting point when we move across any period in the periodic table. At first it increases till the middle of each transition series and then it decreases with the onset of pairing of electrons. If you look at the values of melting points for the first transition series (Fig. 1.7), there is a sharp decrease of melting point at manganese, which has five unpaired *d*

electrons.This is because of a complex crystal structure of manganese. Now, can you understand what may be the reason for the softness and low melting point of Zn, Cd and Hg (Hg is a liquid)? Yes, the explanation can be that the electrons are paired up in these atoms. The melting points of the elements of the first transition series are comparatively lower than those of the elements of the second and third transition series. This trend is very well illustrated in the Fig. 1.7.

The periodic trends in the boiling points are similar to those in the melting points. As the process of boiling requires almost complete breaking of bonds and such metallic bonding exists in the liquid state to some extent, high temperatures are necessary. Therefore, the boiling points of the metals are much higher than melting points.

1.4.3 Ionization Enthalpy

Ionization enthalpy refers to the ease with which an electron may be removed from an atom in the gaseous state. In the case of a transition metal the value is intermediate between those of the *s* and *p*-block elements. The values for the first ionization enthalpies vary over a wide range from 541 kJ mol^{-1} for lanthanum to 1007 kJ mol^{-1} for mercury.

You have already learnt in previous classes about the concept of ionization enthalpy and how it varies periodically with the atomic size. Transition metals also follow the same trends. This is illustrated in Fig. 1.8. Based on this the following examples are given to make you understand this concept better.

EXAMPLE 1.13: How does the ionization enthalpy of the transition elements vary as we move across the period?

SOLUTION: As we move across a period, the effective nuclear charge experienced by ns^2 electrons goes on increasing causing the shells to shrink in size and thus making it difficult to remove the electrons. Thus along a period, the ionization enthalpy increases. This can be checked from the values of the first ionization enthalpy of these elements given in Table 1.5.

EXAMPLE 1.14: Though the second and the third ionization enthalpies(as given in Table 1.5), follow the same pattern, exception is noted for the second ionization enthalpies of Cr and Cu which are comparatively higher. Why is this so?

SOLUTION: Due to the extra stability of $3d^5$ and $3d^{10}$ configurations of Cr and Cu respectively.

EXAMPLE 1.15: Why does the ionization enthalpy tend to increase along the series only slightly as compared to the main group elements (Fig. 1.8)?

SOLUTION: As the decrease in the size of the transition metals is less than that of the main group elements along a period. Since *s* and the *d* electrons do not differ much in energy, the difference in the successive ionization enethalpies is relatively small.

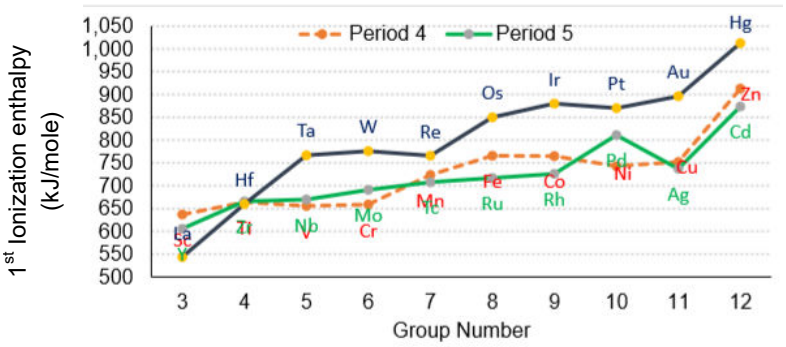


Fig. 1.8: Variation in first ionization enthalpy of the transition elements.

1.4.4 Electrode Potential

When a metal is placed in a solution of its ions a potential difference is set up between the metal and the solution. This concept is illustrated in Fig. 1.9.

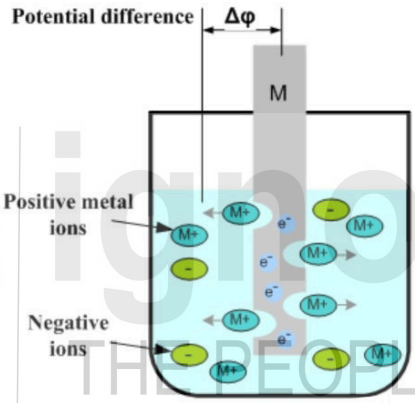


Fig. 1.9: Single Electrode Cell (Half-cell).

The value of this potential difference for a particular metal depends upon the particular metal, the concentration of the metal ions in solution and the temperature. By convention, the potential difference set up in a 1 *M* solution of metal ions at 298K is called the standard electrode potential. Measuring the standard electrode potentials is absolutely impossible. It has to be measured against some reference electrode which is the hydrogen electrode. This consists of hydrogen gas at one atmosphere pressure in contact with a 1*M* solution of its ions at 298 K.

The values of some standard electrode potentials for the elements of first transition series are given in Table 1.7. Electrode potential is a measure of the electropositive character and the reactivity of the metals. You will find that along a period, generally there is a decrease in electropositive character and also the reactivity of metals also decreases. Table 1.7 contains the thermochemical parameters related to the transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials. The observed values of E^{o} and those calculated using the data of Table 1.7 are compared in Fig. 1.10. If you look at Table 1.7, you will see that all the elements of the first transition series, except copper, have negative values and can react with acids (H^{+}) producing hydrogen. A plot of variation of the electrode potential of the transition elements of 3*d* series is

shown in Fig. 1.10. The unique behaviour of Cu, having a positive E^o, accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. 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^o for Mn, Ni and Zn are more negative than expected from the trend.

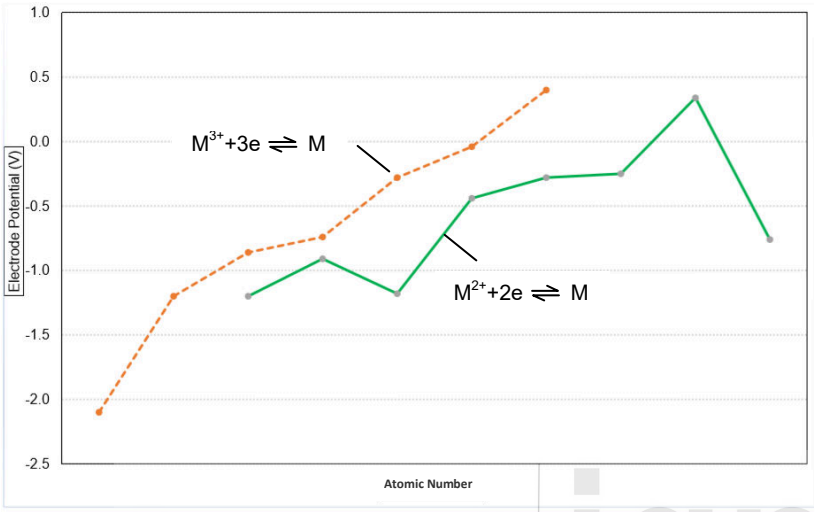


Fig.1.10: Trends in electrode potentials of transition metals of 3*d* series.

EXAMPLE 1.16: Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, what is possible reason for this?

SOLUTION: (Hint: consider its high ΔH^o. The $E^o(M^{2+}/M)$ value for copper is positive (+0.34V))

TABLE 1.7: Thermochemical data (kJ mol^{-1}) for the first row transition Elements and the Standard Electrode Potentials for the Reduction of M^{2+} to M.

Element (M)	$\Delta_O H^o(M)$	$\Delta_1 H_1^o$	$\Delta_1 H_2^o$	$\Delta_{hyd} H^o(M^{2+})$	E^o /V
Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	298	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu	339	745	1958	-2121	-0.34
Zn	130	906	1734	-2059	-0.76

Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	298	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu	339	745	1958	-2121	-0.34
Zn	130	906	1734	-2059	-0.76

1.4.5 Electronegativity

The periodic variation of electronegativity with atomic number for the first six rows of the periodic table is shown in Fig. 1.11

Transition elements have fairly low values of electronegativity. It increases from Sc to Cu with a fall at Mn and Zn. But, this increase in electronegativity is much slower as the additional electron is being added to an inner shell which provides relatively good shielding to the outer electrons from the nucleus. Thereby the elements become slightly less metallic which is reflected in the increasing positive electrode potentials of their ions M^{2+} and M^{3+} (Table 1.5).

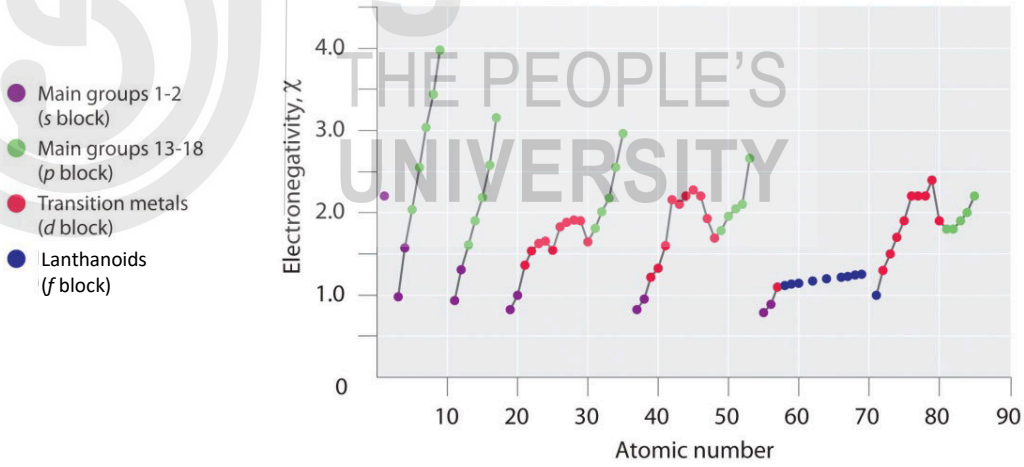


Fig.1.11: Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

1.4.6 Oxidation States

The transition elements usually exist in several different oxidation states which change in units of one, e.g. Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^{+}.

The oxidation states shown by the transition elements may be related to their electronic structures which have been already discussed in section 1.2 of this unit. Recalling the electronic configuration of the transition elements we remember that Cr and Cu have additional stability when the *d* orbitals are exactly half filled or completely filled (Table 1.7) in their ions.

Table 1.7: Oxidation states of transition elements(The solid dots show common oxidation states, and the hollow dots show possible but unlikely states)

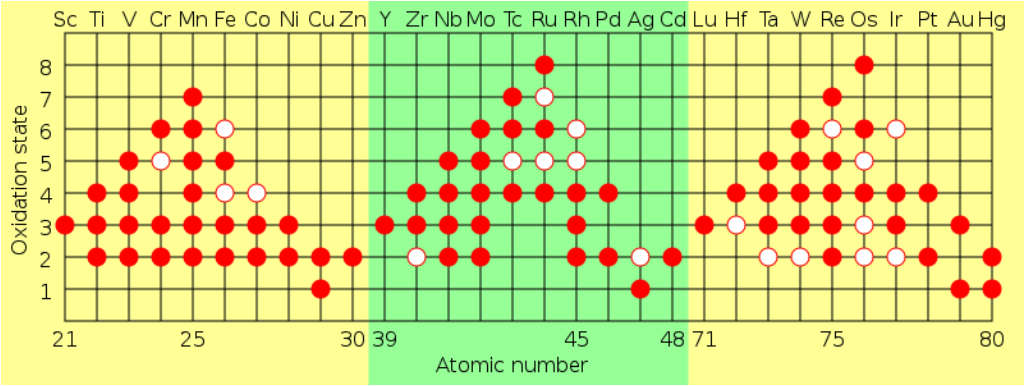


TABLE 1.8: Oxidation states of transition elements of *d*-block (the most common oxidation states are in bold type)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+1	+2	**+2**	+2	**+2**	**+2**	+1	**+2**
	+3	+2	**+3**	+3	**+3**	+3	+3	**+2**	
	+4	+3		+4	+4	+4	+4		
		+4		+6	+6				
		+5	+6	+7					
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	**+4**	+3	+3	+4	+2	**+3**	**+2**	**+1**	**+2**
		+5	+4	**+6**	**+3**	+4	+3	+2	
			+5	+7	+4	+6	+4	+3	
			+6		+5				
					+6				
					+7				
					+8				
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	**+4**	+4	+2	+3	+2	+2	+2	+1	+1
		+5	+3	+4	+3	+3	+3	**+3**	**+2**
			+4	+5	**+4**	**+4**	**+4**		
			+5	+6	+6	+6			
			+6	**+7**	+8				

If you look at Table 1.8 then you will notice that there is a reduced tendency of higher states towards the end of the series. This could be due to steady increase in the effective nuclear charge along the series thus pulling the *d*

orbitals into the electron core and not making them readily available for bonding. For example, the only oxidation state for Zn is Zn(+2) where no *d* orbital is involved. On the other hand, early in the series, it is difficult to form species that do not utilize the *d* electrons i.e., Sc(+2) is virtually unknown and Ti(+5) is more stable than Ti(+2).

By looking at Table 1.7 you can very easily follow the trend in the oxidation states as we go down the group. A full range of oxidation states of the transition elements is shown in Table 1.8. The trend in the stability of oxidation states within the groups is different for the transition elements and the main group elements (*s* and *p*-block elements). For the main group elements, the higher oxidation state becomes less stable going down a group because of inert effect. However for the transition elements the stability of the higher oxidation states increase going down a group.

To illustrate this trend, let us first look at Group 6. It is composed of Cr, Mo and W. We have seen that chromium in +6 oxidation state as in K_2CrO_4 is a good oxidizing agent forming Cr^{3+} as the product. This means that in many instances Cr(+3) is more stable than Cr(+6). In contrast, molybdenum and tungsten in +6 oxidation state in K_2MoO_4 and K_2WO_4 are not easily reduced. This implies that lower oxidation states, e.g., Mo(+3) and W(+3) are not as easy to form as Cr(+3), making the +6 oxidation state more stable. Thus the stability of the +6 state for Group 6 elements will be W^{6+}>Mo^{6+}>Cr^{6+}. We find the same trend in Group 4 which is composed of Ti, Zr and Hf. For all the three elements, most stable oxidation state is +4. However Ti(+2) and Ti(+3) can be formed from Ti(+4) by the use of good reducing agent but lower oxidation states of Zr and Hf are extremely difficult to prepare. Table 1.9 shows how various oxidation states of some elements of period 4 tend to react with respect to oxidation and reduction.

Going from left to right across period 4, $M^{2+}(aq)$ ions are known for the last seven elements from V to Cu and $M^{3+}(aq)$ ions are known for the first seven elements from Sc and Co. Thus, there is an overall increase in stability of $M^{2+}(aq)$ with respect to oxidation as one moves across the series. However, in the case of iron, $Fe^{2+}(aq)$ is less stable than $Fe^{3+}(aq)$ because of the extra stability associated with half-filled (d^5) orbitals in the case of $Fe^{3+}(aq)$. Sc could have an oxidation state of (+2) if both *s* electrons are used for bonding and (+3) when two *s* and one *d* electrons are involved. Ti has an oxidation state (+2) when both *s* electrons are used for bonding, (+3) when two *s* and one *d* electrons are used and (+4) when two *s* and two *d* electrons are used. Similarly, V shows oxidation states of (+2), (+3), (+4) and (+5). In the case of Cr, by using the single *s* electron for bonding, we get an oxidation state of (+1): hence by using varying numbers of *d* electrons oxidation states of (+2), (+3), (+4), (+5) and (+6) are possible. Mn has oxidation states (+2), (+3), (+4), (+5) (+6) and (+7). In case of the first transition series the lowest oxidation state displayed is the number of *s* electrons and the highest oxidation state is the number of *s* and *d* electrons.

The highest oxidation states are often stabilized in the oxide and fluoride compounds, e.g., MnO_4^-, CrO_4^{2-}, VO_2^+, VF_5, etc. In these compounds O^{2-} and F^- are difficult to be oxidized by the central metal because O and F are strong oxidizing agents.

Table 1.9: Reactivity of some oxidation states of first transition series elements in aqueous solution

Reducing agents ⟶	Most stable	⟵ Oxidising agents
–	Sc^{3+}	–
Ti^{2+}, Ti^{3+}	Ti^{4+}	–
V^{2+}, V^{3+}	V^{4+}	V^{5+}(slightly)
Cr^{2+}	Cr^{3+}	Cr^{6+}
–	Mn^{2+}	Mn^{3+}, Mn^{4+}, Mn^{7+}
Fe^{2+}	Fe^{3+}	–
–	Co^{2+}	Co^{3+}
–	Ni^{2+}	–
Cu^{2+}	Cu^{2+}	–

Once the d^5 configuration is exceeded, i.e. in the last five elements, the tendency for all the *d* electrons to participate in bonding decreases. Thus, Fe has a maximum oxidation state of (+6). However, the second and third elements in this group attain a maximum oxidation state of (+8) in RuO_4 and OsO_4. Can you guess why this difference between Fe and the other two elements Ru and Os? Well, the reason is the increased size of the atoms. The oxidation states form a regular 'pyramid' as shown in Table 1.7. The oxidation number of all elements in the elemental state is zero. In addition, several of the elements have zero-valent and other low valent states in complexes. Low oxidation states occur particularly with π bonding ligands such as carbon monoxide and dipyridyl. The higher oxidation states are displayed with electronegative elements like oxygen and fluorine. Compounds in higher oxidation states are oxidizing in nature and covalent while those in lower oxidation states are reducing and ionic. Similar but not identical pyramids of oxidation states are found in the second and third rows of transition elements.

Now refer to Table 1.7 and try out the following examples.

EXAMPLE 1.17: In Group 8 (the iron group) what are the maximum oxidation state shown by the second and third row transition elements?

SOLUTION: The second and third row transition elements show the maximum oxidation state of (+8) compared with (+6) for Fe.

When we say that compounds are stable, it is meant that they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures. Within each of the transition Groups 3–12, there is a difference in stability of the various oxidation states.

SAQ 3

Explain briefly in the space given below, why zinc and cadmium are soft metals.

SAQ 4

a) Explain briefly in the space provided below, the existence of OsO_4 in terms of trends in oxidation states.

b) What are the basic requirements for stabilization of high and low oxidation states of transition metals.

c) Describe and account for the trends in the ionic radii and the stability of high oxidation states upon moving from the second to the third row of the transition series.

1.5 STABILITY OF VARIOUS OXIDATION STATES FOR Mn, Fe AND Cu

Latimer Diagrams

Latimer diagrams, also called reduction potential diagrams, show the different species of an element in varying oxidation states and are widely used to ascertain relative stabilities of different oxidation states. Arrows are put between different species and standard potentials involving two immediate species are written over the arrows.The oxidation state of the element concerned is specified under each species which may differ by one or more electrons. The species with the highest oxidation state is placed at the extreme left and the one with the lowest at the right extreme. The first point to understand here is how to construct a Latimer diagram? You have to remember that in a Latimer diagram, oxidation members decrease from left to right, then the numerical values of the standard potentials (E^o) in volts are written above the line joining the species involved in the particular couple. Typically standard conditions are taken in either strong acid ($[H^+]$ =1 *M*, pH 0) or strong base ($[OH^-]$) =1*M*, pH 14).

Latimer diagram for manganese (in 1 *M* acidic solution at 25 ºC) in oxidation states from +7 to 0 is shown below:

$$\underset{7+}{MnO_4^-} \xrightarrow{+0.564V} \underset{6+}{MnO_4^{2-}} \xrightarrow{+0.274V} \underset{5+}{MnO_4^{3-}} \xrightarrow{+4.27V} \underset{4+}{MnO_2} \xrightarrow{+0.95V} \underset{3+}{Mn^{3+}} \xrightarrow{+1.51V} \underset{2+}{Mn^{2+}} \xrightarrow{-1.18V} Mn$$

The Latimer diagram has in it all the standard potentials for redox reactions of the element Mn. See the last part which connects Mn^{2+} and Mn which gives the potential for the half-cell reaction:

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)\, E^o_{1/2} = -1.18\,V$$

Next look at the point which connects Mn^{4+} and Mn^{3+} which basically represents the reaction:

$$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O(l) \qquad E^o_{1/2} = +0.95\,V$$

After this, let us see how to calculate the standard potential for non-adjacent species from the Latimer diagram. Remember that the standard potentials values (E^o) are not additive. They have to be converted to $\Delta G^o (= -nFE^o)$

values which are additive. We can calculate values for multi-electron reactions by first adding $\Delta G^o (= -nFE^o)$ values and then dividing by the total number of electrons. Example, for conversion of MnO_4^- to Mn^{2+} the standard potential will be:

$$E^o = \frac{1(0.56) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)}{5} = +1.51V$$

Oxygen atom is assigned an oxidation state of -2 and the hydrogen atoms an oxidation state of +1.

5 electrons are involved in this oxidation number change.

The highest oxidation state is listed on the left and the reduction electrode potentials are listed between each species and the next reduced form, with the lowest oxidation state appearing on the right. If the potential on the right of a species is higher than the potential on the left then the species would undergo disproportionation.

It is possible to predict whether a species will disproportionate into a lower and a higher oxidation state from an inspection of the Latimer diagram covering the redox species. If the potential to the right of the species is higher than the potential on the left, then the species will undergo disproportionation. Let us take the following case:

$$M^{2+} \xrightarrow{x \text{ volt}} M^{+} \xrightarrow{y \text{ volt}} M(s)$$

The disproportionation reaction will be as:

$$2M^+(aq) \longrightarrow M(s) + M^{2+}(aq)$$

We have

$M^+ (aq) + e \rightarrow M(s)$; $E^o = y$ volt (right hand side)

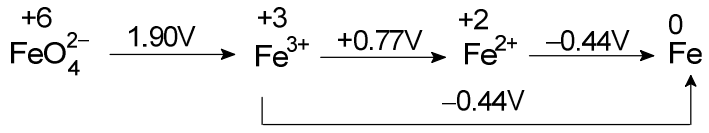
$M^{2+} (aq) + e \rightarrow M^+(aq)$; $E^o = x$ volt (left hand side)

If we now subtract the left hand side (half reaction) from the right hand side (half reaction) of the Latimer diagram we get the disproportionation reaction whose standard potential is given by:

$$E^o = y - x$$

When (y - x) is positive i.e. when the potential to the right of the redox species (of the Latimer diagram) is higher than that to the left, we have $E^o > 0$. This means $\Delta G^o < 0$ and so the reaction is spontaneous i.e. the species will disproportionate.

Latimer diagram for Iron (in acid solution)



SAQ 5

Find the standard potential for the three-electron reduction of MnO_4^- to $MnO_2(s)$ where the three-electron reduction for Mn is given as in section 1.5.

1.6 SUMMARY

Let us now summarise what we have learnt in this unit. This unit focuses on the transition metals and their characteristics. We have learnt about the electronic configuration of the transition elements and how the filling of the orbitals takes place with the increase in atomic number. We learnt that unlike the main group elements, the differentiating electron enters the penultimate (n-1)*d* orbital in transition metals. This reflects in the properties of the transition metals and the periodicity in their properties, In this unit we have studied the variation of size, density, volume, melting and boiling points, ionization enthalpy, electronegativity, electrode potential, oxidation states and reactivity of the transition metals. Also, we have discussed the stability of various oxidation states for Mn, Fe and Cu along with Latimer diagrams. If we would summarise the salient features of the Latimer diagrams, we can say that they are simple visual representations of the standard reduction potentials between various oxidation states of an element. The highest oxidation state is on the left, lowest on the right.

1.7 TERMINAL QUESTIONS

1. How do the following properties vary in the transition elements?
   a) Atomic size
   b) Ionization enthalpy
   c) Stability of various oxidation states.
2. Why are gold and silver used for making ornaments?
3. Explain the following:
   a) Mercury is a liquid.
   b) The most common oxidation states of Ti are 2, 3 and 4.
4. Arrange each of the following groups of elements in order of increasing atomic size:
   a) iron, osmium, ruthenium (b)molybdenum,strontium, zirconium (c) scandium, lanthanum, yttrium.
5. Which one of the following pairs is more stable?
   a) CrO_3, WO_3 b) MnO_4^-, ReO_4^- c) Cr^{2+}, Cr^{3+} d) Mn^{2+}, MnO_4^-
   e) CrO_4^{2-}, MoO_4^{2-} f) Mn_2O_7, Re_2O_7 g) V^{2+}, VO_4^{3-}
6. Which of the following tend to be an oxidizing agent or a reducing agent?
   a) Ti^{2+} b) CrO_4^{2-} c) Cu^+ d) MnO_4^-
7. Yttrium with chlorine does not form YCl or YCl_2 but only YCl_3. How does this agree with the trends in stability of oxidation states?

8. Write a balanced equation for the reaction of each of the following elements with oxygen:

   a. Scandium b. Titanium c. Vanadium d. Chromium e. Manganese
   f. Nickel g. Copper

9. Which of the following is NOT true:

   a) The chemistry of molybdenum is more similar to that of tungsten than of chromium.

   b) Higher oxidation states are most prevalent in the second and third rows of transition elements.

   c) Transition metals have high atomic volumes and are therefore not very dense.

   d) Enthalpies of atomization reach a maximum in the middle of a row.

10. What are Latimer diagrams?

1.8 ANSWERS

Self-Assessment Questions

1. a) 3*d* will have higher energy in potassium. This is because for multi electron atoms, the n*s* orbitals penetrates most, and have the highest increase in effective nuclear charge.

   b) i) Manganese (Mn) ii) Cadmium (Cd) iii) Zinc (Zn) iv) Rhodium (Rh) (v) Titanium (Ti) vi) Niobium (Nb)

   c) i) $[Ar]3d^5$ ii) $[Xe]4f^{19}$ iii) $[Ar]3d^8$ iv) $[Kr]4d^5$ v) $[Ar]3d^2$ vi) $[Ar]3d^5$ vii) $[Xe]4f^{14}5d^9$ viii) $[Kr]4d^3$

2. a) (i) Calcium (ii) Titanium (iii) Molybdenum (iv) Osmium

   b) Due to lanthanoid contraction. Because of the filling in of 4*f* orbitals in the lanthanoids.

3. Zn and Cd have electronic configuration $[Ar]3d^{10}4s^2$ and $[Kr]\ 4d^{10}5s^2$, respectively. Therefore, there is no unpaired electron for metallic bonding. Thus, these metals are soft.

4. The oxidation number of osmium in OsO_4 is +8. The stability of higher oxidation states increases as we go down the group of the transition metals. Osmium being in third transition series is, therefore, stable in oxidation state +8 and exists as OsO_4.

5. For the the three-electron reduction of $MnO_4^-(aq)$ to $MnO_2(s)$,

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27)}{3} = +1.70\,V$$

Terminal Questions

1. See the trends in properties.

2. Because of their noble nature gold and silver are used for making ornaments.

3. a) No metallic bond formation
   b) By giving away two *s* electrons, two *s* and one *d* electrons, two *s* and two *d* electrons respectively for bonding.
4. a) Fe<Ru<Os b) Mo<Zr<Sr c) Sc<Y<La
5. a) WO_3 b) ReO_4^- c) Cr^{3+} d) Mn^{2+} e) MoO_4^{2-} f) Re_2O_7 g) VO_4^{3-}
6. a) Reducing agent b) Oxidising agent c) Reducing agent
   d) Oxidising agent
7. Stability of high oxidation state as we go down a group.
8. a) $4Sc(s)+3O_2(g)\rightarrow 2Sc_2O_3(s)$
   b) $Ti(s)+O_2(g)\rightarrow TiO_2(s)$
   c) $4(V)(s)+5O_2(g)\rightarrow 2V_2O_5(s)$
   d) $4Cr(s)+3O_2(g)\rightarrow 2Cr_2O_3(s)$
   e) $Mn(s)+O_2(g)\rightarrow MnO_2(s)$
   f) $2Ni(s)+O_2(g)\rightarrow 2NiO(s)$
   g) $2Cu(s)+O_2(g)\rightarrow 2CuO(s)$
9. c)
10. Latimer diagrams are simple visual representation of the standard reduction potentials (E°_{red}) between different oxidation states of an element.

Sources of Figures

Fig. 1.1:
https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_(OpenSTAX)/19%3A_Transition_Metals_and_Coordination_Chemistry/19.1%3A_Properties_of_Transition_Metals_and_Their_Compounds) (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace, source cc licensed)

Fig. 1.2:

IUPAC. org

Fig. 1.11:

https://chem.libretexts.org/Courses/Grand_Rapids_Community_College/CHM_120__Survey_of_General_Chemistry/2%3A_Atomic_Structure/2.11%3A_Electron_Configurations%2C_Valence_Electrons%2C_and_the_Periodic_Table)

Sources of Tables

Table 1.7:

https://commons.wikimedia.org/wiki/File:Transition_metal_oxidation_states.svg)

UNIT 2

TRANSITION ELEMENTS-II

Structure

2.1 INTRODUCTION

The transition metals have always held a special interest for inorganic chemists. In the last unit you have learnt about the electronic configurations, general characteristics of the transition elements and Latimer diagrams. In this unit we are going to discuss other important aspects like complex formation, colour, magnetic properties and catalytic properties of transition metals and their compounds.

It is interesting to note at this point that the compounds of the main group metals are almost always white, but those of the transition metals are coloured. A lot of study of compounds of transition metals was done by the Swiss chemist Alfred Werner who in 1893, proposed that the metal ion was central and surrounded by other ions and molecules which acted as electron pair donors. Werner and his students prepared many transition metal compounds for the subsequent eight years to find proof to his theory which has opened a new area in inorganic chemistry.

Expected Learning Outcomes

After studying this unit you should be able to:

- understand why transition metals form coloured compounds;
- discuss about the formation of complexes of transition metal compounds;
- discuss their magnetic properties; and
- discuss their catalytic properties.

2.2 FORMATION OF COMPLEXES

In previous classes you must have heard the word 'complexes', basically these are species where a metal ion is linked to anions or molecules containing lone pair of electrons (ligands) by coordinate bonds. Transition metals have a tendency to form complex ions as they form small, highly charged ions which have high charge density and also have vacant orbitals which have suitable energy to accept lone pairs of electrons donated by other groups or ligands. A transition metal in a high oxidation state forms a cation with high charge density which can form strong bonds with a wide variety of negative or polar ligands. A transition metal ion can form a complex in low oxidation state too, in this case the electrons in the *d* orbitals become involved in π bonding with ligands. The most common geometry is octahedral where six ligands surround the central ion octahedrally. Tetrahedral arrangement of four ligands are found in some metal complexes. Four ligands may be found at the corners of a square in some cases too. Besides these geometries, other geometries like trigonal bipyramid, pentagonal bipyramid, etc., are also present occasionally. Some of the typical complexes of the transition metals are $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{3-}$, $[Cu(NH_3)_4]^{2+}$, etc. The nature of these complexes and the important theories of bonding related to them are discussed later.

2.3 COLOUR OF TRANSITION METAL COMPOUNDS

Many ionic and covalent compounds of transition elements are coloured whereas most of the compounds of the *s* and *p*-block elements are almost always white. When light passes through a material it is deprived of those wavelengths that are absorbed. If absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complementary colour to the colour of the light absorbed. Absorption in the visible and UV regions of the spectrum is caused by changes in electronic energy. Thus the spectra are sometimes called electronic spectra. (These changes are often accompanied by much smaller changes in vibrational and rotational energy.)

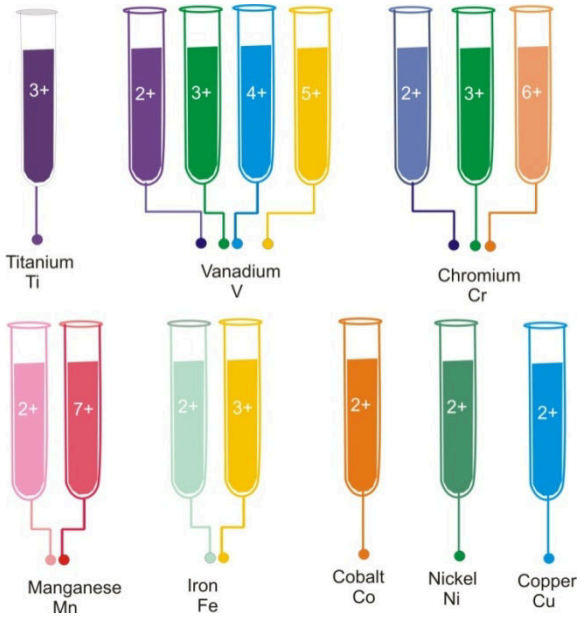


Fig. 2.1: Colours of Transition Metal Ions in their aqueous complexes.

It is always possible to promote an electron from one energy level to another. However, the energy jumps are usually so large that the absorption lies in the UV region. Special circumstances can make it possible to obtain small jumps in electronic energy which appear as absorption in the visible region.

Polarization

NaCl, NaBr and NaI are all ionic, and colourless. AgCl is also colourless. However, AgBr is pale yellow and AgI is yellow. The colour arises because the Ag^+ ion polarizes the halide ions. This means that it distorts the electron cloud, and implies a greater covalent contribution. The polarizability of ions increases with size: thus I^- is the most polarized and AgI is most coloured. So now can you follow why the compounds Ag_2CO_3 and Ag_3PO_4 are yellow, and Ag_2O and Ag_2S are black? Well the reasons are the same, that is polarization of the electron cloud of anion by the Ag^+ ion.

Incompletely filled *d* or *f* shell

In the previous unit you have learnt that as per the latest IUPAC definition of transition metals they have partially filled *d* orbitals, and these are key to the formation of coloured compounds and complexes. As you know, substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound.

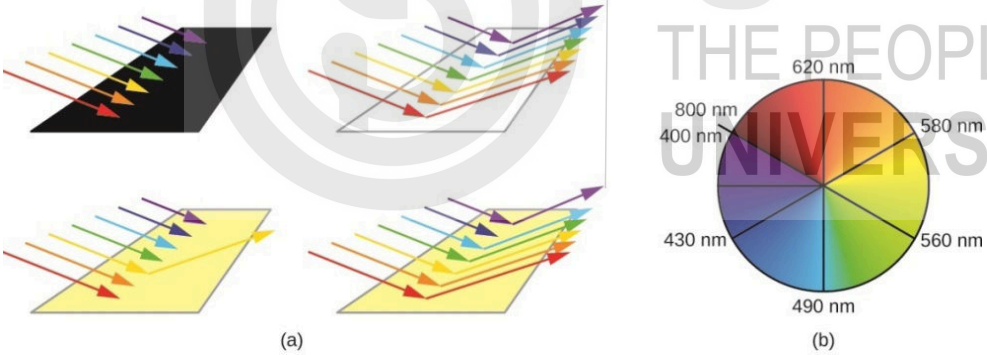


Fig. 2.2:(a) An object is black if it absorbs all colours of light. If it reflects all colours of light, it is white. An object has a colour if it absorbs all colours except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary colour from white light (in this case, indigo). (b) Complementary colours are located directly across from one another on the colour wheel.

EXAMPLE 2.1: Fig. 2.2 depicts a simple colour wheel.a) Copper(II) sulphate solution looks pale blue because when light passes through it, some frequencies of white light are absorbed. What colour does copper(II) sulphate solution absorb? b) When you add an excess of ammonia solution to copper(II) sulphate solution, the colour changes to a very deep blue as the tetraamminediaquacopper(II) ion is formed. What colour is the solution now absorbing from white light?

SOLUTION: The blue colour of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colours of blue and green (Fig. 2.2). If white light (ordinary sunlight, for example) passes through $[Cu(NH_3)_4]SO_4$ solution, some wavelengths in the light are absorbed by the solution. The $[Cu(NH_3)_4]^{2+}$ ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and comes out from the other side will have all the colours in it except for the red. We see this mixture of wavelengths as dark blue. The diagram gives an impression of what happens if you pass white light through *a* $[Cu(NH_3)_4]SO_4$ solution.

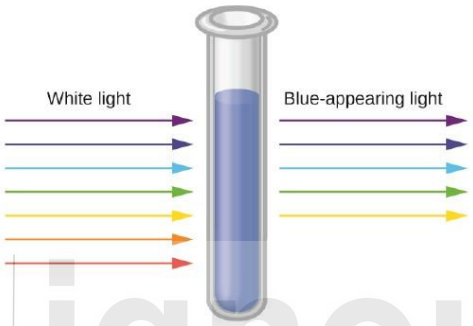


Fig. 2.3: A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary colour, blue.

Colour may arise from an entirely different cause in ions with incomplete *d* or *f* shells. This source of colour is very important in most of the transition metal compounds. In a free isolated gaseous ion the five *d* orbitals are degenerate, that is they have the same energy. However the ion is not bare; when in solution it is surrounded by solvent molecules, when in a complex it is surrounded by other ligands and when in a crystal lattice, it is surrounded by anions. The surrounding groups affect the energy of some *d* orbitals more than others. Thus the *d* orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy, the difference in energy is small. Thus in transition element ions with a partly filled *d* shell it is possible to promote electrons from one *d* level to another *d* level of higher energy. This is known as *d*-*d* transition and corresponds to a fairly small energy difference and so light is absorbed in the visible region. The colour of a transition metal complex is dependent on how large the energy difference is between the two *d* levels. This in turn depends on the nature and number of the ligands, and on the geometry of the complex formed. Thus the octahedral complex $[Ni(NH_3)_6]^{2+}$ is blue, $[Ni(H_2O)_6)^{2+}$ is green and $[Ni(NO_2)_6]^{4-}$is brown-red, that is the colour changes with the ligand.

Certain ligands cause a large split in the energies of *d* orbitals of the central metal atom. Compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, compounds of transition metals with ligands that cause small split in energies of *d* orbitals are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

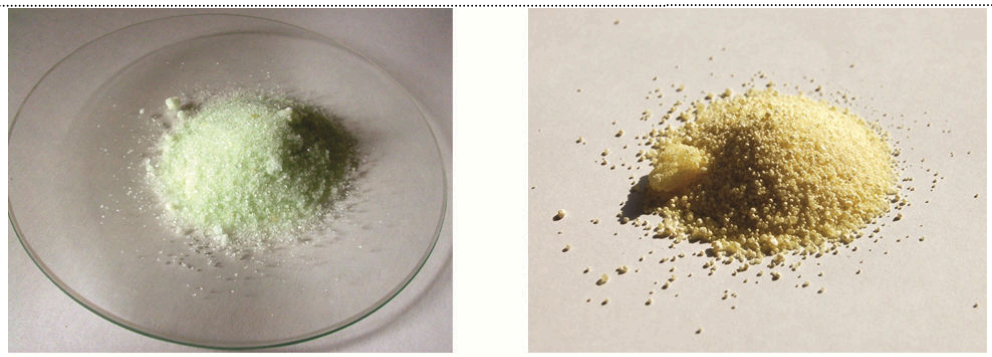


Fig. 2.4: Both (a) hexaaqua iron(II) sulphate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centres, but they absorb photons in different ranges of the visible spectrum.

The source of colour in the lanthanoids and the actinoids is very similar, arising from *f*→*f* transitions. With the lanthanoids the 4*f* orbitals are deeply embedded inside the atom, and are well shielded by the 5*s* and 5*p* electrons. The *f* electrons are practically unaffected by complex formation: hence the colour remains almost constant for a particular ion regardless of the ligand. The absorption bands are also very narrow.

Some compounds of the transition metals are white, for example CuCl and TiO_2. In these compounds it is not possible to promote electrons within the *d* level. Cu^+ has a d^{10} configuration and the *d* level is full. Ti^{4+} has a d^0 configuration and the *d* level is empty. For this reason zinc sulphate is also white. In the series Sc(+3), Ti(+4), V(+5), Cr(+6) and Mn(+7), these ions may all be considered to have an empty *d* shell: hence *d*-*d* transitions are impossible and they should be colourless. However, as the oxidation number increases these states become increasingly covalent and rather than forming highly charged simple ions, oxoions are formed TiO^{2+}; VO_2^+, VO_4^{3-}, CrO_4^{2-} and MnO_4^-. VO_2^+ is pale yellow, but CrO_4^{2-} is strongly yellow coloured, and MnO_4^- has an intense purple colour in solution though the solid is almost black. The colour arises by charge transfer where an electron is momentarily transferred from oxygen to the metal thereby causing temporary reduction of the metal. Since transfer of electron is transfer of charge these spectra are called charge transfer spectra. Charge transfer requires that the energy levels on the two different atoms are fairly close. Charge transfer always produces intense colours.

The *s* and *p*-block elements do not have a partially filled *d* shell so there cannot be any *d*–*d* transitions. The energy to promote an *s* or *p* electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus compounds of *s* and *p*-block elements typically are not coloured. Compounds of transition elements are usually markedly coloured, in contrast to compounds of *s* and *p*-block elements which are mostly white or colourless unless the anion is coloured. For example, the aqua ion $Ti(H_2O)_6^{3+}$, which has one electron in the 3*d* orbital absorbs light of wavelength in the yellow-green region of spectrum and therefore, appears reddish-violet in colour. Table 2.1 gives the relationship between the colour and the wavelength of light.

Table 2.1: Relationship between the colour and wavelength

Wavelength absorbed in nm	Colour absorbed	Colour observed
<400	UV region	White/colourless
400-435	Violet	Yellow-green
435-480	Indigo	Yellow
480-490	Green-blue	Orange
490-500	Blue-blue	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Indigo
595-605	Orange	Green-blue
605-750	Red	Blue-green
>750	Infra-red	White/colourless

Whenever the *d* orbitals are completely filled or empty, there is no possibility of electronic transitions within the *d* orbitals. In such cases, the ions will not show any colour. For example, the compounds of Sc^{3+},Ti^{4+}, Cu^{+} and $Zn^{2+}$are white or colourless. Table 2.2 gives the colour and oxidation states of the metal ions present in some hydrated ions of transition elements.

Table 2.2: Oxidation States and observed colours for some aqua species of the Transition Metal Ions

Element	+2	+3	+6	+7
Sc		Colourless $[Sc(H_2O)_6]^{3+}$		
Ti		Violet $[Ti(H_2O)_6]^{3+}$		
V	Violet $[V(H_2O)_6]^{2+}$	Green $[V(H_2O)_6]^{2+}$		
Cr	Blue $[Cr(H_2O)_6]^{2+}$	Violet/green $[Cr(H_2O)_6]^{3+}$	Orange/yellow $Cr_2O_7^{2-}$, CrO_4^{2-}	
Mn	Pink $[Mn(H_2O)_6]^{2+}$	Red $[Mn(H_2O)_6]^{3+}$	Green MnO_4^{2-}	Purple MnO_4^{-}
Fe	Pale green $[Fe(H_2O)_6]^{2+}$	Yellow/brown $[Fe(H_2O)_6]^{3+}$		
Co	Pink $[Co(H_2O)_6]^{2+}$	Blue $[Co(H_2O)_6]^{3+}$		
Ni	Green $[Ni(H_2O)_6]^{2+}$			
Cu	Blue $[Cu(H_2O)_6]^{2+}$			
Zn	Colourless $[Zn(H_2O)_6]^{2+}$			

Many transition metal compounds have bright colours and thereby they are useful as pigments in paints and dyes.

Fig. 2.5: The Pigment Prussian Blue, $Fe_4[Fe(CN)_6]_3.14H_2O$.

Prussian blue: When Fe^{3+} ions are added to $[FeCN)_6]^{4-}$ ions in water (or Fe^{2+} ions are added to $[FeCN)_6]^{3-}$ ions), a deep blue compound called Prussian blue forms. Its formula is Fe_4 $[Fe(CN)_6]_3$. 14 H_2O. The colour arises from the interaction of the Fe(+2) and Fe(+3) ions in the compound.

Cadmium sulphide, a yellow powder **Titanium dioxide**

Fig. 2.6: Some pigments.

The presence of transition metal ions in crystalline silicates or alumina transforms these ordinary materials into gemstones, some examples are shown in Table 2.3 and Fig, 2.7.

Table 2.3: Some coloured gemstones

Gem	Formula	Colour	Origin of colour
Ruby	Al_2O_3	Red	Cr^{3+} replacing Al^{3+} in octahedral sites
Emerald	$Be_3Al_2(SiO_3)_6$	Green	Cr^{3+} replacing Al^{3+} in octahedral sites
Sapphire	Al_2O_3	Blue	Intervalence transition between Fe^{2+} and Ti^{4+} replacing Al^{3+} in adjacent octahedral sites

Ruby **Emerald** **Sapphire**

Fig 2.7: Some gemstones.

EXAMPLE 2.2: Which one of the following ions is colourless?

i) Cu^{+} ii) Co^{2+} iii) Ni^{2+} iv) Fe^{3+}

SOLUTION:

Ion	outer shell electronic configuration	Colour
Cu^{+}	$3d^{10}4s^{0}$	Fully filled *d* orbitals; no colour.
Co^{2+}	$3d^{7}4s^{0}$	Partially filled *d* orbitals - pink in colour.
Ni^{2+}	$3d^{8}4s^{0}$	Partially filled *d* orbitals - green in colour.
Fe^{3+}	$3d^{5}4s^{0}$	Half filled *d* orbitals; reddish brown

Conclusion:

Correct option: i) Cu^{+}

SAQ 1

Explain briefly why $CuSO_4$ is blue while $ZnSO_4$ is white.

2.4 MAGNETIC PROPERTIES

When you place an iron piece near a magnet, you will see that it is immediately drawn towards the magnet. However, some elements are repelled by the magnets. The property of an element to be attracted or repelled by a magnet differs from element to element. Substances which are weakly repelled by a magnetic field are called **diamagnetic,** while the substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field are called **paramagnetic.** If the force of attraction is very large and the permanent magnetisation is retained, the substance is said to be **ferromagnetic,** e.g. iron and some iron compounds.

A charged particle in motion generates a magnetic field. Electrons are charged particles and they are associated with two types of motion which generate magnetic fields. From the pre-wave mechanical view point, the electron may be regarded as a small sphere of negative charge spinning on its axis. Then from the completely classical considerations, the spinning of charge produces a magnetic moment. Secondly, an electron travelling in a closed path (orbit) around a nucleus, again according to pre-wave mechanical picture, will also produce a magnetic moment. The magnetic properties of any individual atom or ion will result from some combination of these two properties, that is, the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus.

The magnetic moment is usually expressed in units called **Bohr magnetons** (BM). The general equation for the magnetic moment is given by:

$$\mu_{(S+L)} = \sqrt{4S(S+1)+L(L+1)} \quad \ldots (2.1)$$

In the above expression, S is the sum of the spin quantum numbers and L is the sum of orbital angular momentum quantum number of all the electrons. In many compounds including those of the first row transition elements, the orbital contribution is quenched out by the electric fields of the surrounding atoms and as an approximation, the observed magnetic moment may be considered to arise only from unpaired spins. Putting $L = 0$ in the above expression, you can get the spin-only magnetic moment μ_s.

Thus, $\mu_S = \sqrt{4S(S+1)}$ …(2.2)

The spin-only magnetic moment, μ_s can also be related to the number of unpaired electrons, n, in any species, as the total spin quantum numbers $S = n/2$.

Hence, $\mu_S = \sqrt{4S(S+1)} = \sqrt{4n/2(n/2+1)}$

$= \sqrt{n(n+2)}$ …(2.3)

The above expression gives the value of magnetic moment in Bohr magnetons which can be converted into SI unit of Ampere square meter (Am^2) by the following relationship:

1 BM = 9.274 x 10^{-24} Am^2

The magnetic moment is measured by weighing the sample in presence and absence of magnetic field using a magnetic balance known as Gouy balance (Fig. 2.8).

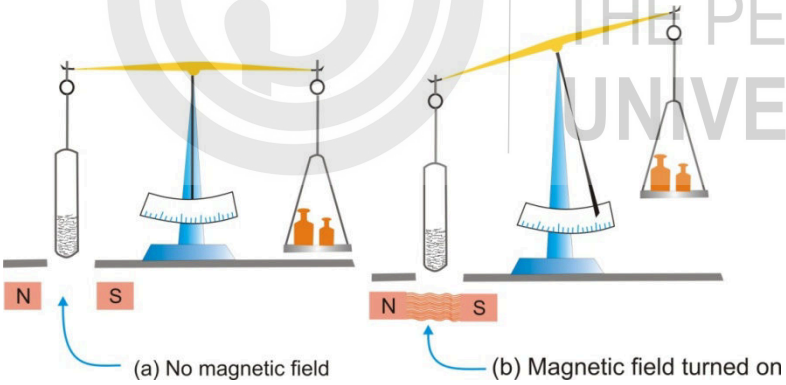


Fig. 2.8: Measurement of molecular paramagnetism using a Gouy balance.

Diamagnetic materials have no magnetic moment and show a slight decrease in weight in the presence of magnetic field. On the other hand, paramagnetic materials show an apparent increase in weight. The magnetic moment can be calculated from the change in weight.

In some case (e.g. Mn^{2+}, or Fe^{3+}, in which all the d orbitals are occupied singly by electron for which m_l = 2, 1, 0, -1 and -2, giving l = 0) the observed magnetic moment values agree very well with the spin-only value as given in Table 2.4. But generally, experimental values differ from the spin-only values. This is because the orbital motion of the electron also makes some contribution to the moment. More detail on the magnetic properties of the transition elements can be studied in higher courses on the subject.

Table 2.4: Predicted and observed magnetic moment values of some transition metal hydrated ions

Ion	Electronic configuration	Unpaired electrons	Magnetic moment μ_s (BM)	
			Calculated	Experimental
$[Ti(H_2O)_6]^{3+}$	$3d^1$ ↑	1	1.73	1.75
$[V(H_2O)_6]^{3+}$	$3d^2$ ↑ ↑	2	2.84	2.75
$[V(H_2O)_6]^{2+}$	$3d^3$ ↑ ↑ ↑	3	3.87	3.86
$[Cr(H_2O)_6]^{2+}$	$3d^4$ ↑ ↑ ↑ ↑	4	4.90	4.80
$[Mn(H_2O)_6]^{2+}$	$3d^5$ ↑ ↑ ↑ ↑ ↑	5	5.92	5.96
$[Fe(H_2O)_6]^{2+}$	$3d^6$ ⇅ ↑ ↑ ↑ ↑	4	4.90	5.00
$[Co(H_2O)_6]^{2+}$	$3d^7$ ⇅ ⇅ ↑ ↑ ↑	3	3.87	4.40
$[Ni(H_2O)_6]^{2+}$	$3d^8$ ⇅ ⇅ ⇅ ↑ ↑	2	2.84	2.90
$[Cu(H_2O)_6]^{2+}$	$3d^9$ ⇅ ⇅ ⇅ ⇅ ↑	1	1.73	1.80

SAQ 2

In $[Co(H_2O)_6]^{2+}$ the observed magnetic moment is higher than the spin-only value. Explain the reason for this in the space provided below.

An enzyme is a biological catalyst which can bring about specific chemical reactions. It is known that several transition metal ions e.g., iron, manganese, cobalt, zinc and molybdenum ions are involved in various processes.

2.5 CATALYTIC PROPERTIES

Many transition metals and their compounds have catalytic properties. These metals can function as catalysts because they can utilize both *d* and *s* electrons for the formation of bonds between reactant molecules and the surface catalyst atoms. This increases the concentration of the reactants at the catalyst surface and weakens the bonds in the reactant molecules with the result that the activation energy is lowered. Compounds of transition metals are able to act as catalysts because of the ease with which the metal can adopt different oxidation states and also because of their ability to form complexes, thus they readily form intermediates. Some of the common catalysts used for important reactions are:

a. $FeSO_4$ and H_2O_2 as Fenton's reagent for the oxidation of alcohols to aldehydes.

b. Pd for hydrogenation, e.g. phenol to cyclohexanol

c. Fe/Mo in manufacture of ammonia by Haber process

d. Pt/PtO as Adams catalyst for reductions

e. Pt/Rh in oxidation of NH_3 to NO in the manufacture of nitric acid by Ostwald's process

f. V_2O_5 in oxidation of SO_2 to SO_3 in the manufacture of sulphuric acid by contact process

g. Ni (Raney nickel) in reduction processes

h. $TiCl_4$ as (Ziegler Natta Catalyst) for polymerisation of ethene.

Transition metals are important catalysts in biological system. A number of transition elements present in very small quantities in plants and animals are essential for the enzymes to function. For example, a cobalt atom lies at the centre of the vitamin B_{12} coenzyme. Molybdenum and iron are contained in nitrogen fixing enzymes.

Apart from their role as catalysts transition metals are important in the biological system. Iron is present in hemoglobin of blood which acts as oxygen carrier. It is also present in myoglobin which acts as oxygen reservoir and in ferredoxins of photosynthetic process.

2.6 ALLOYS

Alloys are a combination of two or more solid metals. Transition elements, (e.g. gold and copper) have similar metallic radii and so they both easily form alloys. Some common alloys, their compositions and their uses are given below in Table 2.5.

Table 2.5: Some common alloys

Name	Composition (%)	Properties	Uses
Brass	Cu 70-85, Zn 15-30	Harder than pure Cu	Taps, utensils, decorative items
Gold, 18-carat	Au 75, Ag 10-20, Cu 5-15	Harder than pure (24 - carat) gold	Jewellery
Stainless steel	Fe 65 -85, Cr 12-20, Ni 2-15, Mn 1-2, C 0.1-1, Si 0.5-1	Can resist corrosion	Tools, chemical equipment

2.7 INTERSTITIAL COMPOUNDS

Transition metals can trap some small atoms like hydrogen, boron, carbon, nitrogen, etc., in vacant spaces in their crystal lattice interstitial compounds, Carbon and nitrogen always occupy octahedral holes; hydrogen is smaller and always occupies tetrahedral holes. As only transition metals form such

compounds, the *d* electrons are, therefore, presumably involved in the bonding. The structure of the metal compounds often changes during the formation of such compounds. The composition of these compounds is generally non-stoichiometric, e.g., $TiH_{1.73,}$ $PdH_{0.56,}$ $VH_{0.56}$, but may approach regular stoichiometry and a regular structure, e.g., TiC and VN. The later transition elements of the first series form non-stoichiometric carbides with irregular structure, such as CrC_3, which are more reactive than the interstitial carbides of the early transition elements. These interstitial compounds are of much importance, e.g., carbon steels are interstitial iron-carbon compounds in which the interstitial carbon prevents the iron atoms from sliding over one another, making iron harder, stronger, but more brittle.

2.8 SUMMARY

Let us now summarise what we have learnt in this unit. This unit focuses on the colour and magnetic properties of the transition metals. We have also learnt about the formation of complexes and catalytic properties of transition element and their compounds.

2.9 TERMINAL QUESTIONS

1. Why do we see different colours among transition elements?
2. Which of the following compounds is expected to be coloured?

   a) Ag_2SO_4 b) CuF_2c) MgF_2 d) CuCl
3. In which case of the aqueous solutions of following salts will be coloured?

   a) $CrCl_3$ b) $Zn(NO_3)_2$ c) $Co(NO_3)_2$ d) $LiNO_3$ e) Potash alum
4. Predict the spin-only magnetic moment for:

   a) Fe^{2+} b) Mn^{7+} c) Cu^{+} d) Ti^{3+}

2.10 ANSWERS

Self-Assessment Questions

1. Cu^{2+} in $CuSO_4$ has $[Ar]3d^9 4s^0$ configuration and its electrons can be promoted to the half-filled *d* orbital. Thus it can undergo *d-d* transition which absorbs mainly in the red region of the visible light and $CuSO_4$ appears blue in colour (blue is complementary colour of red). Because Zn^{2+} in $ZnSO_4$ has the configuration $[Ar]3d^{10}4s^0$, the transition of electron from one *d* orbital to another is not possible and no light is absorbed in the visible region of spectrum by $ZnSO_4$ and therefore, it appears white.
2. The observed magnetic moment at times differs from that of the calculated spin-only magnetic moment due to the contribution of orbital motion of the electron. The observed magnetic moment for $[Co(H_2O)_6]^{2+}$ has contribution from the spin as well as orbital angular momentum and

thus the observed magnetic moment is higher than the calculated spin-only magnetic moment.

Terminal Questions

1. Transition elements have partially filled *d* orbitals, and these are key to the coloured compounds and complexes they form.

2. The theory behind this is: The transition metal ions with partially filled *d* orbitals exhibit colours in aqueous solutions and also in crystals due to *d*- *d* transitions. However, these transitions are not possible with empty or full-filled i.e. d^0 and d^{10} configurations and metal ions with these configurations usually does not show any colour(said to be white). So we can infer:

Compound	Ion	Outer shell electronic configuration	Colour
Ag_2SO_4	Ag^+	$4d^{10}\ 5s^0$	No colour due to fully filled *d* orbitals.
CuF_2	Cu^{2+}	$3d^9\ 4s^0$	Blue coloured since partially filled *d* orbitals.
MgF_2	Mg^{2+}	$2s^2\ 2p^6$	No colour. There are no *d* electrons and no excitation of electron possible in the visible region.
CuCl	Cu^+	$3d^{10}\ 4s^0$	No colour since *d* orbitals are completely filled.

Conclusion: Correct option is: 'b'

3.

Compound	Ion	Outer shell electronic configuration	Colour
$CrCl_3$	Cr^{3+}	$4d^3\ 5s^0$	Partially filled *d* orbitals - green in colour.
$Zn(NO_3)_2$	Zn^{2+}	$3d^{10}\ 4s^0$	No colour since *d* orbitals are fully filled.
$Co(NO_3)_2$	Co^{2+}	$3d^7\ 3s^0$	Partially filled *d* orbitals - pink in colour.
$LiNO_3$	Li^+	$2s^2$	No colour. There are no *d* electrons and no excitation of electron possible in the visible region.
Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$	K^+ Al^{3+}	$4s^2$ $2s^2\ 2p^6$	same as Li^+

Conclusion: Correct options are: 'a' and 'c'.

4.

Ion		Electronic Configuration	Number of unpaired Electrons	Magnetic moment
a)	Fe^{2+}	$[Ar]3d^6 4s^0$	4	4.90 BM
b)	Mn^{7+}	$Ar]3d^0 4s^0$	0	0 BM

c)	Cu^{+}	$[Ar]3d^{10}4s^{0}$	0	0 BM
d)	Ti^{3+}	$[Ar]3d^{1}4s^{0}$	1	1.73 BM

Sources of Figures

Fig. 2.2:

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/24%3A_Complex_Ions_and_Coordination_Compounds/24.07%3A_Colour_and_the_Colours_of_Complexes, LibreTexts content is licensed by CC BY-NC-SA 3.0.)

Fig. 2.4:

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/24%3A_Complex_Ions_and_Coordination_Compounds/24.07%3A_Colour_and_the_Colours_of_Complexes, LibreTexts content is licensed by CC BY-NC-SA 3.0.)

Fig. 2.5:

https://en.wikipedia.org/wiki/Prussian_blue_(medical_use)#/media/File:Pigment Berliner_Blau.JPG,CC0).

Fig. 2.6:

http://woelen.homescience.net/science/index.html, CC BY-SA 3.0)

https://commons.wikimedia.org/wiki/File:Titanium(IV)_oxide.jpg, Wikimedia Commons, the free media repository)

Fig. 2.7:

https://en.wikipedia.org/wiki/Ruby_(color)#/media/File:Ruby_gem.JPG, https://en.wikipedia.org/wiki/Emerald#/media/File:5_Emeralds_from_Colombia.JPG, https://en.wikipedia.org/wiki/Sapphire#/media/File:Geschliffener_blauer_Saphir.jpg, (CC BY-SA 3.0)

UNIT 3

INNER-TRANSITION ELEMENTS

Structure

3.1 INTRODUCTION

In the preceding two units, you have studied the main features of the chemistry of the transition elements which belong to the *d*-block of the periodic table. In this unit you will study the salient features of the chemistry of the transition elements of the *f*–block of the periodic table. As the electrons are filled in the antepenultimate *f*-orbitals which is an inner shell, these elements are also termed as inner-transition elements. As discussed in Unit 1 of this course you should recall that the *f*-block elements comprise two series of elements - the lanthanoid series and the actinoid series. You will observe that in comparison to the elements of *d*-block transition series, the members of lanthanoid series resemble one another much more closely. Usually they have one common stable oxidation state and they occur together in the same ores in nature. Because of the similarity in their chemical properties their separation from each other is very difficult. The chemistry of the actinoids is more complicated because they exhibit more than one oxidation state and their radioactive nature creates problems in the study of their properties. In this unit you will study the general features of the chemistry of lanthanoids and actinoids with emphasis on periodicity in their properties.

Expected Learning Outcomes

After studying this unit you should be able to:

- understand the electronic configuration and position in periodic table of the inner-transition elements;
- understand lanthanoid contraction and its consequences;
- follow the trends in the atomic radii, melting and boiling points, densities and ionization enthalpy of the inner-transition elements;
- get an idea about the various oxidation states of the inner-transition elements;
- have knowledge about the colour of the ions;
- discuss the electrode potentials;
- understand the magnetic properties; and
- discuss the separation of lanthanoids by Ion-Exchange method.

3.2 GENERAL CHARACTERISTICS

The lanthanoids are referred as “rare earth elements” sometimes, but this name is inappropriate as they are not rare, except for promethium, which does not have a stable isotope.

The lanthanoids are silvery white soft metals and tarnish very fast in air. Although lanthanoid means 'like lanthanum' and so should not include lanthanum, lanthanum has become included by common usage. Similarly actinium is included in the actinoid series. The ending 'ide' normally indicates a negative ion, and therefore the terms lanthanoid and actinoid are preferred to lanthanide and actinide. However, lanthanide and actinide are still allowed owing to wide current use. The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. In Unit 1 of this course, in Fig. 1.1, you can see that the inner-transition elements (lanthanoids and actinoids) are placed as two rows separated out from the main periodic table. The lanthanoids have only one stable oxidation state and their chemistry provides a study on the effect of small changes in size and nuclear charge along a series of elements which are quite similar in many respects. The chemistry of the actinoids is, on the other hand, much more complicated. Many of the actinoids form compounds similar to those of the transition metals. Their complication is to some extent due to the wide range of oxidation states in these elements and to also their radioactivity. The earlier members have quite long half-lives compared to the others later in the series. The latter members can only be prepared in nanoscale (nanograms). All these make the study of actinoids very difficult. A general lanthanoid is represented by the symbol Ln and an actinoid by An.

3.2.1 Electronic Configuration and Position in Periodic Table

Now let us look at the electronic configurations and some salient physical properties of the inner-transition elements. The actual ground state electronic

configurations of lanthanoids have been determined from atomic spectroscopy and are given in Table 3.1 along with the metallic and ionic radii, electrode potential and colour of the trivalent lanthanoid ions.

Table 3.1: Some properties of lanthanum and the lanthanoids

Z	Name	Symbol	Electronic configuration outside the [Xe] core		Metallic radius pm	Ionic radius M^{3+} pm	E^{o}(V) M^{3+}/M	Colour of Ln^{3+}
			Ln	Ln^{3+}				
57	Lanthanum	La	$5d^16s^2$	--	187	106	-2.52	Colourless
58	Cerium	Ce	$4f^15d^16s^2$	$4f^1$	183	103	-2.48	Colourless
59	Praseodymium	Pr	$4f^36s^2$	$4f^2$	182	101	-2.46	Pale Green
60	Neodymium	Nd	$4f^46s^2$	$4f^3$	181	100	-2.43	Lilac
61	Promethium	Pm	$4f^56s^2$	$4f^4$	--	98	-2.42	Pale Yellow
62	Samarium	Sm	$4f^66s^2$	$4f^5$	179	96	-2.41	Yellow
63	Europium	Eu	$4f^76s^2$	$4f^6$	204	95	-2.41	Pale pink
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^7$	180	94	-2.40	Colourless
65	Terbium	Tb	$4f^96s^2$	$4f^8$	178	92	-2.39	Pale pink
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^9$	177	91	-2.35	Yellow
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{10}$	176	89	-2.32	Yellow
68	Erbium	Er	$4f^{12}6s^2$	$4f^{11}$	175	88	-2.30	Rose pink
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{12}$	174	87	-2.28	Pale green
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{13}$	194	86	-2.27	Colourless
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}$	174	85	-2.26	Colourless

The ground-state electron configurations of the lanthanoids may be represented as $[Xe]4f^n5d^{0\text{-}1}6s^2$. Lanthanum which has the electronic configuration $[Xe]5d^16s^2$ is excluded from this generalization, but it is included in the table as like the other members it has a stable oxidation state of +3 and has other similarities. The electron configuration of the Ln^{3+} ions vary regularly from $4f^1$ for Ce^{3+} to $4f^{14}$ for Lu^{3+}. Now look at the Table 3.1 and try to understand the examples given below.

EXAMPLE 3.1: In the lanthanoids, which atoms have an electron in the 5*d* orbital? In other elements where has this electron been shifted to?

SOLUTION: By looking at the electronic configurations of atoms in Table 3.1, it can be said that there is an electron in the 5*d* orbital only in Ce, Gd and Lu, in all other elements this electron is shifted to the 4*f* orbital. This sort of shuttling of electrons can be understood in terms of the comparable energies of the 4*f* and the 5*d* orbital.

EXAMPLE 3.2: Does the presence of an electron in the 5*d* orbital affect the properties of the lanthanoids?

SOLUTION: Now, at this stage you should follow that the presence of an electron in 5*d* orbital is not important as the lanthanoids have the prevalence of +3 oxidation state in ionic compounds. So, the Ln^{3+} ions have electronic configurations which varies in a regular manner from [Xe]$4f^1$ for Ce^{3+} to [Xe]$4f^{14}$ for Lu^{3+} as seen from Table 3.1.

EXAMPLE 3.3: The lanthanoids have the general pattern of electronic configuration as [Xe]$4f^n5d^06s^2$, can you find the three exceptions to this case?

SOLUTION: Among the lanthanoids, exceptions to the $4f^n5d^06s^2$ pattern are found in three cases:

(a) At Ce, where the electron configuration is [Xe]$4f^15d^16s^2$. The 4*f* orbitals cannot be contracted as the nuclear charge is not sufficient and thus their energy cannot be lower than 5*d*.

(b) Gadolinium has the [Xe]$4f^75d^16s^2$ configuration, which may be due to the extra stabilization as expected in a half-filled *f* shell.

(c) Lutetium also has the[Xe]$4f^{14}5d^16s^2$ configuration where the last electron is added beyond the capacity of the 4*f* shell.

Table 3.2: Some properties of actinium and the actinoids

Z	Name	Symbol	Electronic configuration outside the [Rn] core		Metallic radius pm	Ionic radius M^{3+} pm	E^o(V) M^{3+}/M	Colour of An^{3+}
			An	An^{3+}				
89	Actinium	Ac	$6d^17s^2$	$5f^0$	--	112	- 2.6	Colourless
90	Thorium	Th	$6d^27s^2$	$5f^1$	179	--	--	--
91	Protactinium	Pa	$5f^26d^17s^2$	$5f^2$	163	104	-1.95	
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	156	103	-1.80	Colourless
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	155	101	-1.86	Red brown
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	155	100	-2.03	Purplish
95	Americium	Am	$5f^77s^2$	$5f^6$	159	98	-2.38	Blue violet
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	173	97	--	Pink
97	Berkelium	Bk	$5f^97s^2$	$5f^8$	174	96	--	Pale Yellow
98	Californium	Cf	$5f^{10}7s^2$	$5f^9$	170	95	--	--
199	Einstenium	Es	$5f^{11}7s^2$	$5f^{10}$	186 $\pm$ 2	--	--	--
100	Fermium	Fm	$5f^{12}7s^2$	$5f^{11}$	186 $\pm$ 2	--	--	--
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{12}$	--	--	--	--
102	Nobelium	No	$5f^{14}7s^2$	$5f^{13}$	--	--	--	--
103	Lawrencium	Lr	$5f^{14}6d^17s^2$	$5f^{14}$	--	--	--	--

Now let us discuss the electronic configuration of the actinoids and this we will do based on the data given in Table 3.2. The ground state electronic configuration of actinium, [Rn] $6d^1 7s^2$ has similarities with that of lanthanum and this maybe the reason that they show similar chemical properties. The electronic configurations of the actinoids following actinium are not known exactly and not as certainly as those of lanthanoids. The difference in energy between 5*f* and 6*d* orbitals in the beginning of actinoids is less than that between 4*f* and 5*d* orbitals for the lanthanoids. Thus both the 5*f* and 6*d* orbitals are involved in accommodating successive electrons. So, if you give a closer look at the data in Tables 3.1 and 3.2 you will see that the filling of 5*f* orbitals in actinoids is not much regular compared to the filling of the 4*f* orbitals in lanthanoids. As you move to the heavier actinoids, i.e. plutonium onwards the 5*f* orbitals become more stable and seem to be of lower energy than the 6*d* orbitals, so the electrons would prefer occupying the 5*f* orbitals.

SAQ 1

Explain briefly:

a) What are inner-transition elements?

b) What are lanthanoids and actinoids? Why are they so called?

c) Write the electronic configurations of the elements of atomic number 61 and 95.

3.2.2 Lanthanoid Contraction

The atomic and ionic radii (Table 3.1 and Fig. 3.1) of lanthanum and the lanthanoids show a steady decrease along the series; this is commonly known as *lanthanoid contraction*. The 4*f* orbitals of the lanthanoids make very little contribution to bonding: their radial distribution functions lie within the 6*s* and 5*d* orbitals. Electrons are removed much easily from the 6*s* and 5*d* orbitals when the lanthanoids form the +3 ion. Lanthanoids thus show mainly ionic bonding. The underlying reason for this has been mentioned earlier – poor shielding by the 4*f* electrons causes the effective nuclear charge to rise steadily across the series. It has already been discussed in Unit 1 of this course that as a consequence of lanthanoid contraction, elements of 4*d* and 5*d* transition series show similarity in properties.

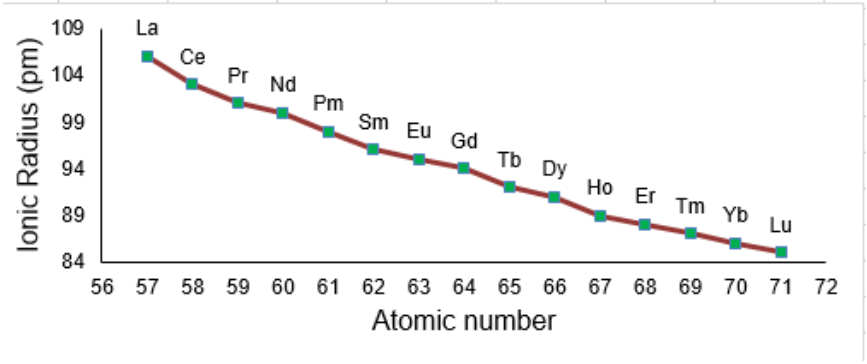


Fig. 3.1: Variation of Ionic radii for the Ln^{3+} ions in pm (picometer).

3.2.3 Atomic Radii

You have studied in previous courses that the atomic size decreases with increase in atomic number along any period due to increase in effective nuclear charge. However, the decrease in atomic radius is small when the differentiating electron enters an inner orbital. This is because the additional inner electron screens the size-determining outer electrons from the nucleus much better than an additional outer electron. For example, decrease in the covalent radius from Sc to Zn, i.e., across ten elements of the 3*d* transition series, is 19 pm. This decrease is almost one-third of the decrease in the covalent radius of the seven elements of *s* and *p*-blocks of the period 3.

The rate of decrease in atomic radius along the lanthanoids (Table 3.1) and also along the actinoids (Table 3.2) is even less than that in the transition series, since the difference in the electronic configurations of these elements is in the number of electrons in the antepenultimate (last but two) shell of electrons. But the cumulative effect of decrease in atomic radius across the fourteen elements of lanthanoids is quite substantial. This decrease in atomic radius across the lanthanoids is known as lanthanoid contraction. Similarly, there is an actinoid contraction across the actinoids. In the actinoids, due to poor shielding by 5*f* electrons, the actinoid contraction is greater from element to element. As a result of lanthanoid contraction, the normal increase in size from Sc – Y – La disappears after the lanthanoids, and pairs of elements such as Zr and Hf, Nb and Ta, Mo and W, etc., possess nearly similar sizes (Table 3.3). The properties of these elements, therefore, are very similar. The similarities in properties within these pairs make their separation very difficult. Thus, due to lanthanoid contraction, the elements of 5*d* and 4*d* transition series resemble each other much more closely than do the elements of 4*d* and 3*d* series.

Table 3.3: Atomic (covalent) radii of the elements preceding and following the lanthanoids in pm(picometer)

21		22	23	24	25	26	27	28	29	30
Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
144		132	122	118	117	117	116	115	117	125
39		40	41	42	43	44	45	46	47	48
Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
162		145	134	130	127	125	125	128	134	144
57	58-71	72	73	74	75	76	77	78	79	80
La	Ce-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
169	165-156	144	134	130	128	126	127	130	134	147

SAQ 2

Explain the term lanthanoid contraction and its consequences.

3.2.4 Melting and Boiling Points, Densities

Table 3.4: Melting and boiling points, densities of lanthanum and the lanthanoids

Element	M. P. ^{o}C	B. P. ^{o}C	Density g cm^{-3}
La	920	3420	6.20
Ce	798	3433	6.77
Pr	931	3520	6.77
Nd	1021	3074	7.01
Pm	1042	-	-
Sm	1074	1794	7.52
Eu	822	1429	5.23
Gd	1313	3273	7.90
Tb	1365	3230	8.23
Dy	1412	2567	8.55
Ho	1474	2700	8.80
Er	1529	2868	9.10
Tm	1545	1950	9.30
Yb	819	1196	6.97
Lu	1663	3402	9.84

In general lanthanoids have high melting points and boiling points. The melting points of the lanthanoids increase at a very fast rate with increasing atomic number from 798 °C for cerium to 1,663 °C for lutetium (more than doubling of the melting point temperatures takes place). The low melting points for the light to middle lanthanoids are thought to be due to a 4*f* electron contribution to the bonding, which is a maximum at cerium and decreases with increasing atomic number to about zero at erbium. The low melting points of europium and ytterbium are due to their divalency.

EXAMPLE 3.4: Now look at Table 3.4, what is the pattern in the variation of the densities and melting and boiling points of the elements? Explain the reason of low values as shown by some.

SOLUTION: The densities and melting and boiling points of the elements show a periodic variation, reaching minima at Eu and Yb. Europium and ytterbium have inner core stable configurations $4f^7$ and $4f^{14}$ to participate in metallic bonding. This leaves only the two outer 6*s* electrons to enter the conduction bands, thus leaving larger cores and weaker binding forces.

3.2.5 Ionization Enthalpy

Now we will discuss about the ionization enthalpies of the lanthanoids which is related to their electronic structures. You already know that 4*f* electrons are poorly screened from the nuclear charge. When an atom of the lanthanoids

ionizes, first the two valence 6*s* electrons and one further electron (from either the 4*f* or 5*d* orbital) are removed. Thereafter, the remaining 4*f* electrons are held tightly by the nucleus. From Table 3.5 and Fig. 3.2 we can see how the ionization energies vary across the lanthanoids.

There are no compounds with Ln(+4) as the fourth ionization enthalpy I_4 is very high. I_4 *is* approximately the same as the sum of the first three ionization enthalpies $(I_1 + I_2 + I_3)$. The nuclear attraction increases across the lanthanoid series which leads to the ionization enthalpies increasing gradually which is related to the electronic structure of the particular atom. If you look at Fig. 3.2 you can see that the variation of I_3 shows three sharp discontinuities, the largest of which are seen between Eu and Gd. Ionisation of Eu^{2+} correspond to removal of an electron from the half-filled $4f^7$, whereas ionization from Gd^{2+}involves a less tightly bound *d* electron. The stable oxidation states shown by the elements is largely determined by their ionization enthalpies. We shall discuss them later.

Table 3.5: Ionization enthalpies for the lanthanoids in kJ/mol

Element	I_1	I_2	I_3
La	538	1067	1850
Ce	528	1047	1949
Pr	523	1018	2090
Nd	530	1034	2128
Pm	536	1052	2140
Sm	543	1068	2260
Eu	547	1085	2425
Gd	592	1172	1999
Tb	564	1112	2122
Dy	572	1126	2220
Ho	581	1139	2200
Er	589	1151	2190
Tm	597	1163	2284
Yb	603	1175	2415
Lu	524	1341	2022

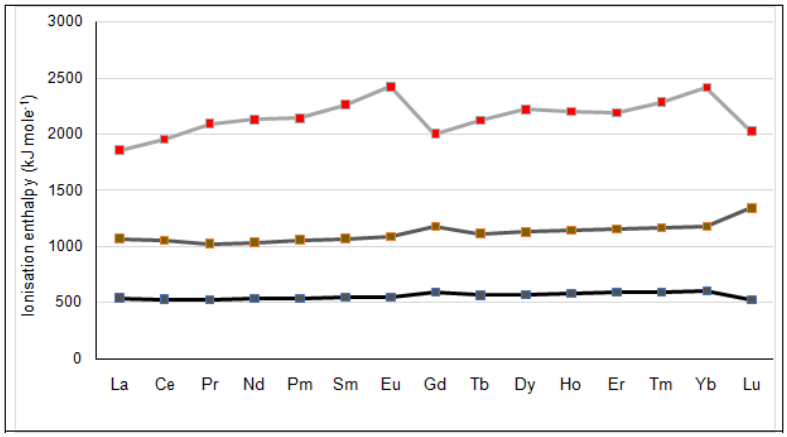


Fig. 3.2: Variation of ionization enthalpies for the lanthanoids.

3.2.6 Oxidation States

As discussed in the section 3.2.5, the first three ionization enthalpies of the lanthanoids is comparatively low and they are strongly electroposive with a principal oxidation state of +3. Refer to the Table 3.1 and follow their electronic configurations to understand that the elements adjacent to lanthanum *(4f^0),* gadolinium (4*f*^{7}*)* and lutetium *(4f*^{14}*)* also exhibit other oxidation states. The oxidation states commonly encountered for the elements are shown in Table 3.6 given below:

Table 3.6: Oxidation states of Lanthanum and Lanthanoids

La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**
3	3, 4	3, (4)	3	3	3 (2)	3 (2)	3
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
3 (4)	3 (4)	3	3	3 (2)	3, 2	3	

*The unstable oxidation states are enclosed in parentheses.

The predominant oxidation state is +3. Some lanthanoids show + 2 or + 4 oxidation states but these are usually less stable than the +3 state. Cerium (+4) is a notable exception. In Table 3.6 you can see that +2 or +4 also exist for some lanthanoids which gain extra stability by attaining half-filled or completely filled configurations, e.g. cerium (+4) and terbium (+4) which have *f*^{0} and *f*^{7} configuration respectively. Lanthanum exhibits only the +3 state as the trivalent ion has a noble gas configuration. Similarly, gadolinium and lutetium form only the M^{3+} ion which have the half-filled *f*^{7} and filled *f*^{14} configuration. The +3 state in the lanthanoids is most common which is very much striking if compared with the variable oxidation states of the *d*-block transition elements dealt in Unit 1.

Following are the examples where number of electrons in ions is different than those with stable *f*^{n} configurations:

f^0 :	La^{3+}, Ce^{4+}, Ac^{3+},Th^{4+},Pa^{5+},V^{6+}
f^7 :	Eu^{2+}, Gd^{3+}, Tb^{4+},Cm^{3+},Bk^{4+}
f^{14} :	Yb^{2+}, Lu^{3+}

Exceptions are the following:

non - f^0	*non* - f^7	*non* - f^{14}
$Pr^{4+}(4f^1)$	$Nd^{4+}(4f^1)$,$Sm^{2+}(4f^6)$	$Tm^{2+}(4f^{13})$

So you must remember that other factors like ionization enthalpies and sublimation energies of the metals as well as lattice energies may be responsible to make the various oxidation states stable.

Table 3.7: Oxidation states of actinium and the actinoids. The more stable states are in bold type; unstable states are enclosed in parentheses.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)			(2)	(2)	2	2	2	--
3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
	4	4	4	4	**4**	4	4	4	(4)					
		5	5	**5**	5	5								
			6	6	6	6								
				(7)	7									

For the actinoids, there is a great range of oxidation states. Can you guess why is it so? It is because the 5*f*, 6*d* and 7*s* levels have comparable energies. Table 3.7 shows the known oxidation states of actinium and the actinoids in which numbers in bold indicate the most stable oxidation state in aqueous solution. The 5*f* orbitals are slightly more diffuse and the actinoids have a chemistry which includes even covalent bonding and a variety of oxidation states for the earlier members of the series. The 5*f* orbitals of the actinoids are more penetrating and provide better shielding from the nuclear charge, they are thus more diffuse than the 4*f* orbitals and they can overlap in a better way with ligand orbitals. The 6*d* orbitals are similarly expected to be more effective in covalent bond formation than their 5*d* counterparts. The most common oxidation state of actionoids is thus +3 as seen from Table 3.7. From the Table 3.7 you can also see that the initial elements of the actinoids show higher oxidation states but not so for those later in the series. Such uneven distribution of oxidation states among actinoids does not recommend learners to study their chemistry in terms of oxidation states.

You will be learning that actinoids have significant similarities with transition metals, form a number of complexes and display a wide multiplicity of oxidation states. This is in contrast to the lanthanoids which resemble the Group 2 metals and mostly form ionic bonds.

SAQ 3

Which is the most common oxidation state of the lanthanoids? Give its configuration.

3.2.7 Colour of Ions

The ions of lanthanoids and actinoids are coloured in the solid state as well as in aqueous solution, as is the case with the ions of transition metals. You have studied in the preceding unit that the colours of transition metal ions arise because of absorption of light due to *d*-*d* electronic transitions. The colours of lanthanoid and actinoid ions arise due to electronic transitions in the 4*f* and 5*f* orbitals. Colours of hydrated lanthanoid and actinoid ions are given in Table 3.1 and 3.2, respectively.

Many trivalent lanthanoid ions are strikingly coloured both in the solid state and in aqueous solution. The colour seems to depend on the number of unpaired *f* electrons. Elements with (n)*f* electrons often have a similar colour to those with (14 - n)*f* electrons (see Table 3.1). However, the elements in other valency state do not all have colours similar to their isoelectronic 3+ counterparts (Table 3.8).

Colour arises because light of a particular wavelength is absorbed in the visible region. The wavelength absorbed corresponds to the energy required to promote an electron to a higher energy level.

Table 3.8: Colours of Ln^{4+}, Ln^{2+} and their isoelectronic Ln^{3+} counterparts

Ce^{4+} Orange-red	$4f^0$	La^{3+} Colourless
Sm^{2+} Blood-red	$4f^6$	Eu^{3+} Pale pink
Eu^{2+} Pale greenish yellow	$4f^7$	Gd^{3+} Colourless
Yb^{2+} Yellow	$4f^{14}$	Lu^{3+} Colourless

Except Lu^{3+}(f^{14}), the lanthanoid ions show absorptions in the visible or UV region of the spectrum. These colours arise from *f-f* transitions. Strictly these transitions are Laporte forbidden (since the change in the subsidiary quantum number is zero) and so the colours are pale because they depend on relaxation of the rule. The *f* orbitals are deep inside the atom and an *f* electron has the subsidiary quantum number $l = 3$, so m_l may have values 3, 2,1,0,-1,-2,-3. Thus a large number of transitions are usually possible. You must remember that for transition elements *d-d* spectra give absorption bands. For transition metal complexes the ligand play an important role in widening the peaks of the absorption bands. It is also possible to get transitions from the 4*f* to the 5*d* level. Such transitions give broader peaks and their position is affected by the nature of the ligands.The peaks of absorption spectra of lanthanoid ions are narrow and very characteristic. Ce^{3+} *and* Yb^{3+} are colourless because they do not absorb in the visible region. However, they show exceptionally strong absorption in the UV region, because of transitions from 4*f* to 5*d. f-d* peaks are broad, in contrast to the narrow *f-f* peaks.

Ligand is any atom or molecule attached to a central atom, usually a metallic element, in a coordination or complex compound. Examples of common ligands are the neutral molecules water (H_2O), ammonia.

Charge transfer spectra are possible due to the transfer of an electron from the ligand to the metal. This is more probable if the metal is in a high oxidation state or the ligand has reducing properties. Generally charge transfer produces intense colours. The strong yellow colour of Ce^{4+} solutions, the blood red colour of $Sm^{2+}$are due to charge transfer.

3.2.8 Electrode Potentials

The standard electrode potentials of lanthanoids for the half-reaction,

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

are given in Table 3.1. The electrode potentials are very low. Therefore, these elements are highly electropositive and reactive metals. The electrode

potential increases from Ce to Lu, which is consistent with the slight decrease in the ionic radius due to lanthanoid contraction. The electrode potentials of the actinoids also are quite low (Table 3.2) and the actinoids also are highly electropositive and reactive metals.

In keeping with the gradually decreasing size from lanthanum to lutetium the standard electrode potentials (M^{3+}/M) of the lanthanoids register an increase from lanthanum (-2.52 volt) to lutetium (-2.26volt) (Table 3.1). The magnitude of the standard potentials shows that the lanthanoids are fairly strong basic elements. Their ionization enthalpies also register an increase from lanthanum to lutetium (Table 3.5) but not gradually. Generally basic properties increase with increasing atomic number across a period. But for the lanthanoids it is not true. Lanthanum (+3) is the most basic while lutetiuim (+3) is the least basic. The metals tarnish in air and burn to give the oxides Ln_2O_3. Exception is for Ce which forms CeO_2. They react with halogens to give the trihalides LnX_3. The lanthanoids dissolve rapidly in dilute acids with evolution of H_2 to produce Ln(+3) salt solution.

The electrode potentials of the actinoids also are quite low (Table 3.2). Therefore, the actinoids also are highly electropositive and reactive metals.

3.2.9 Magnetic Properties

You have learnt in the preceding unit that paramagnetism is associated with the presence of unpaired electrons in a substance. The lanthanoid and actinoid ions, other than f^0 *type* (e.g., La^{3+}. Ce^{4+}, Ac^{3+}, Th^{4+}, Pa^{5+}, U^{6+}) and f^{14} type (e.g. Yb^{2+}, Lu^{3+}, Lr^{3+}), are all paramagnetic, because each of the seven *f* orbitals characterising inner-transition metal species (lanthanoid and actinoid) must contain a single electron before any pairing can take place (Hund's rule).

You have also studied that in case of transition elements, the contribution of orbital motion of electrons to paramagnetism is negligible and can be ignored. The magnetic moments of transition metal ions can be explained in terms of the spin contribution of the unpaired electrons present in *d* orbitals. However in case of the lanthanoids the magnetic moments of only those ions, which have f^0, f^7 and f^{14} configuration agree with the spin only value. In all other cases, the magnetic moment values are higher than those calculated on the basis of spin only formula. This can be explained by taking orbital contribution to magnetic moment also into account. In lanthanoid ions, the 4*f* orbitals are comparatively better shielded from the surroundings by the overlying 5*s* and 5*p* orbitals than the *d* orbitals in transition metal ions. Therefore, the contribution of orbital motion to paramagnetism is not quenched.

The actinoids display magnetic properties similar to that of the lanthanoids, however the magnetic properties of the actinoid ions are complicated than those of the lanthanoid ions. This partially arises from (i) the fact that the 5*f* electrons are nearer the surface of the atom and are easily influenced by the chemical environment, although not to the same extent as do the *d* electrons, and (ii) the less sharply defined distinctions between 5*f* and 6*d* electrons as compared with 4*f* and 5*d* electrons. From the above discussion it is clear that the magnetic moments of the *f*-block (inner-transition) metal ions must be calculated taking into account both spin and orbital contributions.

The magnetic moment of transition elements may be calculated from the equation.

$$\mu_{(S+L)} = \sqrt{4S(S+1)+L(L+1)}$$

(μ_{S+L}) is the magnetic moment in Bohr magnetons calculated using both the spin and orbital momentum contributions. *S* is the resultant spin quantum number and *L* is the resultant orbital momentum quantum number. In the previous unit you have calculated the magnetic moment of the first row transition elements using the spin only formula. This is because the orbital contribution is quenched out by interaction with the electric fields of the ligands in its environment. μ_s is the spin only magnetic moment in Bohr magnetons. *S* is the resultant spin quantum number and *n* is the number of unpaired electrons.)

$$\mu_s = \sqrt{4S(S+1)}$$

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

$La^{3+}(f^0)$, and two of the lanthanoids Gd^{3+} (f^7) and Lu^{3+} (f^{14}) have spin-only values for magnetic moment.

SAQ 4

Gd^{3+} has seven unpaired electrons, find its spin only magnetic moment.

The magnetic moments of the other lanthanoid ions do not obey this simple relationship. Their magnetic moment arises from the unpaired electron spins and that from the orbital motion. This also happens with the second and third row transition elements. Here you must note that the magnetic properties of the lanthanoids are basically not the same as those of the transition elements. In the lanthanoids the spin contribution *S* and orbital contribution *L* couple together to give a new quantum number *J*.

$J = L - S$ when the shell is less than half full

and $J = L + S$ when the shell is more than half full } (as per Hund's third rule)

so the expression for magnetic moment is

$$\mu = g\sqrt{J(J+1)}$$

where

$$g = 1\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Fig. 3.3 shows the calculated magnetic moments for the lanthanoids using both the simple spin only formula, and the coupled spin plus orbital momentum formula. You can see that the calculated values using the coupled spin + orbital momentum formula and experimental values measured at 300 K (26.85 °C) match in most cases. The range of experimental values are shown as bars.

Two cases Eu^{3+} and Sm^{3+} do not show good match. The reason is that with Eu^{3+} the spin orbit coupling constant is very low.

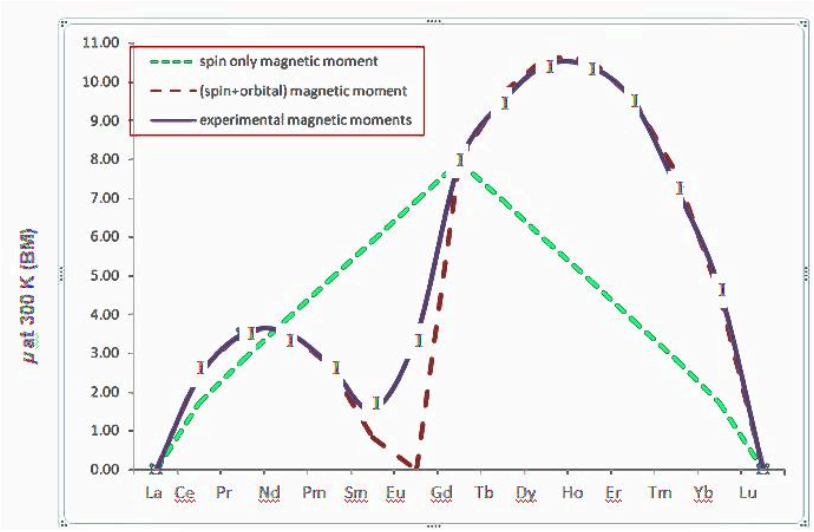


Fig. 3.3: Paramagnetic moments of La^{3+} and the lanthanoid ions at 300K (26.85 °C). Theoretical (Spin-only) values are shown as broken line(green), theoretical (spin + orbital) values are shown as broken line(red) and the observed values as solid line (purple). The range of experimental values are shown as bars.

Table 3.9: Magnetic moments of La^{3+} and the Ln^{3+} ions

	Electronic configuration of M^{3+}	Magnetic moment	
		Calculated (BM)	Observed (BM)
La	[Xe]$4f^0$	0	0
Ce	[Xe]$4f^1$	2.54	2.3-2.5
Pr	[Xe]$4f^2$	3.58	3.4-3.6
Nd	[Xe]$4f^3$	3.62	3.5-3.6
Pm	[Xe]$4f^4$	2.68	2.7
Sm	[Xe]$4f^5$	0.84	1.5-1.6
Eu	[Xe]$4f^6$	0	3.4-3.6
Gd	[Xe]$4f^7$	7.94	7.8-8.0
Tb	[Xe]$4f^8$	9.72	9.4-9.6
Dy	[Xe]$4f^9$	10.63	10.4-10.5
Ho	[Xe]$4f^{10}$	10.60	10.3-10.5
Er	[Xe]$4f^{11}$	9.57	9.4-9.6
Tm	[Xe]$4f^{12}$	7.63	7.1-7.4
Yb	[Xe]$4f^{13}$	4.50	4.4-4.9
Lu	[Xe]$4f^{14}$	0	0

3.3 SEPARATION OF LANTHANOIDS

Deposit of monazite occur in Southern India, South Africa and Brazil.

The separation of lanthanoids is very difficult as most of them generally occur together. Although a large number of minerals are known to contain lanthanoids, only three of them, viz., monazite, bastnaesite and xenotime are of commercial importance. Both monazite and bastnaesite are richer in the lighter lanthanoids,

As all the lanthanoids occur together in nature, their extraction involves two main steps: (i) separation from one another and (ii) reduction of their compounds to metals. Since the lanthanoids are all typically trivalent and are almost identical in size, their chemical properties are almost similar. Therefore, the separation of lanthanoids from one another is almost as difficult as the separation of isotopes. Only cerium and europium can be separated from the remaining lanthanoids by employing conventional chemical methods because of stabilities of Ce^{4+} and Eu^{2+} in aqueous solution. Cerium can be separated from a mixture of lanthanoids by oxidising Ce^{3+} to Ce^{4+} with permanganate or bromate or hypochlorite in an alkaline medium and subsequently precipitating it as CeO_2. Europium can be reduced to Eu^{2+} either by electrolytic reduction with a mercury cathode or by using zinc amalgam. It is then precipitated from the solution as $EuSO_4$.

Earlier the lanthanoids used to be separated from each other by selective precipitation or by **fractional crystallization**. These processes need to be repeated several times and thus are very tedious and not very efficient. However, the individual elements can now be separated with much less difficulty on a large scale by employing more efficient techniques of **solvent extraction** and **ion-exchange chromatography**.

The process of ion-exchange chromatography is the most important, rapid and effective method for the separation and purification of the lanthanoids. In this process, a solution of lanthanoid ions is run down a column of a synthetic ion exchange resin. Ion exchange resins are organic polymers consisting of functional groups such as – COOH, $-SO_3H$ or –OH. In these resins, hydrogen ions are mobile and can be exchanged with other cations. Thus, the lanthanoid ions replace the H^+ ions and get bound to the resin:

$$Ln^{3+} + 3R\text{-}SO_3H \longrightarrow Ln(SO_3R)_3 + 3H^+$$

After the H^+ ions have passed through the column, a solution of a complexing agent such as citric acid, α-hydroxyisobutyric acid or EDTA at the appropriate pH is passed through the column to elute, i.e., to wash off the metal ions in a selective manner:

$$Ln(O_3SR)_3 + (NH_4)_3EDTAH \longrightarrow Ln(EDTAH) + 3NH_4O_3SR$$

As the EDTA solution flows down the column, the lanthanoid ions come off the resin and or a complex with EDTA and then go back on the resin a little lower down the column. This process is repeated many times as the metal ions gradually travel down the column. The smaller lanthanoid ions like Lu^{3+} form stronger complexes with EDTA than the larger ions like La^{3+}. Thus, the smaller and heavier ions spend more time in solution and less time on the column.

Therefore, the heavier ions are eluted from the column first and the lighter ones the last. Using suitable conditions, all the individual elements can be separated. The eluates are then treated with an oxalate solution to precipitate lanthanoids as oxalates which are then ignited to get the oxides:

$$2Ln(EDTAH) + 3(NH_4)_2C_2O_4 \longrightarrow Ln_2(C_2O_4)_3 + 2(NH_4)_3EDTAH$$

$$Ln_2(C_2O_4)_3 \longrightarrow Ln_2O_3 + 3CO + 3CO_2$$

Samarium, europium and ytterbium are prepared by reduction of the oxides with La at high temperatures:

$$Ln_2O_3 + 2La \longrightarrow Ln_2O_3 + 2Ln,\ Ln = Sm \text{ and } Eu$$

Other lanthaniods are obtained by the reaction of $LnCl_3$ or LnF_3 with Ca metal at 1300 K. $LnCl_3$ or LnF_3 are prepared by heating Ln_2O_3 with appropriate ammonium halide:

$$Ln_2O_3 + 6NH_4X \longrightarrow LnX_3\text{-}6NH_3 + 3H_2O$$

$$2LnX_3 + 3Ca \longrightarrow 2Ln + 3CaX_2$$

SAQ 5

Why is the separation of the lanthanoids so difficult? List three important methods used for the separation of lanthanoids.

3.4 SUMMARY

In this unit, you have studied electronic configuration and position of inner-transition elements in the periodic table. Thereafter you have come across the concept of lanthanoid contraction, atomic radii, melting and boiling points, densities, ionisation enthalpy, oxidation states, colour of ions, electrode potentials and magnetic properties of lanthanoids and actinoids which can be summarized as following:

- The lanthanoids and actinoids are characterized by filling of 4*f* and 5*f* subshells, respectively
- For the lanthanoids, actinium and transamericium elements, the tripositive oxidation state is the most stable in every case. However, the oxidation states higher than +3 are quite common for the early actinoids.
- The lanthanoids exhibit greater similarities in their properties in their most prominent oxidation state, +3. Cerium and europium are the only lanthanoids to be stable as Ce^{4+} and Eu^{2+} in aqueous solution.
- All the lanthanoid and actinoid ions which have unpaired electrons are paramagnetic. The magnetic moment of lanthanoid and actinoid ions depends on both spin and angular momentum of the unpaired electrons.
- All the lanthanoids and actinoids are highly electropositive and reactive metals. They react with oxygen, halogens, hydrogen, water and acids.

Also in this unit you have learnt how separation of lanthanoids by ion-exchange method is carried out. Since the lanthanoids are all typically trivalent and are almost identical in size, their chemical properties are almost similar. As all the lanthanoids occur together in nature, their separation is extremely difficult.

3.5 TERMINAL QUESTIONS

1. What are *f*-block elements?
2. Discuss the ways in which the actinoids resemble their lanthanoid congeners.
3. Discuss the ways in which the early actinoids more closely resemble the transition elements.
4. Discuss the position of lanthanoids and actinoids in the periodic table.
5. Why are most of the lanthanoid and actinoid compounds paramagnetic?
6. Why the lanthanoids show very few oxidation states compared to the early actinoids?
7. Compare the chemistry of actinoids with that of the lanthanoids with special reference to: (i) electronic configuration (iii) oxidation state (ii) atomic and ionic sizes.
8. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.
9. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.
10. Why the actinoid contraction is greater from element to element than the lanthanoid contraction?

3.6 ANSWERS

Self Assessment Questions

1. (a) Two series of elements from cerium (atomic number 58) to lutetium (atomic number 71) and thorium (atomic number 90) to lawrencium (atomic number 103) are known as inner-transition elements. The term transition is used because they exhibit transition behavior by exhibiting variable oxidation states, forming coloured ions and exhibiting paramagnetism. The prefix inner is used because in the building up process of their atoms the differentiating electron enters the *f* orbitals of an inner shell.

   (b) The 14 elements form cerium (atomic number 58) to lutetium (atomic number 71) which follow lanthanum (atomic number 57) in the periodic table are called lanthanoids. Similarly, 14 elements from thorium

(atomic number 90) to lawrencium (atomic number 103) which follow actinium (atomic number 89) in the periodic table are called actinoids.

(c) The electronic configuration of the elements of atomic number 61 and 95 is [Xe]$4f^5 6s^2$ and [Rn]$5f^7 s^2$, respectively.

2. The gradual decrease in atomic size of the lanthanoid starting form cerium to lutetium is known as lanthanoid contraction. Because of lanthanoid contraction, the elements from hafnium to mercury that follow the lanthanoids have unusually small sizes.

3. The most common oxidation state of lanthanoids is +3. This oxidation state of the lanthanoid ions arises due to the loss of two 6*s* electrons and the lone 5*d* electron if present, from the atom of the elements. If no electron is present in the 5*d* orbital, then one of the electrons from the 4*f* shell is lost. The lanthanoid ions in this oxidation state have the general configuration [Xe]$4f^{1\text{-}14}$.

4. $\mu_s = \sqrt{7(7+1)} = \sqrt{63} = 7.9\,\text{BM}$

5. The most stable oxidation state of the lanthanoids is +3. The ionic radius of Ln^{3+} ions is quite comparable and varies very little from one element to another. Therefore, the chemical properties of the lanthanoids are almost similar due to which the separation of lanthanoids is very difficult- almost as difficult as the separation of isotopes.

Terminal Questions

1. Those elements, in the building up process of whose atoms the differentiating electron enters the *f* orbitals of an inner shell, are called *f*-block elements. There are two series of *f*-block elements containing 14 elements each. The lanthanoid series contains elements from cerium to lutetium and the actinoid series contains elements from thorium to lawrencium.

2. Actinoids resemble their lanthanoid congeners in the following way:

   - They have the similar electronic configurations.,
   - They exhibit a common oxidation state of +3,
   - They form complexes,
   - Most of them form coloured ions and exhibit paramangnetism.

3. The early actinoids exhibit a large number of oxidation states, in this respect they resemble transition elements.

4. There is no separate place for lanthanoids and actinoids in the periodic table. Therefore, the lanthanoids are placed along with lanthanum and actinoids along with actinium in the periodic table.

5. Most compounds of lanthanoids and actinoids are paramagnetic because they contain lanthanoid and actinoid ions which possess unpaired electrons. Presence of unpaired electrons gives rise to paramagnetism in the compound.

6. The range of oxidation states is much more restricted in the members of lanthanoid series as compared to those of the actinoid series. This is a result of stabilising effects exerted on 4*f* orbitals by increasing ionic charge. By the time an ionic charge of +3 is developed on a lanthanoid ion, the 4*f* orbitals are so stabilized that they become part of the inner core of the electrons. It becomes increasingly difficult to remove further electrons to give rise to higher oxidation states. On the other hand, in the beginning of the actinoid series, the difference in energy of the 5*f* and 6*d* orbitals is much less. Therefore, 5*f* electrons along with 6*d* and 7*s* electrons participate in bonding, resulting in a wider range of oxidation states. However, later the 5*f* orbitals also become more stable and show reluctance to involve themselves in bonding.

7.

	Lanthanoids	Actinoids
(i)	Electronic configuration: $[Xe]\ 4f^n\ 5d^{0-1}\ 6s^2$	$[Rn]\ 5f^n\ 6d^{0-2}\ 7s^2$
(ii)	Oxidation states: mostly +3	Variable oxidation states for early actinoids like transition metals.
(iii)	Atomic and ionic sizes: lanthanoid contraction takes place	Actinoid contraction takes place which is greater than lanthanoid contraction.

8. Lawrencium, Lr, $5f^{14}6d^{1}7s^2$, +3 oxidation states as $6d^{1}7s^2$ can be removed easily and completely filled $5f^{14}$ configuration will be achieved.

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