INORGANIC CHEMISTRY

Topic: 4

TRANSITION ELEMENTS

LONG ANSWER QUESTIONS

1. **What are transition elements? Give the names of the metals of the first transition series.**

Ans: **Transition Metals**

The elements belonging to d-block are metals. The d-block elements are classified into four transition series. These 4 series corresponds the filling of 3d, 4d, 5d and 6d orbitals.

The series of elements, that are formed by filling the 3d, 4d and 5d shells of electrons, comprise the d-block elements. They are often called as transition elements because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which form ionic compounds and elements of p-block which form covalent compounds. In s and p blocks electrons add to the last shell, in d-block electrons are added to the penultimate shell. Typically the transition elements have an incompletely filled d level. The zinc group has d^{10} configuration and compounds of these elements show some differences from other transition elements. The elements make up three complete rows of ten elements and an incomplete fourth row. The position of the incomplete fourth series is discussed along with the f-block elements.

First transition series

This is also called as 3d series which corresponds the filling of 3d orbital. It starts from scandium whose atomic number is 21 and includes 10 elements till zinc whose atomic number is 30.

First transition series (or) 3d series

Element	Atomic number	Symbol	Electronic configuration
Scandium	21	Sc	[Ar] $3d^1$ $4s^2$
Titanium	22	Ti	[Ar] $3d^2$ $4s^2$
Vanadium	23	V	[Ar] $3d^3$ $4s^2$
Chromium	24	Cr	[Ar] $3d^5$ $4s^1$
Manganese	25	Mn	[Ar] $3d^5$ $4s^2$

Element	Atomic number	Symbol	Electronic configuration
Iron	26	Fe	[Ar] $3d^6\ 4s^2$
Cobalt	27	Co	[Ar] $3d^7\ 4s^2$
Nickel	28	Ni	[Ar] $3d^8\ 4s^2$
Copper	29	Cu	[Ar] $3d^{10}\ 4s^1$
Zinc	30	Zn	[Ar] $3d^{10}\ 4s^2$

2. **Write the names and electronic configuration of second transition series.**

Ans: **Second transition series**

This is also called as 4d series which corresponds the filling of 4d orbital. It starts from yttrium whose atomic number is 39 and includes 10 elements till cadmium whose atomic number is 48.

Second transition series (or) 3d series

Element	Atomic Number	Symbol	Electronic configuration
Ytterium	39	Y	[Kr] $4d^1\ 5s^2$
Zirconium	40	Zr	[Kr] $4d^2\ 5s^2$
Niobium	41	Nb	[Kr] $4d^4\ 5s^1$
Molybdenum	42	Mo	[Kr] $4d^5\ 5s^1$
Technetium	43	Tc	[Kr] $4d^5\ 5s^2$
Ruthenium	44	Ru	[Kr] $4d^7\ 5s^1$
Rhodium	45	Rh	[Kr] $4d^8\ 5s^1$
Palladium	46	Pd	[Kr] $4d^{10}\ 5s^0$
Silver	46	Ag	[Kr] $4d^{10}\ 5s^1$
Cadmium	48	Cd	[Kr] $4d^{10}\ 5s^2$

3) **List the typical properties of transition elements. How are their properties correlated?**

Ans: **General Characteristics Of Transition Elements**

(i) Except for mercury, which is a liquid at room temperature all other elements are solid metals exhibiting all the characteristics of a metal.

(ii) The show variable oxidation states unlike s and p block elements.

(iii) They, and some of their compounds, show catalytic properties.

(iv) Their compounds are coloured.

(v) They have great tendency to form complex compounds.

(vi) They form alloys and interstitial compounds.

Conductivity

All the transition metals are good conductors of heat and electricity. Silver is the best conductor of electricity.

Density

Because of small size of their atoms and strong metallic bonding the density and hardness of transition elements are high.

Ionization Energy

The ionization energy (IE) of transition elements are higher than those of s-block elements but lower than p-block elements. In a particular transition series, ionization energy although increases gradually as we move from left to right but this increase is not appreciable.

The increase in ionization energy is due to increase in nuclear charge, the effect of increase in nuclear charge is partly balanced by the increase in screening effect. Consequently, the increase in ionization energy along the period of d-block elements is very small.

Variable Oxidation States

Transition elements usually exist in several different oxidation states and the oxidation states changes in units of one, e.g. Fe^{2+} and Fe^{+3}, Cu^{+1} and Cu^{+2}.

Scandium can have an oxidation number of (+II) if both s electrons are used for bonding and (+III) when two s and one d electrons are involved. Similarly all the elements show variable oxidation states depending upon the number of electrons available for bonding in their s and d sub-shells.

Complexes and Their Properties

The transition elements have an unparalleled tendency to form coordination compounds with the Lewis bases, which are called as ligands.

$CO^{3+} + 6NH_3 \longrightarrow [CO(NH_3)_6]^{3+}$

$Fe^{2+} + 6CN^{-} \longrightarrow [Fe(CN)_6]^{4-}$

s and p block elements form very few complexes. The reason transition elements are so good at forming complex is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by ligands.

Size of Atoms and Ions

The covalent radii of the elements decrease from left to right across a row in the transition series. This is because of the poor screening by the d electrons due to which, the nuclear charge attracts all of the electrons more strongly, hence a contraction in size occurs.

The elements in the first group in the d-block show the excepted increase (due to the addition of extra shell) in size Sc → Y → La. However in the subsequent groups there is an increase between first and second members, but hardly any increase between second and third elements. This is due to lanthanide contraction (discussed in f-block elements).

Magnetic Properties

On the basis of behaviour in a magnetic field, substances are classified as paramagnetic, diamagnetic and ferromagnetic. Those substance which are attracted by the applied magnetic field are called paramagnetic where as those which are repelled by the magnetic field are called diamagnetic. Substances which are very strongly attracted by the applied field are called ferromagnetic.

Paramagnetism is a property due to the presence of unpaired electrons. Thus most of the transition metals are paramagnetic. As the number of unpaired electrons increases, the paramagnetic character also increases.

The magnetic moment is calculated from the following formula $\mu = \sqrt{n(n+2)}$ BM where n is the number of unpaired electrons and B. M stands for Bohr magneton.

Catalytic Properties

Many transition metals and their compounds have catalytic properties. For e.g. V_2O_5, Fe, $FeCl_3$, Ni, Pd etc.

This property of transition elements is due to their variable oxidation states. In some cases the transition metals with their variable valency may form variable unstable intermediate compounds. In other cases the transition metal provides a suitable reaction surface.

Non Stoichiometry

Another feature of the transition elements is that they sometimes form non stoichiometry compounds. These are compounds of indefinite structure and proportions. For example $Fe_{0.94}O$. It is mostly due to the variable valency of transition elements. Sometimes, non stoichiometry is caused by defects in the solid structures.

Alloy Formation

Alloys are homogenous solid solutions of two or more metals obtained by melting the components and then cooling the melt. These are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in the crystal lattice of the other. Since transition metals have similar atomic radii, they form alloys very readily.

3. What is meant by variable oxidation states? How does Mn show its variable oxidation states? Explain.

Variable Oxidation States

Transition elements usually exist in several different oxidation states and the oxidation states changes in units of one, e.g. Fe^{2+} and Fe^{+3}, Cu^{+1} and Cu^{+2}.

Scandium can have an oxidation number of (+II) if both s electrons are used for bonding and (+III) when two s and one d electrons are involved. Similarly all the elements show variable oxidation states depending upon the number of electrons available for bonding in their s and d sub-shells.

In the transition elements, the energies of (n-1)d orbitals and ns orbitals are very close. Hence electrons from both can participate in bonding.

The sum $IE_1 + IE_2$ increases. As a result the standard reduction potentials (E^0) become less and less negative. Hence the tendency to form M^{2+} ion decreases. The greater stability of +2 state for Mn is due to half-filled d-subshell (d^5),

4. **How do you classify magnetic materials? Give two examples for each type.**

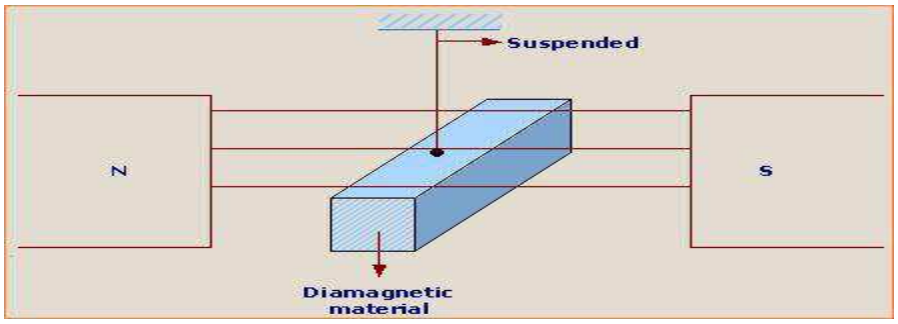
Diamagnetic Substance

Michael Faraday discovered that a specimen of bismuth was repelled by a strong magnet. Diamagnetism occurs in all materials. These materials are those in which individual atoms do not possess any net magnetic moment. [Their orbital and spin magnetic moment add vectorially to become zero]. The atoms of such material however acquire induced dipole moments when they are placed in an external magnetic field.

The diamagnetic materials are Type 1 superconductors as they exhibit perfect conductivity and perfect diamagnetization when cooled to very low temperature. The superconductor repels a magnet and in turn is repelled. Such perfect diamagnetism in superconductors exhibiting the above phenomena is called Meissner effect.

Some important properties are:

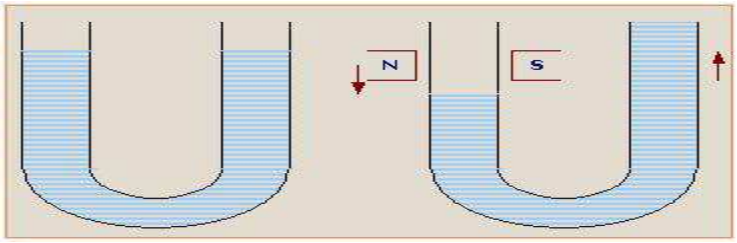
- When suspended in a uniform magnetic field they set their longest axis at right angles to the field as shown



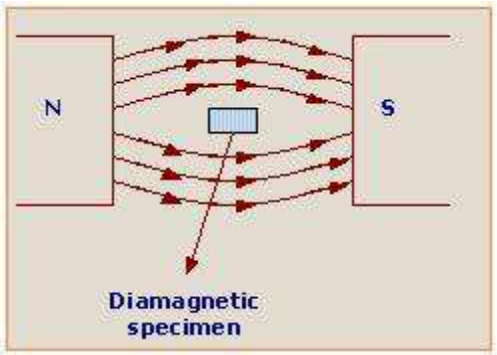
2) In a non-uniform magnetic material, these substances move from stronger parts of the field to the weaker parts. For e.g. When diamagnetic liquid is put in a watch glass placed on the two pole pieces of an electromagnet and current is switched on the liquid accumulates on the sides.

[Note on increasing the distance between the pole, the effect is reversed]

3) A diamagnetic liquid in a U shaped tube is depressed, when subjected to a magnetic field.



4) The lines of force do not prefer to pass through the specimen, since the ability of a material to permit the passage of magnetic lines of force through it is less.



5) The permeability of the substance, that is, $m_r < 1$.

6) The substance loses its magnetization as soon as the magnetizing field is removed.

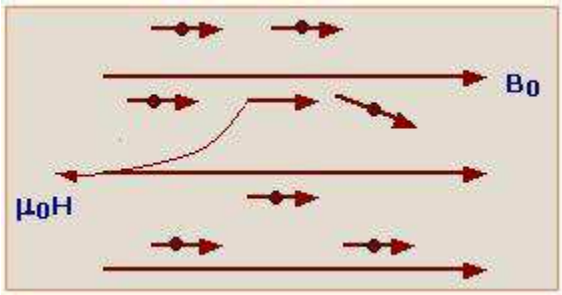
7) Such specimen cannot be easily magnetized and so their susceptibility is negative.

Example: Bismuth, antimony, copper, gold, quartz, mercury, water, alcohol, air, hydrogen etc.

Paramagnetic Substance

Paramagnetic substance is attracted by a magnet very feebly. In a sample of a paramagnetic material, the atomic dipole moments initially are randomly oriented in space.

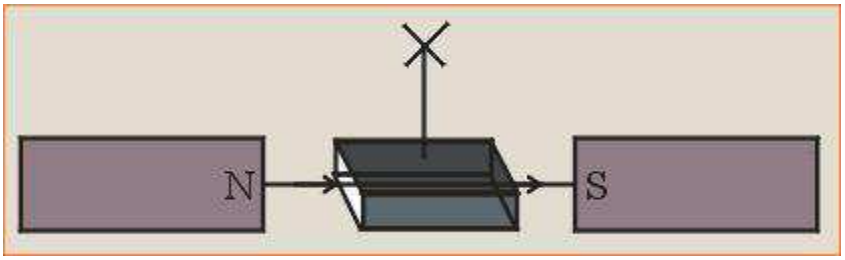
When an external field is applied, the dipoles rotate into alignment with field as shown



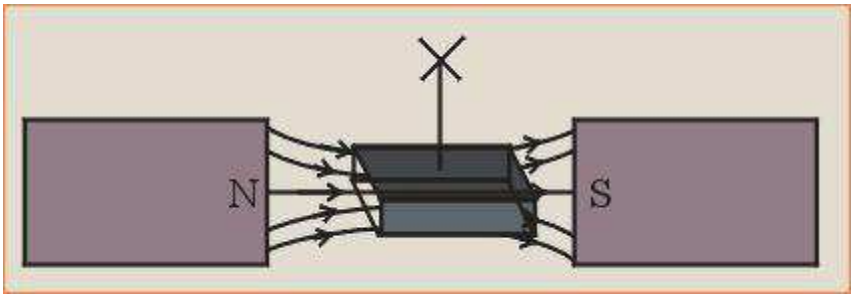
The vector sum of the individual dipole moments is no longer zero.

Some important properties are:

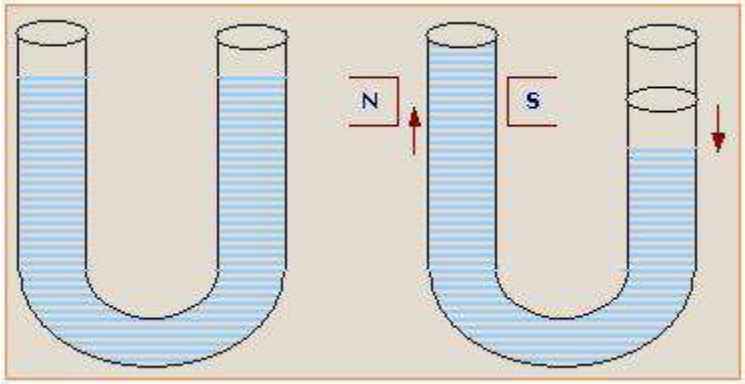
- The paramagnetic substance develops a weak magnetization in the direction of the field.
- When a paramagnetic rod is suspended freely in a uniform magnetic field, it aligns itself in the direction of magnetic field.



- The lines of force prefer to pass through the material rather than air that is $m_r > 1$ that is their permeability is greater than one.



- As soon as the magnetizing field is removed the paramagnetics lose their magnetization.
- In a non-uniform magnetic, the specimen move from weaker parts of the field to the stronger parts (that is it accumulates in the middle).
- A paramagnetic liquid in U tube placed between two poles of a magnet is elevated.



- The magnetization of paramagnetism decreases with increase in temperature. This is because the thermal motion of the atoms tends to disturb the alignment of the dipoles.

Example:

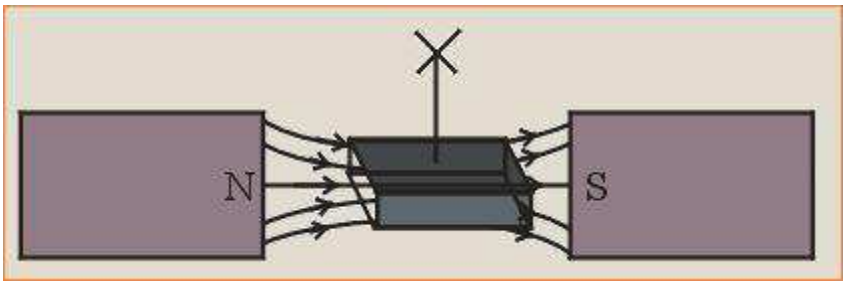
Aluminum, platinum, chromium, manganese, copper sulphate, oxygen etc.,

Ferromagnetic Substance

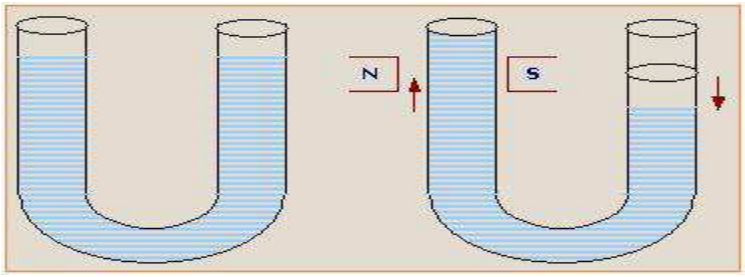
Ferromagnetism, like paramagnetism, occurs in materials in which atoms have permanent magnetic dipole moments. The strong interaction between neighboring atomic dipole moments keeps them aligned even when the external magnetic field is removed.

Some important properties are:

- These substances get strongly magnetized in the direction of field.
- The lines of force prefer to pass through the material rather than air that is $m_r>1$ that is their permeability is greater than one.



- In a non-uniform magnetic, the specimen move from weaker parts of the field to the stronger parts (that is it accumulates in the middle).
- A paramagnetic liquid in U tube placed between two poles of a magnet is elevated.



- For ferromagnetic materials m_r is very large and so its susceptibility i.e., X_m is positive.



- Ferromagnetic substances retain their magnetism even after the magnetizing field is removed.
- The effectiveness of coupling between the neighboring atoms that causes ferromagnetism decreases by increasing the temperature of the substance. The temperature at which a ferromagnetic material becomes paramagnetic is called its

curie temperature. For example the curie temperature of iron is 1418^{o}F, which means above this temperature, iron is paramagnetic.

Example: Iron, cobalt, nickel and number of alloys.

5. **How does a catalyst work in a chemical reaction? Discuss with suitable example. Mention some important catalysts in industry.**

   Ans: The first row transition elements exhibit catalytic properties due to the presence of unpaired electrons which can form complexes. Iron and vanadium are the most important catalysts. Iron is used as catalyst in the manufacture of ammonia. Vanadium is used in the form of vanadium pentoxide in the manufacture of sulphuric acid.

Catalyst	Examples	Function
Metals	Fe, NI, Pt, Ag	Hydrogenation Dehydrogenation
Semiconducting oxides and sulphides	MO, ZnO, MgO, Si_2O_3/MoO_3, MoS_2	Oxidation Desulphurization
Insulating oxides	$A1_2O_3$, SiO_2, MgO	Dehydration
Acids	SiO_2/Al_2O_3 Zeolites	Cracking Polymerization Isomerization

The two important aspects of solid catalysts are (i) activity and (ii) selectivity.

As the reaction is exothermic, the catalyst is heated in the beginning and the temperature is maintained by the heat evolved during the reaction. Initially it is heated to about 450^{o}C.

$$\underset{\text{3 volumes of reactants}}{2SO_2(g) + O_2(g)} \xleftarrow{V_2O_5\ 450^{o}C} \underset{\text{2 volumes of products}}{2SO_3} + 45000 \text{ calories}$$

This is the main chemical reaction occurring in the Contact process. It is a reversible, exothermic reaction accompanied by a decrease in volume.

6. **What are alloys? How they are prepared?**

Ans: **Alloys**

An alloy is a mixture of two or more metals fused together in molten state. Metals when melted tend to dissolve in one another forming alloys. The various properties of a metal like malleability, ductility, strength, hardness, resistance to corrosion and appearance can

be improved by mixing with other metals. Alloys have properties different from its constituents.

Preparation of Alloys

There are four commonly employed methods for the manufacture of alloys: the fusion method, the electro-deposition method, the reduction method, and powder metallurgy.

The Fusion Method

This method uses alloying elements in a fixed proportion and fuses them together in a refractory melting pot or in a brick-lined crucible. The component metal with a higher melting point is melted first and then the other component with a lower melting point is added to the melt. Both metal components are mixed well and allowed to melt further. The molten mass is covered by powdered Carbon to avoid oxidation of the molten alloy components because they are very reactive to the surrounding atmospheric oxygen. The resulting molten mass is allowed to cool at room temperature.

The Electro-Deposition Method

This method involves simultaneous deposition of different component metals from the electrolytic solution containing their salts solution mixture by passing direct electricity.

The Reduction Method

Metal may exist in the form of compounds. Reduction is a chemical process in which a compound of one component can be separated from another component, to get a pure metal. This method is performed in an electric furnace.

Note In all the methods used to prepare alloys, Carbon, salts, and oxides are residuals that may hinder the properties of the produced alloy, which is generally contaminated.

Powder Metallurgy

Powder metallurgy may be defined as the art of producing fine metal powders and then making articles from individual metal powders or alloyed metal powders with or...

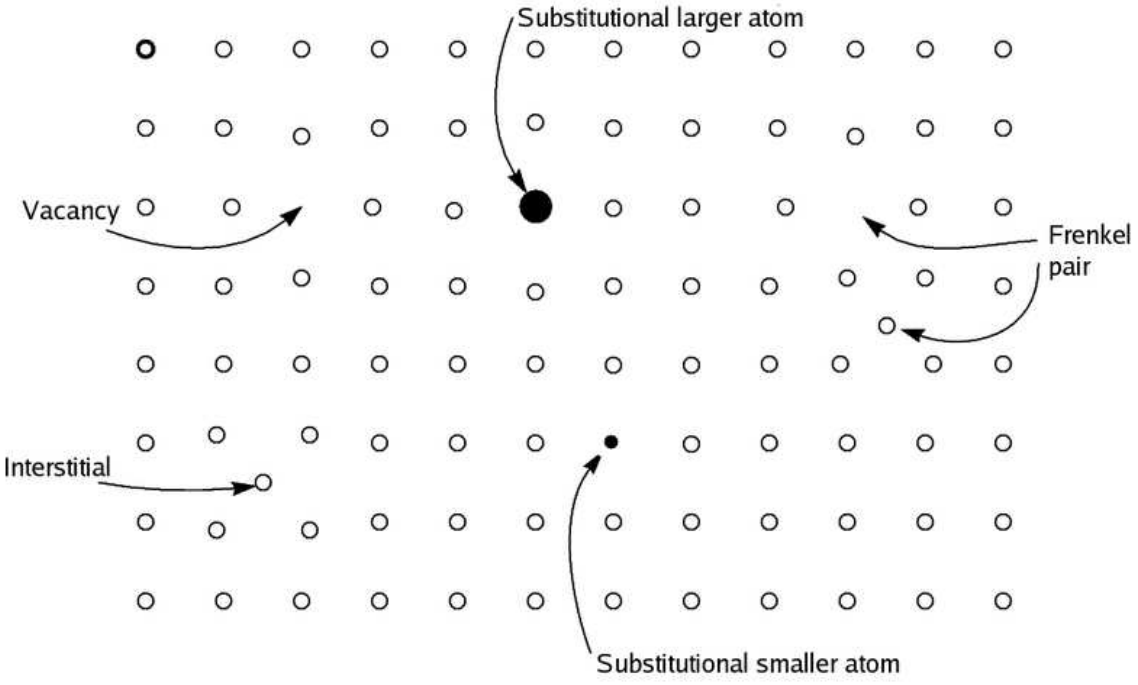
7. Explain about the no-stoichiometric compounds.

Non-stoichiometric compounds are chemical compounds with an elemental composition that cannot be represented by a ratio of well-defined natural numbers, and therefore violate the law of definite proportions. Often, they are solids that contain crystallographic point defects, such as interstitial atoms and vacancies, which result in excess or deficiency of an element, respectively. Since solids are overall electrically neutral, the defect in an ionic compound is compensated by a change in the charge of

other atoms in the solid, either by changing their oxidation state, or by replacing them with atoms of different elements with a different charge.

Nonstoichiometry is pervasive for transition metal oxides, especially when the metal is not in its highest oxidation state. For example, although wüstite (ferrous oxide) has an ideal (stoichiometric) formula FeO, the actual stoichiometry is closer to $Fe_{0.95}O$. The non-stoichiometry occurs because of the ease of oxidation of Fe^{2+} to Fe^{3+} effectively replacing a small portion of Fe^{2+} with two thirds their number of Fe^{3+}. Thus for every three "missing" Fe^{2+} ions, the crystal contains two Fe^{3+} ions to balance the charge. The composition of a non-stoichiometric compound usually varies in a continuous manner over a narrow range. Thus, the formula for wüstite is written as $Fe_{1-x}O$, where x is a small number (0.05 in the previous example) representing the deviation from the "ideal" formula. Nonstoichiometry is especially important in solid, three-dimensional polymers that can tolerate mistakes. To some extent, entropy drives all solids to be non-stoichiometric. But for practical purposes, the term describes materials where the non-stoichiometry is measurable, usually at least 1% of the ideal composition.

Non-stoichiometric compounds are also known as berthollides (as opposed to the stoichiometric compounds or daltonides).



8. Mention any four alloys and mention their uses.

(a) Steel

Steel contains normally 0.1 to 0.5% of carbon. Silver is alloyed with copper. The ornaments made with silver copper alloy have 80% silver and 20% copper. Silver is used in silver plating. Silver salts are used in photography.

(b) Stainless steel

It contains 18% chromium and 8% Nickel. It is used in preparation of household utensils, shaving blades etc.

(c) Invar

It is an alloy of steel which contains 36% of nickel. When steel is alloyed with any metal it is called as alloy steel. It does not expand on heating.

(d) Nickel Steel

This is also an alloy of steel with 3.5% nickel. It is used extensively in cable preparation. This is flexible than stainless steel.

(e) Chrom steel

This is also an alloy of steel with 1.5% - 20% of chromium. This is used in cutlery.

(f) Alnico

This is also an alloy of steel. It contains 12% Aluminium, 20% nickel and 5% cobalt. It contains high magnetic properties and hence used in preparation of permanent magnets.

(g) Bronze

This is an alloy of copper which contains 90% of copper and 10% of tin. It is used in preparation of statues.

(h) Gun metal

This is also an alloy of copper. It contains copper, 10% tin and 2% zinc. It is used mostly in all automobiles for gears and bearings.

(i) Bell metal

This is also an alloy of copper. It contains 80% copper and 20% tin. It is used in bells.

(j) German silver

It is also an alloy of copper. It contains 25 to 40% of copper, 25-35% of zinc and 10-35% nickel. It is used in preparation of utensils.

(k) Dental alloy

This is an alloy of silver. It contains some amounts of silver, tin and mercury. This is used in filling teeth.

(l) Coinage silver

This is also an alloy of silver. It contains 50% silver, 40-50% copper and 5-10% of nickel. It is used in making coins.

9. Discuss the colour of transition metal compounds with suitable examples.

Ans: **Transition Metal compoundsIons**

Transition metal complex ions are called as d-block elements. Transition metal complex ions have an incompletely filled d sub shell. Atoms in the periodic table have a single d electron in their outermost shell i.e. from scandium and yttrium thus those elements are considered as transition metals complex ions. Complex ions are those ions which are having a metal ion at its centre with a number of other molecules or anion surrounding it and this complex which is formed is called as co ordination complex. Metal complex and the surrounding ligands are attached to each other by the co ordinate bonds.

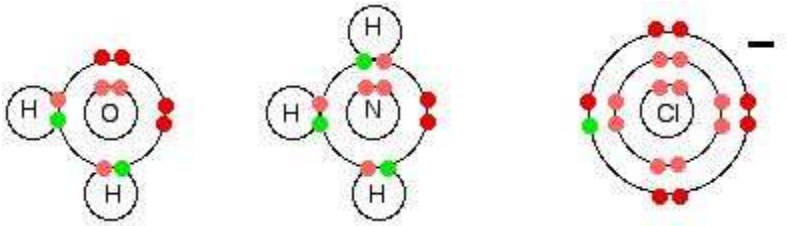
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.9559	47.867	50.9415	51.9961	54.938	55.845	58.9332	58.6934	63.546	65.4089
Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.9058	91.224	92.9064	85.94	98	101.07	102.9055	106.42	107.8682	112.411
Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium
71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
174.967	178.49	180.9497	183.84	186.207	190.23	192.217	195.084	196.9666	200.59
Lutetium	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury

Characteristics of complex ions in Transition metal:

- Variable oxidation states
- Magnetic properties
- Formation of colored compounds
- Formation of complexes
- Electrode potential and low reactivity

Ex: water, ammonia and chloride ions.

All these ions have active lone pairs of electrons in the outer energy level which are used to form co-ordinate bonds with the metal ion.



Examples for Transition Metal with Complex Ions

1. $[Fe\ (H_2O)_6]^{2+}$
2. $[Co\ (NH_3)_6]^{2+}$
3. $[Cr\ (OH)_6]^{3-}$
4. $[CuCl_4]^{2-}$

Properties of transition metal

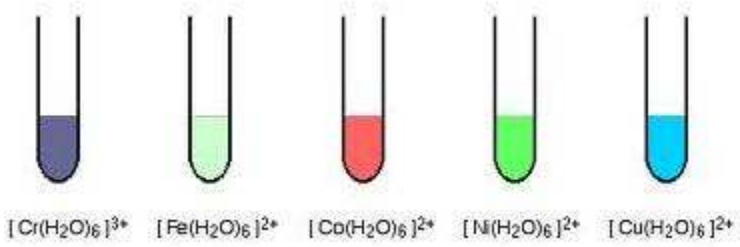
1. The color of the transition metal complex ions is due to d - d electronic transitions.
2. Formation of complexes in many oxidation states, due to the relatively low reactivity of unpaired d electrons.
3. Formation of paramagnetic compounds due to the presence of unpaired d electrons.

Color and Oxidation State of Transition Metal with Complex Ions:

<u>Color of transition metal with complex ions:</u>

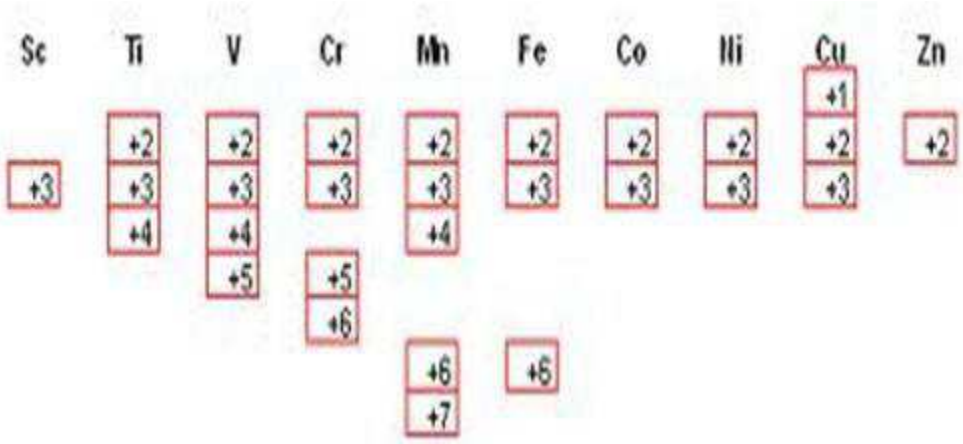
An electron jumps from one d- orbital to another d-orbital due to d-d transition. In transition metal complex ions, the d orbitals don't have the same energy. The splitting pattern of the d orbitals can be calculated by using crystal field theory. The theory in which the extent of the splitting depends on the particular metal, its oxidation state and the nature of the ligands. Color of the transition metal ion is also due to charge transfer because an electron jumps from ligand to metal orbital gives rise to ligand to metal charge transfer. Color of the dichromate and permanganate ions is due to ligand to metal charge transfer.

Colors for some common transition metal



Oxidation states of the transition metal with complex ions:

Transition metal complex ions exhibits two or more oxidation states. For example, compounds of vanadium are known in all oxidation states between −1, such as $[V(CO)_6]^-$, and +5, such as VO_4^{3-}. The element which belongs to groups between 13-17 exhibits multiple oxidation states. Common oxidation state of all the transition metal complex ions differs by two. The maximum oxidation states of transition metal complex ions is +7 for manganese and the minimum oxidation state is -2 for $[Fe(CO)_4]^{2-}$ complex.



10. Explain the magnetic properties of first transition series metal ions.

Ans: Magnetic Properties

On the basis of behaviour in a magnetic field, substance are classified as paramagnetic, diamagnetic and ferromagnetic. Those substance which are attracted by the applied magnetic field are called paramagnetic where as those which are repelled by the magnetic field are called diamagnetic. Substances which are very strongly attracted by the applied field are called ferromagnetic.

Paramagnetism is a property due to the presence of unpaired electrons. Thus most of the transition metals are paramagnetic. As the number of unpaired electrons increases, the paramagnetic character also increases.

The magnetic moment is calculated from the following formula $\mu = \sqrt{n(n+2)}$ BM where n is the number of unpaired electrons and B. M stands for Bohr magneton.

Illustration 1: Why does Mn(II) show maximum papamagentic character amongst the bivalent ions of the first transition series?

Solution: Mn^{2+} has maximum number of unpaired electrons i.e. $3d^5$.

Illustration 2: A substance is found to have a magnetic moment of 3.9 B.M. How many unpaired electrons does it contain?
Solution: Using the formula, $\mu = \sqrt{n(n+2)}$, B.M. n = 3

SHORT ANSWER QUESTIONS

1. Mention any 5 characteristics of transition elements.
Ans: General Characteristics Of Transition Elements

(i) Except for mercury, which is a liquid at room temperature all other elements are solid metals exhibiting all the characteristics of a metal.

(ii) The show variable oxidation states unlike s and p block elements.

(iii) They, and some of their compounds, show catalytic properties.

(iv) Their compounds are coloured.
(v) They have great tendency to form complex compounds

2. Whys are d-block elements are called transition elements?

Ans: The elements belonging to d-block are metals. The d-block elements are classified into four transition series. These 4 series corresponds the filling of 3d, 4d, 5d and 6d orbitals.

The series of elements, that are formed by filling the 3d, 4d and 5d shells of electrons, comprise the d-block elements. They are often called as transition elements because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which form ionic compounds and elements of p-block which form covalent compounds. In s and p blocks electrons add to the last shell, in d-block electrons are added to the penultimate shell. Typically the transition elements have an incompletely filled d level. The zinc group has d^{10} configuration and compounds of these elements show some differences from other transition elements. The elements make up three complete rows of ten elements and an incomplete fourth row. The position of the incomplete fourth series is discussed along with the f-block elements.

3. The transition elements have high boiling and melting points. Why?

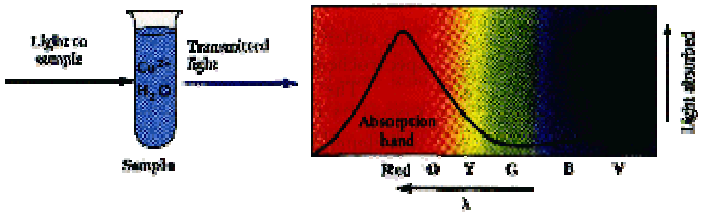
Ans: All the transition metals have metallic character. The atoms in the metals are bound by strong metallic bonds with strong inter atomic bonds. Therefore the melting and boiling points are high.

4. **The sizes of terminal elements of each transition series are greater than their preceding elements. Explain.**

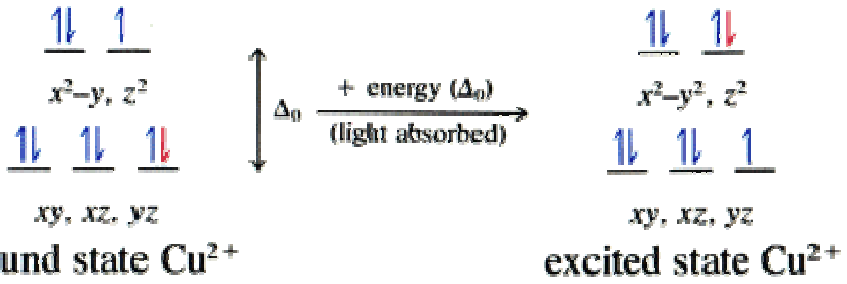
   Ans: In these elements, the last electron normally enters the d orbital which is the penultimate shell, this is due to the aufbau principle of increasing order of energy level filling of orbitals i.e. the last electron goes to (n-1) d orbital. Hence these elements are named as d-block elements and they are called as transition metals because they form the bridge between the representative elements. These elements have partly filled d-subshells in their elementary form or in their simple ions. The electrons in the outer most orbit are sheilds by inner d-electrons. Threrefore the size of terminal elements is more thant the preceding ones.

5. **Write short notes on d-orbital splitting.**

Ans: When light passes through a solution containing transition metal complexes, we see those wavelengths of light that are transmitted. The solutions of most octahedral Cu (II) complexes are blue. The visible spectrum for an aqueous solution of Cu (II), $[Cu(H_2O_6]^{2+}$, shows that the absorption band spans the red-orange-yellow portion of the spectrum and green, blue and violet are transmitted.



The absorption band corresponds to the energy required to excite an electron from the t_{2g} level to the e_g level.



Recall, the energy possessed by a light wave is inversely proportional to its wavelength. The Cu(II) solution transmits relatively high energy waves and absorbs the low energy wavelengths. This indicates that the band gap between the two levels is relatively small for this ion in aqueous solution.

d-Orbital Splitting

The magnitude of the splitting of the d-orbitals in a transition metal complex depends on three things:

- the geometry of the complex
- the oxidation state of the metal
- the nature of the ligands

VERY SHORT ANSER QUESTIONS

1. **Define d-block elements.**

Ans: The elements in which the differentiating electron enters the d-orbital of the penultimate shell are called d - block element

2. Mention d-block elements which are not considered as transition elements.

Ans: The IIB group elements Zn, Cd ans HG are not considered as transition elements but they are present in d-block elements.

3. **Write any two characteristics of transition elements.**

Ans:

i) Except for mercury, which is a liquid at room temperature all other elements are solid metals exhibiting all the characteristics of a metal.

(ii) The show variable oxidation states unlike s and p block elements.

(iii) They, and some of their compounds, show catalytic properties.

(iv) Their compounds are coloured

4. **Why do transition metals show a number of oxidation states?**

Ans: Transition elements usually exist in several different oxidation states and the oxidation states changes in units of one, e.g. Fe^{2+} and Fe^{+3}, Cu^{+1} and Cu^{+2}.

In the transition elements, the energies of (n-1)d orbitals and ns orbitals are very close. Hence electrons from both can participate in bonding. Therefore they show a number of oxidation states.

SOLVED PROBLEMS OF TRANSITION ELEMENTS

Board Level Questions

Problem 1: The chemical reactivity of lanthanides resemble to which other elements of the periodic table?

Solution: The chemical reactivity of the starting lanthanides resemble calcium due to similar first and second ionization energy. But latter lanthanides resemble Al due to ability of showing +3 oxidation state and similarity in I.E.

Problem 2: Enthalpies of atomization of transition elements are higher than those of alkali and alkaline earth metals. Explain.

Solution: The number of unpaired electrons in transition elements are more when compared to these in alkali and alkaline earth metals. As a result, the metallic bonds in transition metals are stronger and enthalpies of atomization are higher than those of alkali and alkaline earth metals.

Problem 3: Explain the following:

(a) Chromium is a typical metal while mercury is a liquid metal.

(b) Zinc readily liberates H_2 from cold dil. H_2SO_4 but not form cold conc. H_2SO_4.

Solution:
(a) Chromium has five unpaired electrons in its d-orbitals which make its metallic bond very strong, whereas in mercury there is no unpaired d-electrons so its metallic bond is very weak, hence it is a liquid.

(b) Since, conc. H_2SO_4 act as an oxidizing agent hence does not evolve H_2 when it reacts with zinc.

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + H_2O$$

Problem 4: Compare thermal stability of ZnO, CdO and HgO.

Solution: ZnO > CdO > HgO

Problem 5: Cu^+ ion has $3d^{10}4s^0$ configuration and colourless but Cu_2O is red and Cu_2S is black. Explain.

Solution: Cu^+ ion has $3d^{10}4s^0$ configuration, i.e. it has no unpaired electron hence there is no d-d transition possible and it is colourless. But Cu_2O and Cu_2S are coloured due to charge transfer of electrons from O^{2-} or S^{2-} to the vacant orbital of Cu^+ ion.

Problem 6: While Cu, Ag and Au are considered as transition elements but Zn, Cd and Hg are not considered as transition elements although all the mentioned elements have complete d-orbitals. Explain.

Solution: Although Cu, Ag and Au have their d – orbitals complete in the elemental state. They do have incomplete d orbitals in their compound state. So they are included in the transition elements.

$Cu^{+2} = 3d^9$

$Au^{+3} = 5d^8$

Zn, Cd and Ag have their d-orbitals complete in their elemental state as well as compound state. So they are not included in the transition elements.

$Zn^{+2} = 3d^{10}$

$Hg^{+2} = 5d^{10}$

Problem 7:

(i) CrO_3 is an acid anhydride. Explain.

(ii) Between Na^+ and Ag^+ which is a stronger Lewis acid and why?

Solution:

(i) $CrO_3 + H_2O \longrightarrow H_2CrO_4$, i.e CrO_3 is formed by loss of one H_2O molecule from chromic acid.

(ii) Between Na^+ and Ag^+, Ag^+ is stronger Lewis acid. Because Ag^+ has pseudo noble gas configuration which makes it more polarizing.

Problem 8: **It is well known that alkali and alkaline earth metals displace hydrogen from dilute acids. But most of the transition elements do not behave so. Explain**.

Solution: Alkali and alkaline earth metals have positive oxidation potential. But most of the transition elements have negative oxidation potentials. So they are not as good oxidizing agents as the alkali and alkaline earth metal are.

Problem 9: In the melting point curves of transition metals, one observes a dip in the curves at the end i.e. Cu, Ag & Au and Zn, Cd & Hg have lower melting points when compared to other transition metals. Explain.

Solution: In the last two groups of transition elements i.e. Cu, Ag, Au, Zn, Cd and Hg all the electrons are paired which can not take part in metallic bonding. As a result, metallic bond in these elements is weak resulting in the lower melting points of these metals.

Problem 10: Enthalpies of atomization of transition elements are higher than those of alkali and alkaline earth metals. Explain.

Solution: The number of unpaired electrons in transition elements are more when compared to those in alkali and alkaline earth metals. As a result, the metallic bonds in transition metals are stronger and enthalpies of atomization are higher than those of alkali and alkaline earth metals.

Problem 11: Explain the following:

(a) Scandium forms no coloured ions, yet it is regarded as a transition element.

(b) Transition elements have many irregularities in electronic configurations.

Solution:

(a) Scandium in the ground state has one d electron. Hence it is regarded as transition element.

(b) In the transition elements, the (n – 1)d subshell and ns subshell have very small difference in energy. The incoming electron may enter into either ns or (n-1)d subshell. Hence they show irregularities in their electronic configurations.

Problem 12: Explain the following

(a) Chromium is a typical metal while mercury is a liquid metal.

(b) Cobalt (II) is stable in aqueous solution but in the presence of strong ligands, it is a easily oxidised to cobalt (III).

Solution:

(a) chromium has 5 unpaired electrons in its d – orbitals which make its metallic bond very stronger. Whereas in mercury there are no unpaired d electrons, so its metallic bond is very weak.

(b) CO(III) has greater tendency to form complex than CO(II) hence in the presence of ligands CO(II) changes to CO(III).

Problem 13: Write down the products of the following reactions.

(a) $CuSO_4$ solution is treated with KI solution.

(b) $AgNO_3$ solution is added to $Na_2S_2O_3$ solution.

Solution:

(a) Free iodine is liberated along with the formation of a white precipitate of cupric iodide.

$$CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$$

$$2CuI_2 \longrightarrow 2CuI + I_2$$

(b) A white precipitate of $Ag_2S_2O_3$ is obtained which turns yellow, brown and finally black on keeping.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

black ppt.

Problem 14: Explain the following

(a) Zinc readily liberates H_2 form cold dil.H_2SO_4 but not from cold conc. H_2SO_4.

(b) Blue colour of the $CuSO_4$ solution is discharged slowly when an iron rod is dipped into it.

Solution:
(a) Conc. H_2SO_4 is a covalent compound. Hence does not contain H^+ ions. Dilute H_2SO_4 contains H_3O^+ which reacts with Zn and liberates H_2.

$$H_2SO_4 + H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$$

$$Zn + 2H_3O^+ \longrightarrow Zn^{2+} + 2H_2O + H_2O \uparrow$$

(b) Fe is more electropositive than Cu, hence it displaces copper form $CuSO_4$ solution.

$$Fe_{(s)} + CuSO_{(aq)} \longrightarrow FeSO_{4(aq)} + Cu_{(s)}$$

Problem 15: An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations.

Solution:

$$Hgl_2 + 2Nal \longrightarrow Na_2[Hgl_4]$$

(orange) coloured due to residual Hgl2)

$$Hgl_2 + Nal(excess) \longrightarrow Na_2[Hgl_4]$$

(orange) (colourless because there is no residual Hgl2)

$$2Na_2[Hgl_4] + 2NaOCl + H_2O \longrightarrow 2Hgl_2 + NaCl + 4NaOH + 2Nal_3$$

(orange)