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GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

19.1 INTRODUCTION

You have already learnt in the chapter on periodic classification that each period of the periodic table starts with the filling of ns subshell and ends with the filling of np subshell (n is the Principal quantum number and also the number of the period). The long form of the periodic table is based on the filling of electrons in various levels in order of increasing energy as given by Aufbau principle (lesson 14) In the fourth period, filling of the 4th shell commences with the filling of s subshell at potassium (At. No. 19). This is followed successively by the filling of $3d$ and $4p$ subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number starts getting filled instead of the second subshell of quantum number that was being filled. This group of elements that occur in between the $4s$ - and $4p$ - block elements is referred to as $3d$ block elements or elements of first transition series (see periodic table in lesson 15). In this lesson you will study more about these elements.

19.2 OBJECTIVES

After reading this lesson, you will be able to

- list the general characteristics of the transition elements.
 - define transition or d -block elements,
 - write electronic configuration of transition elements of $3d$ series,
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- explain variable oxidation states, magnetic properties, colour of the ions / compound and catalytic properties of the elements of first transition series and their compounds,
- explain the formation of coordination complexes by transition metal ions.

19.3 MORE ABOUT TRANSITION ELEMENTS

Transition elements are defined as "Elements whose atoms or ions have partially filled d subshells either in the elemental form (oxidation number zero) or in any of their common oxidation states when present in the combined form".

There are four transition series. The first transition series begins at scandium (At. No. 21) and ends at copper (At. No. 29) whereas second, third and fourth series begin with yttrium (At. No. 39), lanthanum (At. No. 57) and actinium (At. No. 89) and end at silver (At. No. 47), gold (At. No. 79) and at element having atomic number 111 (a synthetic element yet to be synthesized)—respectively. These series are also referred to as 3d, 4d, 5d and 6d series. It may be noted that although elemental copper, silver and gold as well as Cu^{1+} , Ag^{1+} and Au^{1+} have a d^{10} configuration but Cu^{2+} has a $3d^9$, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration and that is why these elements are classified as transition elements. On the other hand, zinc, cadmium and mercury do not have partially filled d subshell either in the elemental state or in any of their compounds/ions. These elements, therefore, are not transition or d block elements. However, zinc, cadmium and mercury are often considered along with d-block elements for the purpose of discussion.

d-Block elements are those elements in which the d subshell is partially filled, i.e., the incoming last electron enters the d subshell.

19.4 GENERAL CHARACTERISTICS

19.4.1 Physical Properties

In case of elements of the first transition series, i.e., 3-d block elements. Hence all the members of this series are metals. All these metals are characterized by high density, high tensile strength, ductility and malleability, high thermal and electrical conductivities, high melting and boiling points. Nearly all crystallize in simple form (table 19.1). These properties indicate that atoms in these elements are held together by strong metallic bonds that are present in molten state as well. Some of the properties of the elements of the first transition series are given in Table 19.1

Table 19.1: Properties of some transition elements.

Element (Symbol)	Z	Crystal form	m.p. c	Density, g cm^{-3}	Atomic radius (\AA)
Scandium (Sc)	21	fcc	1514,	2.989	1.44
Titanium (Ti)	22	hcp	1660,	4.54	1.32
Vanadium (V)	23	bcc	1890,	6.11	1.22

Chromium (Cr)	24	bcc	1857,	7.18	1.17
Manganese (Mn)	25	bcc	1245,	7.44	1.17
Iron (Fe)	26	bcc	1535,	7.87	1.16
Cobalt (Co)	27	fcc	1495,	8.90	1.16
Nickel (Ni)	28	fcc	1453,	8.90	1.15
Copper (Cu)	29	fcc	1083,	8.96	1.17

Z denotes atomic number.

bcc = body centered cubic, fcc = face centered cubic and hcp = hexagonal close packed.

19.4.2 Alloy and Interstitial Compound Formation

From the table 19.1 it may be observed that the atomic sizes of metals of first transition series are quite close to each other. Thus in the crystal lattice, any one of these elements can easily replace another element of similar size giving solid solutions and smooth alloys. Transition elements, therefore, form a number of alloys. Chromium, vanadium and manganese are used to produce alloy steels and stainless steel, copper forms brass, bronze etc. Besides, transition metals also form a number of interstitial compounds in which they take up atoms of small size, like hydrogen, carbon and nitrogen etc. These are located in the vacant spaces of their lattices and are bound firmly there in. The products thus obtained are hard and rigid. For example. Steel and cast iron become hard due to formation of an interstitial compound with carbon. In such compounds, malleability and ductility may marginally decrease but tenacity is considerably enhanced.

19.4.3 Electronic Configuration

Transition elements owe their position in the periodic table to the belated filling of their pen-ultimate, i.e., inner orbitals. You have already learnt that orbitals are filled in the order of their increasing energy. Though shells of lower principal quantum number (lower n value) are expected to be lower in energy than those of higher principal quantum number (higher n value), subshell having higher azimuthal quantum number, i.e. l value but belonging to lower Principal quantum number may have higher energy than a subshell with lower l value and higher n value. It is observed that relative energies of the orbitals do not vary uniformly and the order even reverses at certain values of atomic number as is shown in Fig. 19.1 for the first transition series elements. The general electronic configuration of transition elements is $(n-1)d^{1-10} ns^1$ to 2.

INTEXT QUESTION 19.1

1. Define the term transition element.

.....

2. How many elements comprise the first transition series ? Give names of all these elements.

.....

3. Where as copper, silver and gold are transition elements, zinc, cadmium and mercury are not included amongst transition elements? Explain.
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4. Which of the following elements are transition elements? Justify your answer giving reasons.

Copper (29), Silver (47), Zinc (30) Gold (79), Aluminum (13).

.....

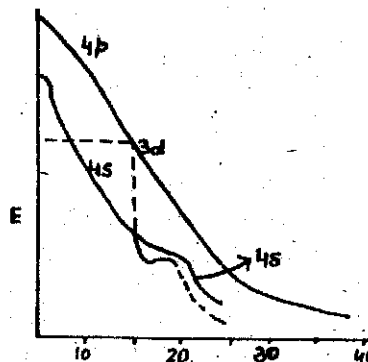


Fig. 19.1: Variation of energy of orbitals vs atomic number.

19.4.4 Filling up of Electrons in Transition Elements

It is observed from the figure 19.1 that s orbitals ($l=0$ and $n=4$) are of lower energy than $3d$ orbitals with $l=2$ and $n=3$, till potassium (atomic number 19). The energy of both these orbitals is almost same at calcium with atomic number 20, but the energy of $3d$ orbitals decreases on further increase of nuclear charge and becomes lower than even $4s$, and hence than $4p$, in case of scandium (atomic number 21). Thus after filling of $4s$ orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to $3d$ orbital instead of $4p$ as the former is of lower energy than the latter. This means that 21st electron enters the underlying Principal quantum level with $n=3$ rather than the outermost level with $n=4$ which started filling at potassium (atomic number 19), the first element of the fourth period. In the case of next nine elements following calcium, the incoming electron is filled in the d subshell, the configuration of the $4s$ subshell remaining almost unaltered. Since half-filled and completely filled subshells are stabler than the one in which one electron is short, an electron is promoted from $4s$ to $3d$ in case of the element with atomic number 24 and 29. consequently, configuration of chromium and copper have only one $4s$ electron. Electronic configurations of elements of first transition series are given in Table 19.2

Table 19.2: Electronic configuration of some transition elements.

Element	Symbol	Z	Electronic configuration
Scandium	Sc	21	$1s^2, 2s^2, 2p^6, 3d^1, 4s^2$
Titanium	Ti	22	$1s^2, 2s^2, 2p^6, 3d^2, 4s^2$
Vanadium	V	23	$1s^2, 2s^2, 2p^6, 3d^3, 4s^2$
Chromium	Cr	24	$1s^2, 2s^2, 2p^6, 3d^5, 4s^2$
Manganese	Mn	25	$1s^2, 2s^2, 2p^6, 3d^5, 4s^2$
Iron	Fe	26	$1s^2, 2s^2, 2p^6, 3d^6, 4s^2$
Cobalt	Co	27	$1s^2, 2s^2, 2p^6, 3d^7, 4s^2$
Nickel	Ni	28	$1s^2, 2s^2, 2p^6, 3d^8, 4s^2$
Copper	Cu	29	$1s^2, 2s^2, 2p^6, 3d^{10}, 4s^2$
Zinc	Zn	30	$1s^2, 2s^2, 2p^6, 3d^{10}, 4s^2$

We see that in case of zinc, the 30th electron goes to 4s level and not 3d level which is already full at copper. Thus by definition, zinc cannot be called a member of d-block series. Besides, no compound of zinc is known in which it has a partially filled d-subshell. Thus it does not fit into the definition of a transition element either. Hence zinc cannot be rightly called either a transition element or a d-block element. However, zinc and other members of group 12, viz., cadmium and mercury are discussed along with 3d, 4d and 5d transition elements for the sake of convenience.

It is important to understand at this point the process of ionization (i.e., oxidation) of transition elements. From what has been said above regarding filling of the orbitals, it is logical to conclude that during ionisation electrons will be lost first from the (n-1)d subshell and then from the 4s level. This, however, is not the case. The reason for deviation from the expected behavior is that once the filling of 3d subshell commences at Scandium (at. no. 21) the energy of 3d subshell decreases and becomes even lower than that of 4s subshell. Consequently, on ionisation, the first row transition elements lose electrons from the 4s subshell followed by the loss from the 3d level. In some cases, however, for example, scandium, all the electrons beyond the core of 18 electrons are lost in single step. It is important to note that though 3d orbitals are of higher energy than 4s orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of the same energy.

19.4.5 Variable Oxidation States

s-Block, d-block and f-block elements show positive oxidation state (except H which shows -1 oxidation state also) whereas most p-block elements show both positive and negative oxidation states. The number of electrons used for bonding by an electropositive element is equal to its positive oxidation state. A characteristic property of chemistry of d-block elements is their ability to exhibit a variety of oxidation states in their compounds. It is due to the fact that for bonding along with its ns electrons, it can also use inner (n-1)d electrons as well because of very small difference in their energies. Thus, depending upon

the number of d electrons involved in bonding, different oxidation states arise; the lowest oxidation state is usually equal to the number of s electrons present (except Sc). For example, copper has an electronic configuration of $3d^{10}4s^1$ and shows oxidation state of +1 besides the usual oxidation state of +2. The highest oxidation states are observed in combination with fluorine or oxygen, which are in order, the two most electronegative elements. The different oxidation states of elements of the first transition series are shown below.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*
+3	(+2)	+2	+2	+2	(+1)	(+1)	(+1)	+1	(+1)
	+3	+3	+3	(+3)	+2	+2	+2	+2	+2
	+4	+4	+4	+4	+3	+3	(+3)	(+3)	
		+5	(+5)	(+6)	+6	(+4)	(+4)		
			+6	+7					

(* Given for comparison only.)

Here the rare oxidation states are given in the parenthesis. An examination of the common oxidation states given above reveals the following:

Except scandium, the most common oxidation state is +2 which arises from the loss of two 4s electrons. This means that after scandium, d-orbitals become more stable than the s-orbital. Compounds having elements with oxidation states +2 and +3 have ionic bonds whereas bonds are essentially covalent in higher oxidation states, e.g., in case of permanganate ion, MnO_4^- , all bonds formed between manganese and oxygen are covalent. Considering the acidbase character of the oxides, it can be inferred that increase in oxidation state leads to decrease in basic character of the oxide and vice versa. Since transition metals exhibit multiple oxidation states their compounds in the higher oxidation states are strong oxidizing agents as they tend to accept electrons and come to stable lower states.

Transition metals also form compounds in low oxidation states such as +1. The bonding in compounds of transition metals in low oxidation states is not always very simple. Formation of several bonds by a metal atom would result in an accumulation of negative charge on the central atom. Such compounds are expected to be unstable. If, however, there are vacant orbitals on the combining atoms such as sulphur or molecules such as carbon monoxide, d-electrons can be donated to the combining molecules and thereby prevent the accumulation of negative charge on the metal. A good example of this type is provided by the case of carbonyls such as nickel tetracarbonyl $Ni(CO)_4$, iron carbonyl, $Fe(CO)_5$, and chromium carbonyl, $Cr(CO)_6$ in which the central metal atom is in zero oxidation state.

19.4.6 Magnetic Properties

Substances possess either of the two type of magnetic behavior, viz diamagnetism or paramagnetism. Diamagnetic substances are either repelled or remain unaffected by an applied magnetic field whereas paramagnetic substances are attracted towards the applied field.

There is a strong correlation between the magnetic behaviour, electronic configuration and oxidation state. Magnetic moment μ Paramagnetism arises due to the presence of unpaired electron or electrons. Since transition metal ions generally contain unpaired electrons a large number of transition metal ions exhibit paramagnetic behaviour.

$$\mu = (n(n + 2))^{1/2}$$

Paramagnetism of paramagnetic material can be calculated (in Bohr Magneton, B.M.) by using the expression: n is the number of unpaired electrons.

Transition metals, and many of their compounds show paramagnetic behaviour due to the presence of unpaired electrons either in the atom or in the ion or molecule.

The magnetic moments arise from the spin and orbital motions of electrons in atoms, ions or molecules. The magnetic characteristics increase as the number of unpaired electrons increases. The magnetic moments of some of the ions of the first transition series are given in table 19.3.

Table 19.3: Magnetic moments of some of the ion of transition elements.

Ion	Electronic configurations	Number of unpaired electrons	Calculated magnetic moments (BM)
Sc ³⁺	3d ⁰	0	0
Ti ³⁺	3d ¹	1	1.73
Ti ²⁺	3d ²	2	2.83
V ²⁺	3d ³	3	3.87
Cr ²⁺	3d ⁴	4	4.90
Mn ²⁺	3d ⁵	5	5.92
Fe ²⁺	3d ⁶	4	4.90*
Co ²⁺	3d ⁷	3	3.87*
Ni ²⁺	3d ⁸	2	2.83
Cu ²⁺	3d ⁹	1	1.73

* Experimental values are significantly high because of ferromagnetic behaviour

Compounds containing Sc³⁺, Ti⁴⁺, V⁵⁺, Cr⁶⁺, Mn⁷⁺ and Cu⁺ ions are diamagnetic since their ions do not contain any unpaired electrons.

Ferromagnetism is a special type of paramagnetism in which permanent magnetic moment is acquired by the substance. Elemental iron, cobalt and nickel of the first transition series show ferromagnetism

19.4.7 Colour of Ions and Compounds

Most of the compounds of d-block elements are coloured or they give coloured solution when dissolved in water. This property of transition elements is in marked contrast to the s-, and p-block elements which often yield white colour compounds. In transition metal compounds is generally associated with incomplete (n-1)d sub-shell of the transition metal. When white light interacts with a substance, a part of it is absorbed. For example, if red portion is absorbed, the remainder appears blue. This is observed in case of copper sulphate solution. Since most compounds of transition elements are coloured, there must be energy transitions which can use up some of the energy of the visible light.

In a free atom or ion all five d-orbitals have same energy. Any electron in 'd' level is free to move amongst these five orbitals. However, in the presence of a ligand or a combining anion, the set of five d orbitals is split because of their different spatial orientation. Under these conditions, a small amount of energy (contained in the white light of the visible region) is able to promote an electron from the lower level to the higher level. When more than one electron is present, inter-electron repulsion between excited and non-excited electrons requires different transition energies. This results in different colours of the ions having different electronic configurations. Colours of the hydrated ions of the elements of first transition series is given in Table 19.4

Table 19.4: Colours of hydrated ions of some of the transition elements.

Hexa hydrated ion of	Number of d electrons	Colour of solid/ solution
Ti ³⁺	1	violet
V ³⁺	2	blue
V ²⁺	3	violet
Cr ³⁺	3	violet
Mn ³⁺	4	violet
Fe ³⁺	5	yellow/colourless
Mn ²⁺	5	light green
Fe ²⁺	6	pale green
Co ²⁺	7	pink
Ni ²⁺	8	green
Cu ²⁺	9	blue

Transition metal compounds are generally coloured in the solid state and give coloured solution when dissolved in water. This is due to the presence unpaired electron or electrons in inner d-orbitals.

It may be noted that majority of transition metal compounds are coloured both in solid state and in solution. This property has been extensively used for the detection and estimation of the metal ions. Further, transfer of electron from an unpaired to a paired situation rarely occurs. For this reason ion having a d³⁺ configuration are very light

coloured since it involves promotion of an electron from the lower level to the higher one where it will exist in the paired form. Since the energy difference between the two levels, is dependent upon the nature of the anion surrounding the central metal atom, different compounds of any particular element may have different colours.

INTEXT QUESTION 19.2

1. What are d-block 'elements'?
.....
2. How many elements are there in 3rd block group ?
.....
3. Is zinc regarded an a d-block element ? Give reasons.
.....
4. In what ways electronic configuration of d-block elements differ from those of s-and p-block elements?
.....
5. Copper (I) salts are diamagnetic whereas Copper (II) salts are paramagnetic. Explain.
.....
6. All compounds of scandium, titanium, vanadium, chromium and manganese in which the element is in oxidation state 3, 4, 5, 6 and 7 respectively, are diamagnetic. Explain
.....
7. Why do transition elements normally show variable oxidation states. Mention exception, if any.
.....

19.4.8 Complex formation

Transition metals exhibit a strong tendency for complex transition with different ligands. A co-ordination complex is one in which a metal is bound by ligands, each donating a pair of electrons (ligand is a chemical species, may be a molecule, ion or radical capable of donating a pair of electrons to the central metal atom in co-ordination compound). The complex is either a neutral or ionic species with a positive or negative charge. A complex ion is composed of two different inseparable parts, e.g., $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ag}(\text{NH}_3)_2]^+$ etc. Such ions have two portions—

- (i) the central metal ion e.g., Fe^{2+} or Ag^+ in the above case, and
- (ii) the surrounding ligands, e.g., :NH_3 , CN^- , OH^- , Cl^- , CO , NO

Ligands are capable of donating one or more pair of electrons e.g., cyanide anion and ammonia molecule are ligands in the above cases; each donates a pair of electrons to the central metal atom. The ease of complex formation is related to

- (i) high positive charge density, (these elements have small cation size and high cationic charge).
- (ii) availability of vacant d orbitals on the central metal atom.

Transition metal ions possess high charge density and vacant d orbitals or hybridized orbitals, all transition metal ions show high tendency to form coordination complexes

19.4.9 Catalytic Properties

An element (for its compound) which has partly filled d-shell and is capable of exhibiting variable oxidation states and complex formation ability acts as a good catalyst as it can provide favourable reaction sites for the reactants. Many transition elements and their compounds are used as catalyst. Nickel is an excellent catalyst for the hydrogenation of olefins and finely divided iron in Haber's process for the synthesis of ammonia gas. Vanadium pentoxide acts as an excellent catalyst in Contact Process for the manufacture of sulphuric acid.

INTEXT QUESTIONS 19.3

1. Give the formula and name of:
 - (i) cationic complex species containing a
 - (a) transition element, and
 - (b) non-transition element
 - (ii) anionic complex species containing a
 - (a) transition element, and
 - (b) non-transition element.

.....
 2. Why do transition element act as good catalysts?

.....
 3. Name some of the common catalysts you have studied.

.....
-

19.5 WHAT YOU HAVE LEARNT

- In case of scandium, ($z=21$), subshell of the previous principal quantum number starts getting filled instead of the second subshell of the quantum number that was being filled.
- All four transition series are designated as 3d, 4d, 5d and 6d respectively. The last series is still incomplete.
- Elements whose atoms or ions have partly filled d-subshell are called d-block elements.
- d-Block elements exhibit variable oxidation states.
- Transition metals and many of their compounds show paramagnetic due to the presence of unpaired electrons either in the atom, ion or molecules.
- Most of the compounds of d-block elements are either coloured or give coloured solutions when dissolved in water.
- The elements of first transition series have high density, high tensile strength, high thermal and electrical conductivity, high melting and boiling points.
- The elements of the first transition series are ductile and malleable.
- Transition elements form a number of alloys and interstitial compounds.
- The general electronic configuration of transition elements is $(n-1)d^{1 \text{ to } 10} ns^{1 \text{ to } 2}$
- d-block elements exhibit variable oxidation states.
- Transition metals and many of their compounds show paramagnetic behaviour due to the presence of unpaired electrons either in the atom, ion or molecule.
- Most of the compounds of d-block elements are either coloured or give coloured solutions, when dissolved in water.

19.6 TERMINAL EXERCISE

1. Explain:

Iron forms FeF_3 and FeI_2 but not FeF_2 or FeI_3 , though both FeCl_2 and FeCl_3 are formed.

.....

2. Why KMnO_4 is deeply coloured while MnSO_4 is feebly coloured?

.....

3. Why does a transition metal form alloys with other transition metals easily?

.....

4. Why do transition metals form interstitial compounds? What is the advantage of preparing such compounds?
.....
5. Name the elements (S) of the first transition series that does not form:
(i) any paramagnetic species,
(ii) any diamagnetic species, in one or more of the oxidation states.
.....
6. Identify the species (of the first transition series) that will have the same number of unpaired electrons (and hence μ) as Fe^{2+} . Calculate the magnetic moment in BM of these species.
.....
7. Explain, why in case of chromium ($z=24$) the configuration $3d^5 4s^1$ might be lower in energy than $3d^4 4s^2$?
.....
8. What is the electronic configuration of copper ($z=29$)? Explain the existence of copper (I) salts?
.....
9. Why are paramagnetic substances usually coloured?
.....
10. A substance having an unpaired electron is paramagnetic. Does it mean that all paramagnetic materials have odd number of electrons? State if you have come across any exception to this rule.
.....
11. A substance having no unpaired electron is diamagnetic. Does it mean that all substances having even number of electrons are diamagnetic?
.....

CHECK YOUR ANSWERS

INTEXT QUESTIONS 19.1

1. Transition elements are defined as those elements which have partially filled d-subshell either in the elemental state or in any of the common oxidation states when in the combined form.
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2. There are nine elements from Sc($z=21$) to Cu ($Z=29$) in the first transition series. These are scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper.
3. Electronic configuration of Cu^{2+} , Ag^{2+} and Au^{3+} is $3d^9$, $4d^9$ and $5d^8$ respectively in which d subshell is partially filled. Hence copper, silver and gold are transition elements. On the other hand, in case of Zn^{2+} , Cd^{2+} and Hg^{2+} the d-subshell has 10 electrons in each case and is, therefore, completely filled. Moreover, there is no other oxidation state in which zinc, cadmium and mercury are known to form compounds which have partially filled d subshell. Hence zinc, cadmium and mercury are not transition elements.
4. (i) Copper (29) has an electronic configuration of $[\text{Ar}]3d^{10}4s^1$. It readily forms compounds in oxidation state +2 ; Cu^{2+} has a configuration of $[\text{Ar}]3d^94s^0$ wherein the d-subshell is partially filled, Hence copper is a transition element.
- (ii) Silver (47) has an electronic configuration of $[\text{Kr}]4d^{10}5s^1$. Though unstable, its compounds in +2 and +3 oxidation states are known. Since d-subshell is partially filled in each of these oxidation states, silver is considered a transition element.
- (iii) Zinc (30) has a configuration of $[\text{Ar}]3d^{10}4s^2$. Zinc forms compounds only in +2 oxidation state wherein its configuration is $3d^{10}4s^0$. Since d-subshell is completely filled, zinc is not a d-block element.
- (iv) Gold (79) has a configuration of $[\text{Xe}]4f^{14}5d^{10}6s^1$ and exhibits +1 and +3 oxidation states. In the +3 state it has a partially filled d-subshell. Hence Gold (79) is a transition element.
- (v) Aluminium (13) has configuration of $[\text{Ne}]3s^23p^1$. It does not have any electron in the d-subshell Hence it is not a member of d-block group.
- (vi) Cadmium (48), tin (50) and antimony (51) have the configuration of $[\text{Kr}]4d^{10}5s^2$, $[\text{Kr}]4d^{10}5s^25p^2$ and $[\text{Kr}]4d^{10}5s^25p^3$ respectively. Oxidation states shown by these elements are 2 ; 2 & 4, and 3 & 5 respectively. In none of these states d-subshell is partially filled. Hence none of these elements are transition elements.

INTEXT QUESTION 19.2

1. d-Block elements are those elements in which the incoming electron occupies the penultimate d-subshell.
2. There are nine elements in 3d block group.
3. No, zinc is not regarded as a d-block element as the 30th electron in case of zinc goes to fill the 4s subshell; the 3-d level gets completely filled at Cu ($z=29$.)
4. In case of s- and p-block elements, the electrons enter the outermost shell but in case of d-block elements the incoming electron enters the penultimate shell.
5. Copper (I) ion has no unpaired electrons whereas copper (II) ion has one unpaired electron in d-subshell. Consequently the later is paramagnetic.
6. The ions Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+} , Mn^{7+} do not contain any unpaired electron; all

electrons present in 3d and 4s subshell have been lost to generate these oxidation states.

7. Since (n-1)d and ns electrons are of different energy, the total number of (n-1)d and ns electrons are lost successively in more than one step. This results in variable oxidation state however, in case of scandium all 3 electrons of 3d and 4s subshells are lost simultaneously. Hence it shows only one oxidation state of +3 and in an exception.

INTEXT QUESTION 19.3

1. (i) (a) $[\text{Cr}(\text{NH}_3)_6]^{3+}$, Hexaammine chromium (III) -
(b) $[\text{Zn}(\text{NH}_3)_4]^{2+}$, Tetra-amminezinc (II).
- (ii) (a) $[\text{Fe}(\text{CN})_6]^{3-}$, Hexacyanoferrate (III)
(b) $[\text{Zn}(\text{OH})_4]^{2-}$, Tetrahydroxyzincate (II).
2. Since transition elements, in free and combined state can easily change from one oxidation state to another, presence of electrons in d subshell provides an easy pathway for the reactants to react.
3. Iron and molybdenum in the manufacture of ammonia by Haber's process and vanadium pentoxide in the oxidation of sulphur dioxide to sulphur trioxide in the Contact process.

TERMINAL EXERCISES

1. Fluorine being most electronegative oxidises iron to +3 state. Therefore, FeF_2 is not formed. On the other hand iodine with a positive character is not able to oxidise iron to +3 state and form only FeI_2 , chlorine with intermediate value of electronegativity oxidises iron to +2 as well as +3 states under different experimental conditions.
2. Colour of KMnO_4 is due to MnO_4^- , the permanganate ion in which the electrons are transferred from oxygen atom to manganese atom. In case of MnSO_4 , Mn^{2+} ion has a d^5 configuration. Transfer of electron from lower energy level to higher energy level in which pairing takes place is an unfavourable process. Hence compounds containing Mn^{2+} are feebly coloured.
3. Since the atomic radii of most of the transition elements are quite close to each other and these also crystallize in the identical shape, transition elements form alloys with other elements easily.
4. Because of the availability of empty space in the crystal lattice, most transition elements accommodate a number of non-metals like H, B, C, N etc., in the interstices to form interstitial compounds. These compounds are chemically inert, hard and have high electrical conductivity and melting points.
- 5 (i) Scandium does not form any paramagnetic compound as in oxidation state +3 it has no unpaired electron. It does ; not exhibit any other oxidation state.
(ii) Iron does not form any diamagnetic species in any of the oxidation states.

- 6 Cr^{2+} has the same number of unpaired electrons as Fe^{2+} viz, 4. Its magnetic moment—

$$\begin{aligned}\mu &= [n(n+1)]^{1/2} \quad n = 4 \\ &= [4(4+2)]^{1/2} = (24)^{1/2} = 4.9 \text{ BM}\end{aligned}$$

7. Since half-filled and completely filled subshells are stabler than otherwise, the configuration $3d^4 4s^2$ changes to $3d^5 4s^1$ in which both the d-subshell and the s-subshell are half-filled.
8. Electronic configuration of copper ($z=29$) changes from $3d^9 4s^2$ to $3d^{10}4s^1$ as completely filled subshell is stabler than otherwise. Loss of the only electron explains the existence of copper (I) salt.
9. A paramagnetic substance has unpaired electrons. If the unpaired electron is / are in the d or f subshell of the metal atom or ion, the substance is coloured otherwise the substance may not be coloured for example paramagnetic O_2 and NO are not coloured,
10. All substances having odd number of electrons must be paramagnetic but all paramagnetic substances do not necessarily contain odd number of electrons. Oxygen which contains 16 electrons is paramagnetic and all transition elements having partially filled d-subshell show paramagnetism though the number of electrons may be even (Refer Table 19.4).
11. It is true that a substance having no unpaired electron is diamagnetic. But a substance having even number of electrons may have unpaired electrons in multiple of 2. Thus a substance having even number of electrons may not be diamagnetic.