

SOME IMPORTANT POINTS

Group 15 Elements

- a) Valence shell electronic configuration = ns^2np^3 . The s orbital is completely filled and p orbitals are half-filled, making the electronic configuration **extra stable**.
- b) There is a considerable increase in covalent radius from N to P due to the addition of new energy shell and due to strong shielding effect of the s and p electrons present in the inner shells. However, there is only a small increase in covalent radii from As to Bi due to **poor shielding** of the valence electrons by the d and/or f electrons present in the inner shells of the heavier elements. Thus, the increase in effective nuclear charge reduces the effect of addition of a new energy shell to some extent. Same is true for ionic radii.
- c) The **ionization enthalpy** of group 15 elements is much greater than that of group 14 elements in the corresponding periods because of the **extra stable** half-filled p orbitals and **smaller size**.
- d) The melting points of group 15 elements first increase from N to As and then decrease up to Bi. The melting points increase down the group due to increase in their atomic size. The unexpected decrease in the melting points of Sb and Bi is because of their tendency to form 3 covalent bonds instead of 5 covalent bonds due to **inert pair effect**. This results in the weakening the attraction among their atoms thereby lowering their melting points. Bi has still lower melting point than Sb because of its large size. And, as a result, Bi has still weaker interatomic forces than Sb.
- e) Metallic character increases on moving down the group. N and P are non metals, As and Sb are metalloids and Bi is a metal. On moving down the group, the **atomic size** and the **screening effect** of the intervening electrons **increases**. As a result the **ionization enthalpy decreases**. In other words, valence electrons are lost more readily and hence the metallic character increases.
- f) The stability of +5 oxidation state decreases and that of +3 oxidation state increases on moving down the group due to **inert pair effect**.
- g) N is restricted to a maximum covalency of 4 since only 4 orbitals (one s and three p) are available for bonding. That is the reason why N does not form NF_5 or NCl_5 . The heavier elements have **vacant d orbitals** in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PCl_5 and AsF_5 etc.

- h) N differs from the rest of the members of this group (**Anomalous behaviour**) due to its smaller size, high electronegativity, high ionization enthalpy and non availability of d orbitals.
- i) Nitrogen exists as a diatomic molecule. On the contrary, Phosphorus, Arsenic and Antimony form single bonds as P—P, As—As, Sb—Sb. The reason being, Nitrogen has unique ability to form **p pi—p pi** multiple bonds with itself. Heavier elements of this group do not form **p pi—p pi** multiple bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- j) The single N—N bond is weaker than the single P—P bond because of high **interelectronic repulsion** of the non-bonding electrons, owing to the small bond length. As a result, the **catenation** tendency is weaker in nitrogen.
- k) Nitrogen, due to the **absence of d orbitals**, cannot form **d pi—p pi bonds** as the heavier elements can, e.g., $R_3P=O$, $R_3P=CH_2$.
- l) The **reducing character** of the hydrides of group 15 increases in the order: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$. As we move from NH_3 to BiH_3 , the thermal stability of the hydrides decreases (With the increase in size of the central atom, the M—H bond strength decreases). That is, their tendency to liberate hydrogen increases and hence their reducing character increases from NH_3 to BiH_3 . Therefore, NH_3 is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst the given hydrides.
- m) The **basic nature** of the hydrides of group 15 elements decreases as we move from NH_3 to BiH_3 . All the hydrides of group 15 elements behave as **Lewis bases** since they possess a lone pair of electrons on the central atom. As the size of the central atom increases, the **lone pair of electrons occupies a larger volume**. In other words, the electron density on the central atom decreases and consequently its tendency to donate a pair of electrons decreases and hence the basic strength decreases as we move from NH_3 to BiH_3 .
- n) All the trihalides of group 15 elements **except** those of nitrogen are stable. In case of nitrogen, **only NF_3** is known to be **stable**. The instability of trihalides of nitrogen is because of the weakness of N—X bond due to large difference in the size of N and X atoms. Further, since the difference in size of N and F is small, the N—F bond is quite strong. Therefore, NF_3 does not undergo hydrolysis with water, dilute acids or alkalis.
- o) The elements of group 15 have 5 electrons in their respective valence shells. Since it is difficult to lose all 3 or 5 electrons from the valence shell to form E^{+3} or E^{+5} ions, therefore, higher elements have no tendency to form ionic compounds.

Instead, they form covalent compounds by sharing of electrons. **Pentahalides are more covalent than trihalides** because it is difficult for the elements to lose all 5 valence electrons when compared to losing 3 valence electrons.

- p) PH_3 has lower boiling point than NH_3 because unlike NH_3 , PH_3 molecules are not associated through **hydrogen bonding** in liquid state.
- q) Dinitrogen is rather **inert** at room temperature because of the **high** bond enthalpy of N_2 .
- r) NO_2 is an **odd (electron) molecule**, which on **dimerisation** is converted to stable N_2O_4 molecule with even number of electrons.
- s) Some metals like Al, Cr, Ni, and Fe do not dissolve in **conc. HNO_3** because of the formation of a passive film of oxide on the surface (**PASSIVITY**).
- t) White phosphorus is **less stable** and therefore, **more reactive** than red phosphorus under normal conditions because of **angular strain** in the P_4 molecule where the angles are only 60° (Each P in P_4 molecule is sp^3 hybridized). Like white phosphorus, **red phosphorus** also exists as P_4 tetrahedra but these are joined together through covalent bonds to give a **polymeric structure**. **White phosphorus** consists of **discrete** tetrahedral P_4 molecule.
- u) PCl_5 , in gaseous and liquid phases has a trigonal bipyramidal structure. The 3 **equatorial** bonds are equivalent, while the 2 **axial** bonds are **longer** than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.
- v) Phosphorus has empty d orbitals. In the **solid state**, PCl_5 exists as an **ionic** solid, $[\text{PCl}_4]^+[\text{PCl}_6]^-$ in which the cation is tetrahedral and the anion is octahedral.
- w) In oxoacids of phosphorus, the P—H bonds are **not** ionisable. Only those H atoms which are attached to oxygen in P—OH form are **ionisable**. Thus, H_3PO_3 and H_3PO_4 are **dibasic** and **tribasic**, respectively as the structure of H_3PO_3 has two P—OH bonds and H_3PO_4 three.
- x) **INERT PAIR EFFECT**: In case of elements of 4th, 5th and 6th period of the p block elements which come after d block elements, the electrons present in the intervening d and f orbitals do not shield the s electrons of the valence shell effectively. As a result, **ns^2 electrons** remain more tightly held by the nucleus and hence **do not** participate in bonding. This is called **inert pair** effect. As a result,

down the group a higher oxidation state becomes less stable with respect to the lower oxidation state.

Group 16 Elements

- a) Group 16 elements have **lower** ionization enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 elements have **extra stable** half filled p orbitals electronic configuration.
- b) The electron gain enthalpy of O is less than S because of the **compact nature** of O atom. As a result of which, the **electron-electron repulsions** in the relatively small 2p- subshell are comparatively large and hence the incoming electrons are not accepted with the same ease as in case of other elements.
- c) Oxygen exists as a **diatomic** gas at room temperature while other elements exist as **octaatomic** solids. Due to small size and high electronegativity, O atom forms **p pi—p pi multiple bonds** with other O atom to form O=O molecule. The intermolecular forces of attraction between oxygen molecules are weak van der Waals' forces and hence oxygen exists as a diatomic gas at room temperature. However, the rest of the elements of this group, do not form **p pi—p pi multiple bonds** due to their large size and hence do not exist as diatomic molecules. Instead, they prefer to form single bonds and exist as octaatomic solids.
- d) S—S bonds are stronger as compared to O—O bonds. Therefore, S has a stronger tendency for **catenation** than oxygen. The O—O bond is weak due to small size, the lone pairs of electrons on oxygen atoms repel the bond pair of O—O bond to a greater extent than the lone pairs of electrons on the sulphur atoms in S—S bond.
- e) The anomalous behaviour of oxygen is due to its **small size** and **high electronegativity**. As a result of small size and high electronegativity, strong **hydrogen bonding** exists between water molecules which are not found between hydrogen sulphide molecules. It is due to this reason that water is a liquid and hydrogen sulphide is a gas.
- f) Oxygen atom has a very small size. The **absence of d orbitals** in oxygen **limits** its **covalency** to 4 and in practice, **rarely exceeds 2**. Since electronegativity of oxygen is very high, it shows only negative oxidation state as **-2** except in the case of OF₂ (Oxygen difluoride) where its oxidation state is **+2**. Since oxygen does not have d orbitals in its valence shell, the 2p electrons on excitation have to go to 3s orbital. So the electron has to be excited from K shell to L shell which requires too much energy. Therefore, the electrons in oxygen do not get unpaired. Therefore, oxygen behaves as a divalent element only.

- g) Except oxygen, all other elements of group 16 show positive oxidation states of +2, +4 and +6 due to **promotion of electrons** to vacant d orbitals. However, due to **inert pair effect**, the stability of +6 oxidation state decreases down the group. Thus, +6 oxidation state is most stable in case of S and least stable in case of Po.
- h) Fluorine is the strongest oxidizing agent. Therefore, an element shows its maximum oxidation state in its compound with fluorine.**
- i) The **acid strength** of hydrides of group 16 elements increases down the group from H_2O to H_2Te . The atomic size increases down the group. As a result, the distance between the central atom and hydrogen increases and the cleavage of X—H bond (where, X= O, S, Se, Te, etc.) becomes easier. Therefore, the tendency to **release** hydrogen as proton increases down the group.
- j) Hydrides of group 16 elements except that of oxygen (water) are reducing agents. The **reducing character** increases from H_2S to H_2Te . This is due to the decrease in their **thermal stability**. As the size of the X atom in H_2X (where, X=O, S, Se, Te, etc.) increases, the bond H—X becomes weaker and thus breaks on heating.
- k) SF_6 is extremely **stable** due to **steric** reasons. Because of its **inertness** and good **dielectric properties**, it is used as a gaseous insulator in high voltage generators and switch gears.
- l) A binary compound of oxygen with another element is called **oxide**. An oxide that combines with water to give an acid is termed **acidic oxide**. e.g. SO_2 , CO_2 , NO_2 , N_2O_5 , Cl_2O_7 . The oxides which give a base with water are known as **basic oxides**. e.g. Na_2O , CaO , BaO . **Oxides of some metals in higher oxidation state also have acidic character**. e.g. Mn_2O_7 , CrO_3 , V_2O_5 . Metal oxides which show characteristics of both acidic as well as basic oxides are called as **amphoteric oxides**. e.g. ZnO , Al_2O_3 . Oxides which are neither acidic nor basic are called **neutral oxides**. e.g. CO , NO , H_2O , N_2O .
- m) Formation of ozone from oxygen is an **endothermic process**, it is necessary to use a **silent electric discharge** in its preparation to prevent its decomposition.
- n) Ozone is **thermodynamically unstable** with respect to oxygen since its decomposition into oxygen results in the liberation of heat (**change in enthalpy is negative**) and an increase in entropy (**change in entropy is positive**). These two effects reinforce each other, resulting in **large negative Gibb's energy change** for its conversion into oxygen. Therefore, **high concentrations of ozone can be dangerously explosive**.

- o) Ozone undergoes decomposition easily to give nascent oxygen. Therefore, ozone acts as a powerful **oxidizing agent**. NO released from the exhaust systems of supersonic jet aeroplanes can get oxidized in the presence of ozone to NO_2 . This reaction is believed to be one of the causes of **depletion of ozone layer**.
- p) The chemical reactions of **sulphuric acid** are as a result of the following **characteristics**: low volatility, strong acidic character, strong affinity for water and ability to act as an oxidizing agent.
- q) Sulphuric acid is a **dense oily liquid**. Care should be taken while preparing dilute sulphuric acid from conc. sulphuric acid because conc. sulphuric acid has a strong **affinity for water**. When water is added to sulphuric acid, a large amount of **heat is produced**, which may **spurt** the acid **out** of the container. Therefore, dilute sulphuric acid is prepared by adding slowly and carefully conc. sulphuric acid to water with constant stirring.
- r) **Greater the value of dissociation constant (K_a), stronger is the acid.**

Group 17 Elements

- a) The halogens have the **smallest** atomic radii in their **respective periods** due to **maximum** effective nuclear charge.
- b) Halogens have **little tendency** to lose electron. Thus, they have very **high** ionization enthalpy. Due to **increase** in atomic size, ionization enthalpy decreases down the group.
- c) Halogens have **maximum** negative electron gain enthalpy in the corresponding periods. This is because they have a strong tendency to **accept** an additional electron to attain the electronic configuration of the nearest noble gas. As the size of the halogens increases, the electron gain enthalpies become less and less negative. However, electron gain enthalpy of Fluorine is less negative than that of Chlorine. This is due to the **small size** of fluorine atom. As a result of which strong **electron-electron repulsions** are presenting the relatively compact 2p orbitals of fluorine. Thus, **amongst halogens, Cl has the most negative electron gain enthalpy**.
- d) Due to **small size** and **higher nuclear charge**, each halogen has the **highest** electronegativity in its period.
- e) All the **halogens** are **coloured**. The colour is due to the fact that their molecules **absorb** light in the **visible region** as a result of which their **electrons** are **excited**

- to higher energy levels while the **remaining light** is **transmitted**. **The colour of halogens is actually the colour of the transmitted light.**
- f) The enthalpy of dissociation of F_2 is **smaller** when compared to that of Cl_2 . A reason for this anomaly is the relatively **large electron-electron repulsion** among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2 .
- g) Fluorine is a **stronger oxidizing agent** than chlorine. It is due to: low enthalpy of dissociation of F—F bond and high hydration enthalpy of fluoride ion.
- h) The fluorine atom has **no** d orbitals in its valence shell and therefore **cannot** expand its octet. Therefore, it exhibits **only -1** oxidation state.
- i) F **does not** show positive oxidation states while other halogens do (**+1, +3, +5, +7**). This happens when halogens **share** their unpaired electrons with more electronegative elements like **F** and **O** in interhalogens, oxides and oxoacids. Since F is the most electronegative element known, it **cannot** share its electron with an element more electronegative than itself and hence it cannot show an oxidation state of +1.
- j) The relative **oxidizing power of halogens** can be illustrated by their **reactions with water**. Fluorine oxidizes water to oxygen. Chlorine and Bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of Iodine with water is non-spontaneous. Iodide ion is oxidized by oxygen in acidic medium.
- k) **Anomalous properties of fluorine**: Ionization enthalpy, electronegativity, bond dissociation enthalpy and electrode potentials are all **higher** for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, melting point and boiling point and electron gain enthalpy are quite **lower** than expected.
- l) The **anomalous behaviour** of fluorine is **due to** its small size, highest electronegativity, low F—F bond dissociation enthalpy and non-availability of d orbitals in valence shell.
- m) Most of the reactions of fluorine are **exothermic** due to the small and strong bond formed by it with other elements.
- n) HF is a liquid due to strong **hydrogen bonding**.

- o) Fluorine forms **two oxides**- OF_2 and O_2F_2 . However, only **OF_2 is thermally stable** at 298 K. Both are strong **fluorinating agents**. O_2F_2 oxidizes Pu to PuF_6 and the reaction is used in removing Pu as PuF_6 from spent nuclear fuel.
- p) If a metal exhibits more than one oxidation state, the halides in **higher oxidation state** will be **more covalent** than the one in lower oxidation state. For e.g. SnCl_4 , PbCl_4 , SbCl_5 and UF_6 are more covalent than SnCl_2 , PbCl_2 , SbCl_3 and UF_4 respectively.
- q) **Chlorine water** on standing **loses its yellow colour** due to the formation of HCl and HOCl . **HOCl so formed, gives nascent oxygen** which is responsible for oxidizing and **bleaching** properties of chlorine. Bleaching effect of chlorine is **permanent**.
- r) Due to high electronegativity and small size, fluorine forms **only one** oxoacid, HOF .
- s) When two different halogens react with each other, **interhalogens compounds** (XX') are formed. **As the ratio between radii of X and X' increases, the number of atoms per molecule also increases**. Thus, Iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 .
- t) Interhalogen compounds are **more** reactive than halogens (except fluorine). This is because $\text{X—X}'$ bond in interhalogens is **weaker** than X—X bond in halogens except F—F bond.

Group 18 Elements

- a) All noble gases have general electronic configuration, **ns^2np^6** . All noble gases are **monoatomic**. Since their valence shell is completely filled, they react with a few elements only under certain conditions. Due to **stable electronic configuration** these gases exhibit **very high ionization enthalpy** and they have **no** tendency to accept electrons (therefore have large positive values of electron gain enthalpy).
- b) Noble gases have **low** boiling points because being monoatomic they have **no** interatomic forces **except** weak dispersion forces (due to which they are **liquefied** at very low temperatures).
- c) Noble gases are **slightly soluble in water** as a result of **dipole-induced dipole interaction**. When water, a polar molecule, comes near a noble gas, it induces dipole in the noble gas by distorting or polarizing its otherwise symmetrical electron cloud.

- d) He and Ne do **not** contain d orbitals in their valence shells and hence their electrons **cannot** be promoted to higher energy levels. Therefore, He and Ne do **not** form compounds with fluorine.
- e) PtF_6 oxidizes O_2 to O_2^+ . So, **Bartlett** thought that PtF_6 should also oxidize Xe to Xe^+ because the **ionization enthalpies** of O_2 (1175 kJ/mol) and Xe (1170 kJ/mol) are **quite close**. This is how noble gas compounds were discovered.
- f) Fluorine and oxygen are the **most electronegative** elements and hence are **very reactive**. Therefore, they form compounds with noble gases particularly Xe.

d and f Block Elements

- a) A transition element is defined as the one which has **incompletely filled d orbitals** in its ground state or in any one of its oxidation states. The electronic configuration of these elements is $(n-1) d^{1 \text{ to } 10} ns^{1 \text{ to } 2}$. With partly filled d orbitals these elements exhibit certain **characteristic properties** such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour.
- b) Zn, Cd and Hg have **full d¹⁰** configuration in their ground state as well as in their common oxidation states and hence, are **not** regarded as transition metals.
- c) **Half and completely filled sets of orbitals are relatively more stable.**
- d) In the formation of metallic bonds $(n-1) d$ and ns electrons participate. Presence of **unpaired d electrons** and relatively **low ionization energies** of transition elements are responsible for the formation of metallic bonds. **Greater** the number of unpaired d electrons, **stronger** is the bonding due to the overlapping of unpaired electrons between different metal atoms.
- e) High melting points of transition metals are attributed to the involvement of greater number of electrons from $(n-1) d$ in addition to the ns electrons in the interatomic metallic bonding. **The strength of metallic bond depends upon the number of unpaired d electrons. Greater is the number of unpaired electrons stronger is the metallic bonding.** Because of stronger metallic bonding, transition elements have high melting points.
- f) Heat required to break the metal lattice to get free atoms is called **enthalpy of atomization**. Transition elements exhibit **high** enthalpies of atomization. This is because of **large number** of unpaired electrons in their atoms which results in **stronger** interatomic attraction and hence **stronger** bonding between atoms.

- g) The atomic radii of the second and third transition series are almost the same. This is due to **lanthanoid contraction** (imperfect shielding of one electron by another in the 4f orbital). Thus, Zr and Hf have very similar and chemical properties.
- h) There are **no** unpaired electrons in Zn, Cd and Hg. Thus, they are **soft** and have **low melting points**. Hg is a liquid at ordinary temperature.
- i) In a particular series, the metallic strength increases upto the middle with increasing number of unpaired electrons (upto d^5 configuration). The melting points decrease after middle because of increasing pairing of electrons. The lower melting point of Mn (I transition series), Tc (II transition series) and Re (III transition series) can be explained on the basis that they have **exactly half filled d orbitals** (stable electronic configuration). Therefore, the electrons are held tightly by the nucleus so that the delocalization is less resulting in weaker metallic bonds.
- j) As we move along a transition series from left to right, the density increases. Atomic radius decreases on moving across the period. Hence, the **atomic volume decreases**. Since, the **atomic mass increases** on moving across the period, the **density increases**.
- k) It is **difficult** to obtain oxidation state **greater than two** for Cu, Ni and Zn because of the **high** values of third ionization enthalpies of these elements.
- l) **Third** ionization enthalpy of Mn is high because the third electron has to be removed from the stable half filled 3d orbital ($3d^5$).
- m) Third ionization enthalpy for change from Fe^{2+} to Fe^{3+} is **very small** because loss of third electron gives the **stable** configuration of $3d^5$.
- n) The first ionization enthalpies of 5d elements are higher as compared to those of 3d and 4d elements. This is because the **weak shielding** of nucleus by 4f electrons in 5d elements results in **greater effective nuclear charge** acting on the outer valence electrons.
- o) **Transition metal ions with incompletely filled d orbitals will be coloured.**
- p) **The large positive E^0 value for Mn^{3+}/Mn^{2+} shows that Mn^{2+} is much more stable than Mn^{3+} (Mn^{3+} can be reduced to Mn^{2+}). **Negative value of E^0 for Cr^{3+}/Cr^{2+} shows that Cr^{2+} is less stable than Cr^{3+} (Cr^{2+} can be oxidized to Cr^{3+}).****

- q) When a magnetic field is applied to substances, **paramagnetic** substances are **attracted** in the magnetic field. Many of the transition metal ions are paramagnetic. Paramagnetism arises from the **presence of unpaired electrons** in the **d orbitals**.
- r) Transition metals form **coloured ions** due to the **presence of unpaired d electrons**. As a result, light is absorbed in the visible region to cause excitation of unpaired d electrons (**d—d transition**) and colour observed corresponds to the **complementary colour** of the light absorbed. Cu^+ , Zn^{2+} , Cd^{2+} are **colourless** due to the absence of unpaired d electrons.
- s) **Cu^{2+} (aq) is more stable than Cu^{1+} (aq)**. This is due to the much **more** negative standard enthalpy of hydration value of Cu^{2+} (aq) than Cu^{1+} (aq), which more than compensates for the second ionization enthalpy of copper.
- t) **Many of the transition metals and their compounds are used as catalysts.** One of the reasons provided is that, transition element with **varying oxidation states** may form **intermediate compounds** with one of the reactants. These intermediates provide a **new path with lower activation energy**. Further, they get decomposed on reaction with the other reactant regenerating the catalyst. Another reason given is that, transition metal **provides** a suitable **large surface area** with valencies on which the reactants are **adsorbed**. As a result, the **concentration** of the **reactants** on the surface of the catalyst **increases**, which **increases the rate of the reaction**.
- u) **The transition metals form a large number of complex compounds.** This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation.
- v) **Alloy formation is due to almost similar sizes of transition metals.** As a result, the transition metal atoms can replace each other in crystal lattice. Alloys are generally harder, have higher melting points and more resistant to corrosion than the individual metals.
- w) **Transition metals form interstitial compounds.** Small atoms like H, C or N can be trapped inside the crystal lattices of metals. These compounds are usually non-stoichiometric and are neither typically ionic nor covalent. E.g. TiC , Mn_4N , Fe_3H etc.
- x) **Disproportionation of an oxidation state:** When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation.

- y) **Lanthanoid contraction:** The regular decrease in the atomic and ionic radii with increasing atomic number is known as lanthanoid contraction. As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f subshell, there is **imperfect shielding** of one electron by another in this subshell due to the shapes of these f orbitals. **The imperfect shielding is unable to counterbalance the effect of the increased nuclear charge.** Lanthanoid contraction causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. As a result, these elements occur together in nature which makes the separation of the elements in the pure state difficult.
- z) The ionization enthalpies of early actinoids are **lower** when compared to the ionization enthalpies of the early lanthanoids. When 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons will therefore, be more effectively shielded from the nuclear than the 4f electrons of the corresponding lanthanoids. **Because the outer electrons are less firmly held, they are available for bonding in the actinoids.**

Coordination Compounds

- a) The number of coordinating or ligating groups present in a ligand is called the **denticity** of that ligand. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate ligand**. Ligand which can ligate through two different atoms is called **ambidentate ligand** (e.g. NO_2^- and SCN^- ions).
- b) The **coordination number** of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. The coordination number of the complex ions, $[\text{PtCl}_6]^{2-}$, $[\text{Ni}(\text{NH}_3)_4]^{2+}$, $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ are 6, 4, 6 and 6 respectively.
- c) **It is important to note that the coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.**
- d) Complexes in which a metal is bound to only one kind of donor groups are known as **homoleptic** complexes. e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$. Complexes in which a metal is bound to more than one kind of donor groups are known as **heteroleptic** complexes. e.g. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

- e) **2004 IUPAC Recommendations**: Ligands will be sorted alphabetically irrespective of charge. Name of anionic ligands will end with- ido so that chloro would become chlorido etc.
- f) Optical isomers are mirror images that cannot be superimposed on one another. These are called **enantiomers**.
- g) **Linkage isomerism** arises in a coordination compound containing ambidentate ligand.
- h) **Coordination isomerism** arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
- i) **Ionization isomerism** arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.
- j) **Solvate isomerism** (hydrate isomerism) arises when water is involved as a solvent. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.
- k) In the formation of a complex, if **inner d orbitals** are used in hybridization (d^2sp^3), the complex is called an **inner orbital complex** or **low spin complex** or **spin paired complex**. An **outer orbital** or **high spin** or **spin free complex** is one which uses the **outer d orbitals** in hybridization (sp^3d^2).
- l) The arrangement of ligands in order of their increasing CFSE values is known as **spectrochemical series**. The ligands with small CFSE values are called **weak field ligands**, whereas those with large value of CFSE are called **strong field ligands**.
- m) **Colour in coordination compounds**: When ligands approach a transition metal ion, the degenerate d orbitals split into 2 sets- one with lower energy and the other with higher energy. When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of the light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

- n) **It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For e.g. removal of water from $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating renders it colourless. Similarly, anhydrous copper sulphate is white, but copper sulphate pentahydrate is blue in colour.**

SOME IMPORTANT QUESTIONS

[I] SOME QUESTIONS BASED ON INERT PAIR EFFECT

1. Bi is a strong oxidizing agent in the pentavalent state (or) Pentavalent Bi is a strong oxidizing agent.
2. +2 oxidation of Pb is more stable than +4 oxidation state.
3. PbCl_4 is less stable than SnCl_4 , but PbCl_2 is more stable than SnCl_2 .
4. BiCl_3 is more stable than BiCl_5 .
5. The stability of +5 oxidation state decreases and that of +3 state increases down the group 15.
6. The stability of +6 oxidation state decreases down the group 16 and the stability of +4 oxidation state increases.
7. Tin (II) is a reducing agent whereas Pb (II) is not.

[II] SOME QUESTIONS BASED ON PRESENCE OR ABSENCE OF d- ORBITALS

1. Nitrogen does not form pentahalide.
2. PCl_5 is known but NCl_5 is not known.
3. NCl_3 gets readily hydrolysed while NF_3 does not.
4. F exhibits only -1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states.
5. ClF_3 exists but FCl_3 does not.
6. He and Ne do not form compounds with fluorine.
7. $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not (R= Alkyl group).
8. OF_6 compound is not known.
9. Oxygen shows covalency of two while sulphur shows covalency upto six.
10. Oxygen does not show oxidation states of +4 and +6 like sulphur.
11. PCl_5 is ionic in the solid state.

[III] SOME QUESTIONS BASED ON PROPERTIES OF TRANSITION ELEMENTS

1. Transition metals and many of their compounds show paramagnetic behaviour.
2. The enthalpies of atomization of the transition metals are high.
3. The transition metals generally form coloured compounds.
4. Transition metals and their many compounds act as good catalyst.

5. Transition metals form a large number of interstitial compounds.
6. Transition metals form alloys readily.
7. Transition elements show variable oxidation states.
8. Sc forms no coloured ions, yet it is regarded as a transition element.
9. Cr is a typical hard metal while Hg is a liquid.
10. The paramagnetic character in 3d transition series elements increases upto Mn and then decreases.
11. Mn exhibits more number of oxidation states than V.
12. Zn^{2+} salts are white while Ni^{2+} salts are blue.
13. Though Cu, Ag and Au have completely filled sets of d orbitals yet they are considered as transition metals.
14. Mn (II) shows maximum paramagnetic character amongst the bivalent ions of the first transition series.
15. Cr^{3+} exhibits paramagnetism while Sc^{3+} does not.
16. Third ionization enthalpy of Mn is unexpectedly high.
17. The second ionization enthalpies of both Cr and Cu are higher than those of the next element.
18. Transition metal fluorides are ionic in nature whereas bromides and chlorides are usually covalent in nature.
19. The largest number of oxidation states is exhibited by the elements in the middle of the first row transition elements.
20. The +2 oxidation state of Mn is quite stable while the same is not true for iron.
21. Cr^{2+} is reducing and Mn^{3+} oxidizing when both have d^4 configuration.
22. Cu^+ ion is not stable in aqueous solution.
23. In the series Sc (Z=21) to Zn (Z=30), the enthalpy of atomization of Zn is the lowest.
24. There is irregular variation of ionization enthalpies (first and second) in first series of the transition elements.
25. +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.
26. Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.
27. The d^1 configuration is very unstable in ions.
28. The lower oxide of transition metal is basic, the highest is acidic.
29. A transition metal exhibits higher oxidation states in oxides and fluorides.
30. The highest oxidation state is exhibited in oxo-anions of a metal.
31. A transition series contains 10 elements.
32. Copper (I) compounds are white and diamagnetic while copper (II) compounds are coloured and paramagnetic.
33. V_2O_5 acts as a catalyst.
34. In the transition series with an increase in atomic number, the atomic radius does not change very much.
35. Ni^{2+} ion has lower magnetic moment than Co^{2+} .
36. Fe has higher melting point than Cu.

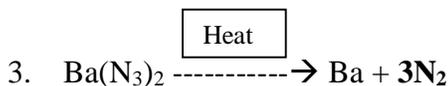
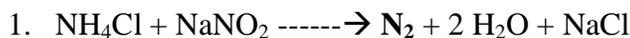
[IV] SOME QUESTIONS BASED ON LANTHANOID CONTRACTION

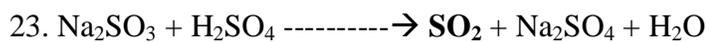
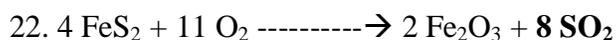
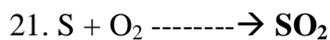
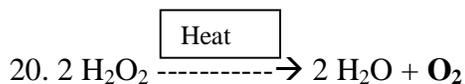
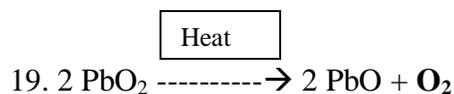
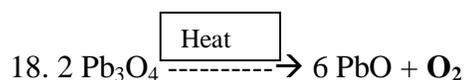
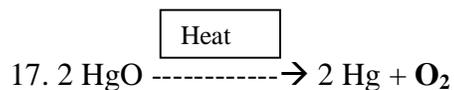
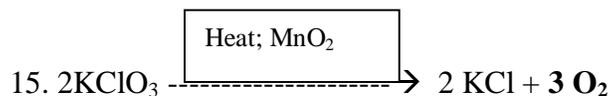
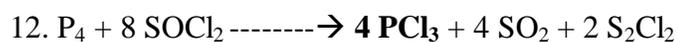
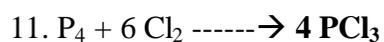
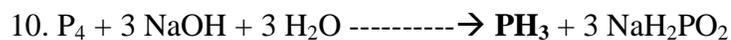
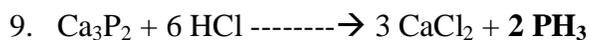
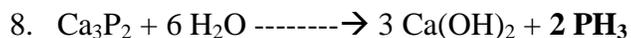
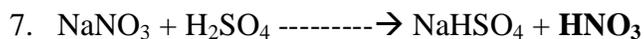
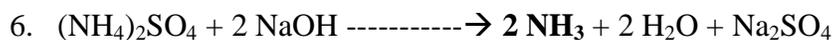
1. Zr and Hf exhibit similar chemical properties.
2. Nb and Ta exhibit similar chemical properties.
3. Zr and Hf occur together in minerals and they exhibit similar properties.
4. Second and third transition series elements show similar size.
5. The properties of third transition series are very similar to second transition series.
6. Separation of lanthanoid elements is difficult.
7. The size of the trivalent cations in the lanthanoid series decreases steadily as the atomic number increases.

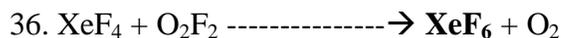
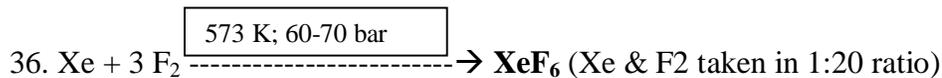
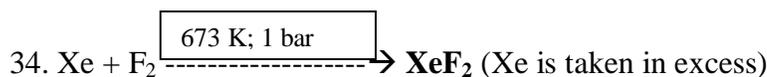
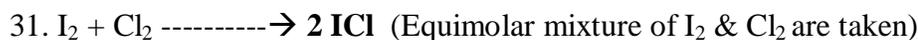
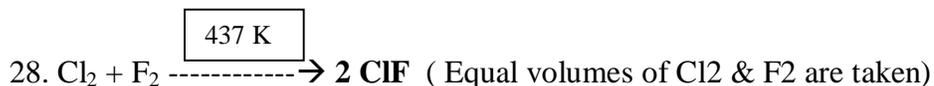
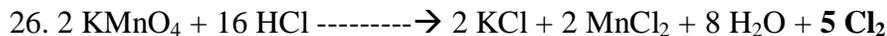
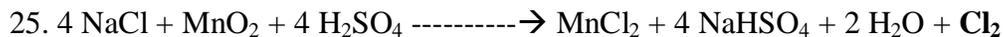
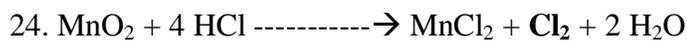
[V] SOME QUESTIONS BASED ON COMPARISON OF REDUCTION POTENTIAL VALUES

1. E^0 for Mn^{3+}/Mn^{2+} couple is much more positive than for the Fe^{3+}/Fe^{2+} .
2. The E^0 values in respect of the electrodes of Cr (Z=24), Mn (Z=25) and Fe (Z=26) are: $Cr^{3+}/Cr^{2+} = -0.4V$, $Mn^{3+}/Mn^{2+} = +1.5V$, $Fe^{3+}/Fe^{2+} = +0.8V$. On the basis of the above information compare the feasibilities of further oxidation of their +2 oxidation states.
3. For M^{2+}/M and M^{3+}/M^{2+} systems, E^0 values for some metals are as follows: $Cr^{2+}/Cr = -0.9V$; $Cr^{3+}/Cr^{2+} = -0.4V$; $Mn^{2+}/Mn = -1.2V$; $Mn^{3+}/Mn^{2+} = +1.5V$; $Fe^{2+}/Fe = -0.4V$; $Fe^{3+}/Fe^{2+} = +0.8V$. Using this data comment upon: a) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+} , and b) the ease with which Fe can be oxidized when compared to the similar process for either Cr or Mn metals.
4. E^0 value for Cr^{3+}/Cr^{2+} is $-0.40V$ while for Mn^{3+}/Mn^{2+} it is $+1.50V$. Cr^{2+} is a strong reducing agent while Mn^{2+} is not.

SOME IMPORTANT PREPARATIONS







IUPAC NAMES OF SOME COORDINATION COMPOUNDS

1. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2] \text{Cl}_3$ = Tetraamminediaquacobalt(III) chloride
2. $[\text{Cr}(\text{en})_3] \text{Cl}_3$ = Tris(ethane-1,2-diamine)chromium(III) chloride

3. $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^- = \text{Amminebromidochloridonitrito-N-platinate(II)}$
4. $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2 = \text{Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate}$
5. $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 = \text{Iron(III) hexacyanoferrate(II)}$
6. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 = \text{Pentaamminechloridocobalt(III) chloride}$
7. $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] = \text{Potassium trioxalatoferrate(III)}$
8. $\text{K}_2[\text{PdCl}_4] = \text{Potassium tetrachloridopalladate(II)}$
9. $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl} = \text{Diamminechlorido(methylamine)platinum(II) chloride}$
10. $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 = \text{Hexaamminecobalt(III) sulphate}$
11. $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+} = \text{Pentaamminenitrito-O-cobalt(III) ion}$
12. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]_3[\text{Cr}(\text{CN})_6] = \text{Tetraamminedichloridocobalt(III)hexacyanochromate(III)}$
13. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] = \text{Sodium pentacyanonitrosoniumferrate(II)}$
14. $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}] = \text{Potassium pentacyanonitrosylcobaltate(II)}$
15. $\text{Na}_2[\text{CrF}_4\text{O}] = \text{Sodium tetrafluoridooxochromate(IV)}$
16. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3 = \text{Tetraaquadichloridochromium(III) nitrate}$
17. $(\text{NH}_4)_3[\text{Cr}(\text{SCN})_6] = \text{Ammonium hexathiocyanato-S-chromate(III)}$
18. $\text{Na}_2[\text{Cr}(\text{CH}_3\text{COO})_4(\text{en})] = \text{Sodium ethylenediaminetetraacetatochromate(II)}$
19. $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl} = \text{Pentaamminecarbonatocobalt(III) chloride}$
20. $[\text{Pt}(\text{py})_4][\text{PtCl}_4] = \text{Tetrapyridineplatinum(II)tetrachloridoplatinate(II)}$

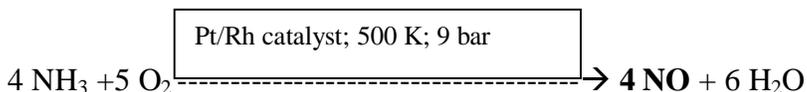
COMMERCIAL PREPARATION OF SOME COMPOUNDS

1. HABER'S PROCESS OF MANUFACTURE OF NH₃:

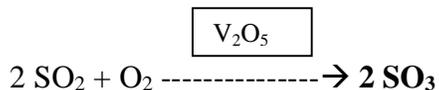


The **optimum conditions** for the production of ammonia are: **Pressure**= 200 atm;
Temperature= About 700 K; **Catalyst**: Iron oxide; **Promoters**: K₂O and Al₂O₃

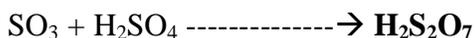
2. OSTWALD'S PROCESS OF MANUFACTURE OF NITRIC ACID:

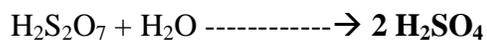


3. CONTACT PROCESS OF MANUFACTURE OF SULPHURIC ACID:

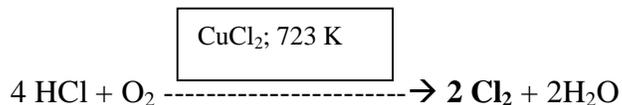


The **optimum conditions** for the production of SO₂ are: **Pressure**= 2 bar;
Temperature= About 720 K; **Catalyst**= V₂O₅

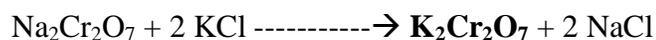
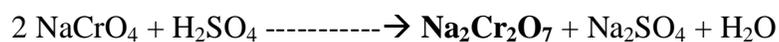
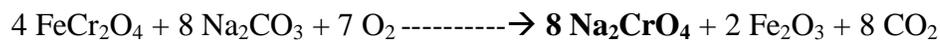




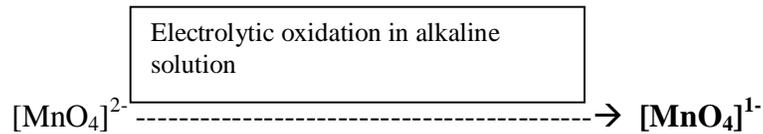
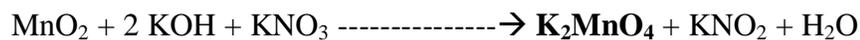
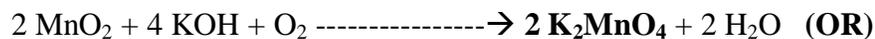
4. DEACON'S PROCESS:



5. PREPARATION OF POTASSIUM DICHROMATE:



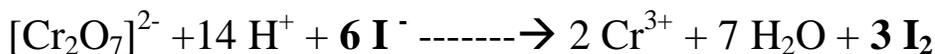
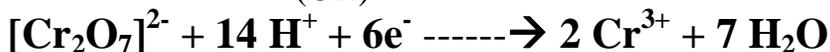
6. PREPARATION OF POTASSIUM PERMANGANATE:



SOME OXIDIZING PROPERTIES OF POTASSIUM DICHROMATE



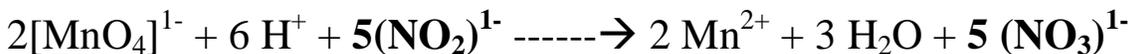
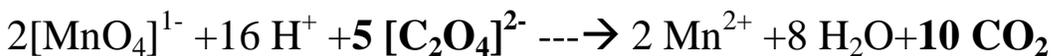
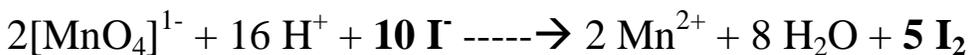
(OR)



SOME OXIDIZING PROPERTIES OF POTASSIUM PERMANGANATE



(OR)



SOME ADDITIONAL IMPORTANT TOPICS

1. Main Postulates of Werner's Theory: i) Metals show two types of valences in coordination compounds- Primary & Secondary. ii) The Primary valences are normally ionizable and are satisfied by negative ions. iii) The Secondary valences are non ionizable and are satisfied by neutral molecules or negative ions (Ligands). iv) The ions/groups bound by the secondary linkages to the metal have characteristics spatial arrangements (coordination polyhedra) corresponding to different coordination numbers.
2. **Double salts** dissociate completely into simple ions when dissolved in water. However, **complex ions** such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4[\text{Fe}(\text{CN})_6]$, do not dissociate into Fe^{2+} and $(\text{CN})^{-1}$ ions. Mohr's salt and Potash alum are double salts.
3. Some limitations of VBT: i) It does not explain the **colour** exhibited by coordination compounds. ii) It does not distinguish between **weak** and **strong ligands**. iii) It does not give a quantitative interpretation of the **thermodynamic** or **kinetic stabilities** of coordination compounds. iv) It does not give quantitative interpretation of **magnetic data**.
4. CRYSTAL FIELD THEORY: The CFT considers the metal—ligand bond to be ionic arising purely from **electrostatic interactions** between the metal ion and the ligand. Ligands are treated as **point charges** in case of anions and as **dipoles** in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion are **degenerate**. The degeneracy of the d orbitals is **lifted** when ligands approach the metal atom/ion. This is due to **ligand-electron metal-electron repulsions**. It results in **splitting** of the d orbitals into lower energy and higher energy orbitals. The pattern of splitting depends upon the nature of the crystal field.
5. Some limitations of CFT: i) CFT does not take into account the **covalent character** of bonding between the ligand and the central atom. ii) In CFT, ligands are assumed as point charges. Hence, it means that anionic ligands should exert the greatest splitting effect. But, the **anionic ligands** are found at the **low end** of the **spectrochemical series**.
6. Synergic bonding interactions in a carbonyl complex: The bond between metal and CO in metal carbonyls is strong due to the following reasons: i) The M—C **sigma bond** is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant d orbital of the metal. ii) The M—C **pi bond** is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant **antibonding** orbital of CO. Thus, the Metal to Ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

7. Stability of a complex & factors affecting stability of a complex ion: Stability of a complex in solution means the measure of resistance to the replacement of a ligand by some other ligand. i) Greater the charge and smaller the size of the central metal ion, more is its charge density and greater will be the stability of the complex. ii) For different metal ions with same charge, stability of the complexes increases as the size decreases. iii) More the basicity of the ligand more is the stability of the complex. iii) For anionic ligands the complexes are more stable if ligand has greater charge and smaller size. iv) Chelating ligands form more stable complexes.
8. Chelate effect: When a polydentate ligand forms a coordination complex having a ring structure, it is called chelate complex. A **chelate complex** is always more **stable** than the complex formed by monodentate ligands. The stabilization of coordination compound due to chelation is called chelate effect.
9. Mischmetall: It is an alloy which consists of a lanthanoid metal (about 95%), Fe (about 5%) and traces of S, C, Ca and Al. Mischmetall is used in Mg based alloy to produce bullets, shell and lighter flint.
10. **Permanganate titrations in presence of HCl are unsatisfactory since HCl is oxidized to Cl₂.**
11. Effect of increasing pH on Potassium dichromate solution: In aqueous solution, [Cr₂O₇]²⁻ ions are in equilibrium with [CrO₄]²⁻ ions.

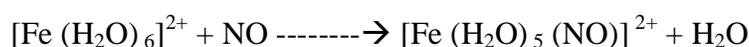
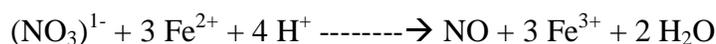


On adding an alkali, the H⁺ ions are used up, and the reaction shifts in the forward direction (**Le Chatelier Principle**), producing a yellow chromate solution. On the other hand, when an acid is added, the concentration of H⁺ ions is increased, and the reaction shifts in the reverse direction, producing an orange dichromate solution.

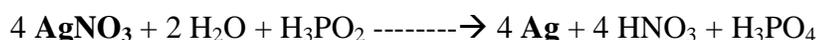
12. The +3 oxidation states of La (Z= 57), Gd (Z= 64) and Lu (Z= 71) are especially stable because they have empty, half filled and completely filled 4f subshell respectively. All lanthanoids except La³⁺ and Lu³⁺ contain unpaired electrons and hence are paramagnetic. The stable oxidation state of lanthanoids is +3. Ions with oxidation state +2 or +4 tend to change to +3 by loss or gain of electrons. Thus, Ce⁴⁺ is a good oxidizing agent i.e., it readily gains electron to change to Ce³⁺.
13. In actinoids, **5f, 6d and 7s** subshells are **close in energy**. Hence, they show a **large number of oxidation states**. Moreover, they are radioactive with short half-lives. Hence, their properties cannot be studied easily. As we move across

actinoids series, we see a gradual decrease in the size of atoms or M^{3+} ions with increasing atomic number. This is called actinoid contraction. The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

14. **Brown Ring Test:** This test depends upon the ability of Fe^{2+} to reduce nitrates to NO, which reacts with Fe^{2+} to form a **brown coloured complex**. An aqueous solution of nitrate salt is taken in a test tube. Freshly prepared ferrous sulphate solution is added into it. Now, conc. sulphuric acid is slowly added through the sides of the test tube. A **brown ring** is formed at the junction of two layers- aqueous layer and acid layer.



15. H_3PO_2 is a good **reducing agent** as it contains **two** P—H bonds. It reduces $AgNO_3$ to metallic silver.



16. Ozone is obtained when silent electric discharge is passed through pure, cold and dry dioxygen taken in an ozonizer. Sparkless electric discharge is used in its preparation, since it produces less heat and thus prevents the decomposition of ozone back to oxygen.

17. **Main postulates of VBT:**

i) The metal ligand bond arises by donation of pair of electrons by ligands to the central metal atom. **ii)** To accommodate these electrons the metal ion must possess requisite number of vacant orbitals of equal energy. These orbitals of the metal atom undergo hybridization to give hybrid orbitals. **iii)** Sometimes the unpaired (n-1)d orbitals pair up before bond formation making (n-1)d orbitals vacant. The central metal atom makes available number of d-orbitals equal to its co-ordination number. **iv)** The metal ligand bonds are thus formed by donation of electron pairs by the ligands to the empty hybridized orbitals. These bonds are equal in strength and directional in nature. **v)** Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3 (or $sp^3 d^2$), dsp^2 and sp^3 hybridization respectively.

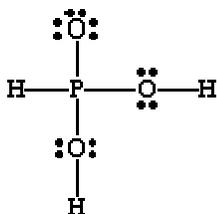
18. Ammonia gas is highly **soluble** in water. Its aqueous solution is **weakly basic** due to the formation of OH^- ions.

19. **White phosphorus** is poisonous. It is insoluble in water but soluble in CS_2 . It glows in dark (Chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 . It is more reactive when compared to red phosphorus. **Red phosphorus** is obtained by heating white phosphorus at 573 K

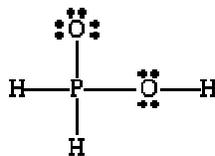
in an inert atmosphere for several days. It is non poisonous and insoluble in water as well as in CS_2 . It does not glow in the dark.

20. **Black phosphorus** has two forms- **alpha** black phosphorus and **beta** black phosphorus. Red phosphorus is heated in a sealed tube at 803 K, when alpha black phosphorus is obtained. Beta black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.
21. White phosphorus dissolves in boiling NaOH solution in an atmosphere of CO_2 giving phosphine. When pure, PH_3 is non inflammable but becomes inflammable due to the presence of P_2H_4 or P_4 vapours. To **remove** these impurities phosphine is absorbed in **HI** to form phosphonium iodide which on treating with **KOH** gives off phosphine.
22. P in PH_3 is sp^3 hybridized. It has **3 bond pairs and one lone pair** of electrons. Since, lp-bp repulsions are stronger than bp-bp repulsions, the tetrahedral angle decreases. As a result, PH_3 is pyramidal. In the case of PH_4^+ ion there are **4 bond pairs and no lone pairs** of electrons. Thus, PH_4^+ assumes tetrahedral geometry.
23. Beta sulphur is stable above 369 K and transforms into alpha sulphur below it. Alpha sulphur is stable below 369 K and transforms into beta sulphur above this. At 369 K both the forms are stable. This temperature is called **transition temperature**.
24. The composition of bleaching powder is $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
25. **Aqua regia** is 3 parts conc. HCl and 1 part conc. HNO_3 . It is used for dissolving noble metals.

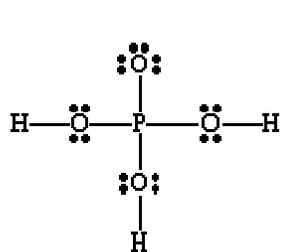
STRUCTURES OF SOME IMPORTANT COMPOUNDS



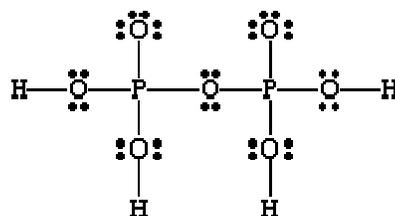
Phosphorous acid, H_3PO_3



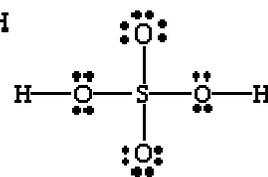
Hypophosphorous acid, H_3PO_2



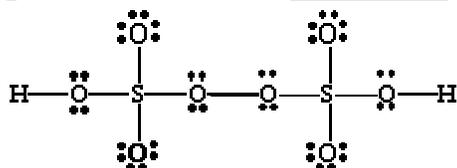
Phosphoric acid, H_3PO_4



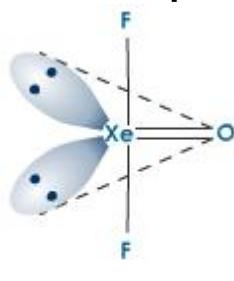
Diphosphoric acid, $H_4P_2O_7$
(pyrophosphoric acid)



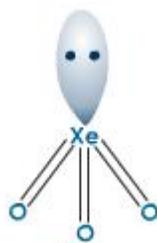
Sulfuric Acid, H_2SO_4



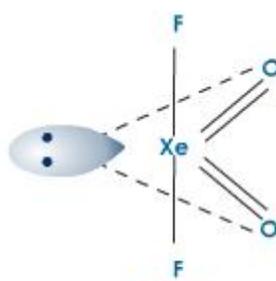
Peroxodisulfuric acid, $H_2S_2O_8$



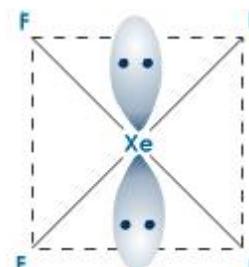
$XeOF_2$
T-shaped



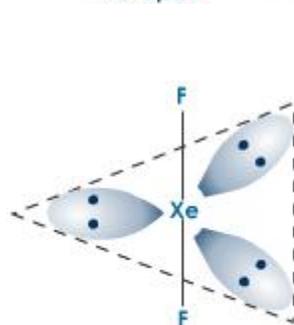
XeO_3
Trigonal pyramidal



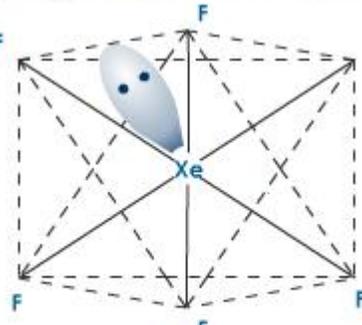
XeO_2F_2
Distorted trigonal bipyramidal



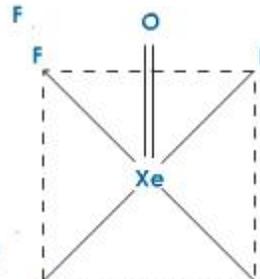
XeF_4
Square planar



XeF_2
Linear



XeF_4
Distorted octahedral

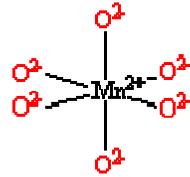


$XeOF_4$
Square pyramidal

CRYSTAL FIELD THEORY

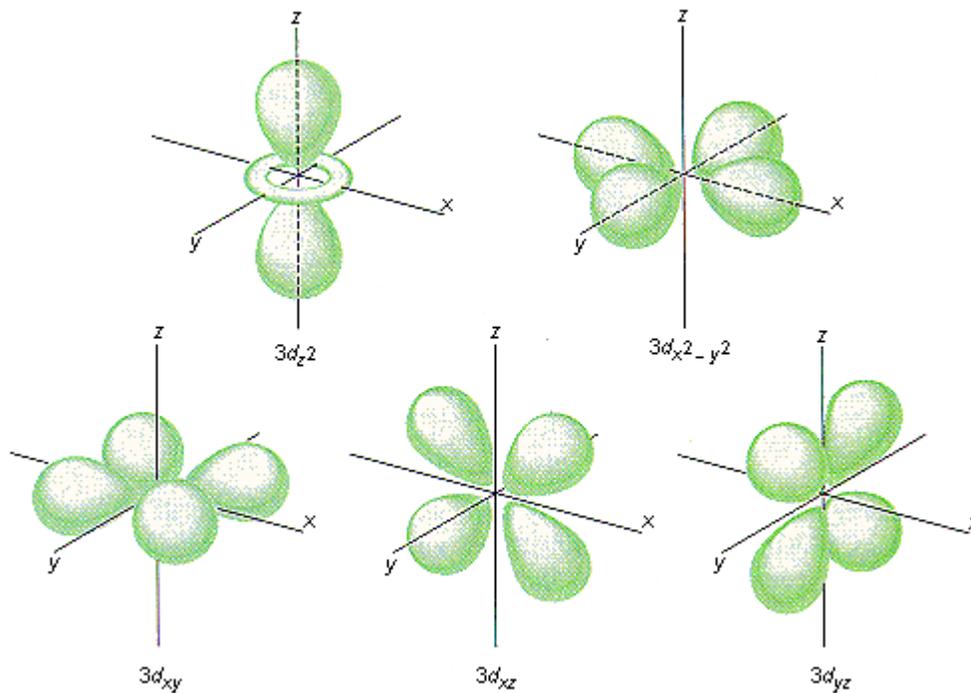
Octahedral Crystal Fields

Each Mn^{2+} ion in manganese (II) oxide is surrounded by six O^{2-} ions arranged toward the corners of an octahedron, as shown in the figure below. MnO is therefore a model for an *octahedral* complex in which a transition-metal ion is coordinated to six ligands.

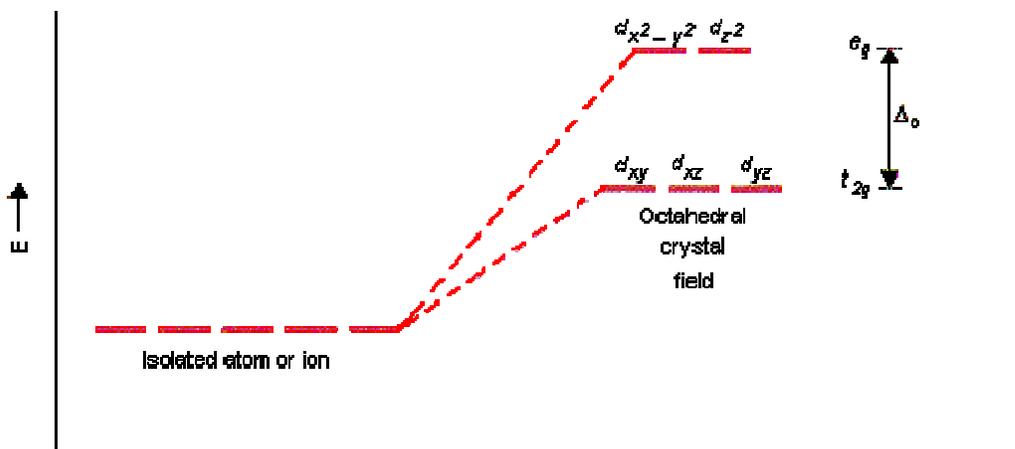


What happens to the energies of the $4s$ and $4p$ orbitals on an Mn^{2+} ion when this ion is buried in an MnO crystal? Repulsion between electrons that might be added to these orbitals and the electrons on the six O^{2-} ions that surround the metal ion in MnO increase the energies of these orbitals. The three $4p$ orbitals are still degenerate, however. These orbitals still have the same energy because each $4p$ orbital points toward two O^{2-} ions at the corners of the octahedron.

Repulsion between electrons on the O^{2-} ions and electrons in the $3d$ orbitals on the metal ion in MnO also increases the energy of these orbitals. But the five $3d$ orbitals on the Mn^{2+} ion are no longer degenerate. Let's assume that the six O^{2-} ions that surround each Mn^{2+} ion define an XYZ coordinate system. Two of the $3d$ orbitals ($3d_{x^2-y^2}$ and $3d_z^2$) on the Mn^{2+} ion point directly toward the six O^{2-} ions, as shown in the figure below. The other three orbitals ($3d_{xy}$, $3d_{xz}$, and $3d_{yz}$) lie between the O^{2-} ions.



The energy of the five 3d orbitals increases when the six O^{2-} ions are brought close to the Mn^{2+} ion. However, the energy of two of these orbitals ($3d_{x^2-y^2}$ and $3d_{z^2}$) increases much more than the energy of the other three ($3d_{xy}$, $3d_{xz}$, and $3d_{yz}$), as shown in the figure below. The crystal field of the six O^{2-} ions in MnO therefore splits the degeneracy of the five 3d orbitals. Three of these orbitals are now lower in energy than the other two.



By convention, the d_{xy} , d_{xz} , and d_{yz} orbitals in an octahedral complex are called the t_{2g} orbitals. The $d_{x^2-y^2}$ and d_{z^2} orbitals, on the other hand, are called the e_g orbitals.

The easiest way to remember this convention is to note that there are three orbitals in the t_{2g} set.

$$t_{2g}: d_{xy}, d_{xz}, \text{ and } d_{yz} \quad e_g: d_{x^2-y^2} \text{ and } d_z^2$$

The difference between the energies of the t_{2g} and e_g orbitals in an octahedral complex is represented by the symbol Δ_o . This splitting of the energy of the d orbitals is not trivial; Δ_o for the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion, for example, is 242 kJ/mol.

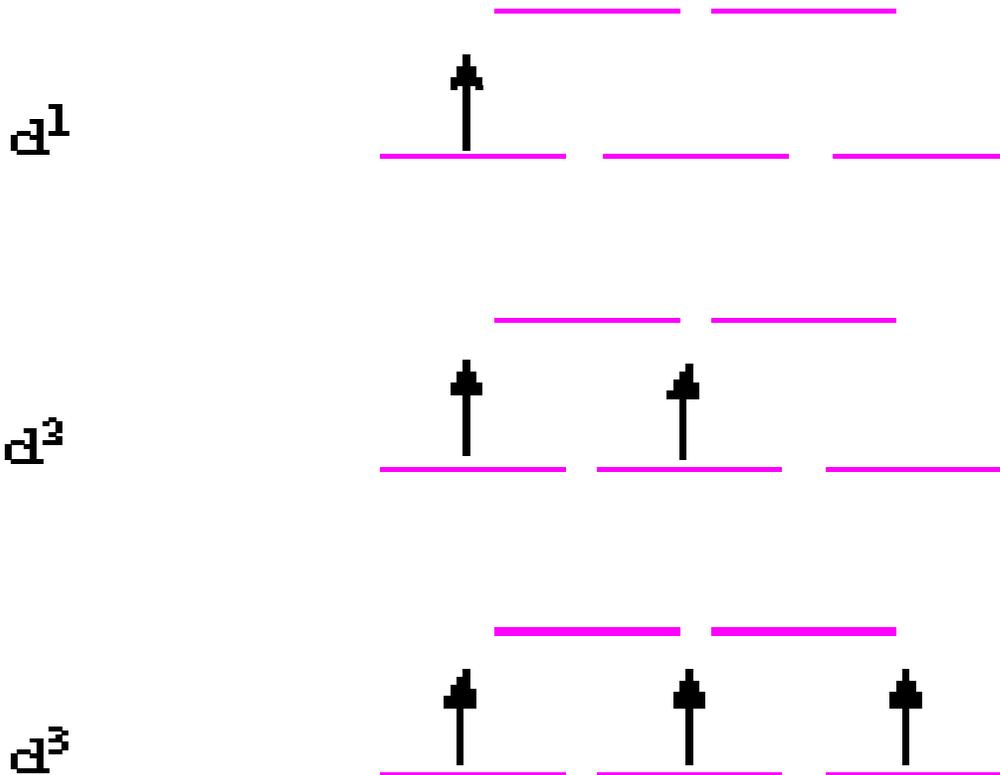
The magnitude of the splitting of the t_{2g} and e_g orbitals changes from one octahedral complex to another. It depends on the identity of the metal ion, the charge on this ion, and the nature of the ligands coordinated to the metal ion.

High-Spin Versus Low-Spin Octahedral Complexes

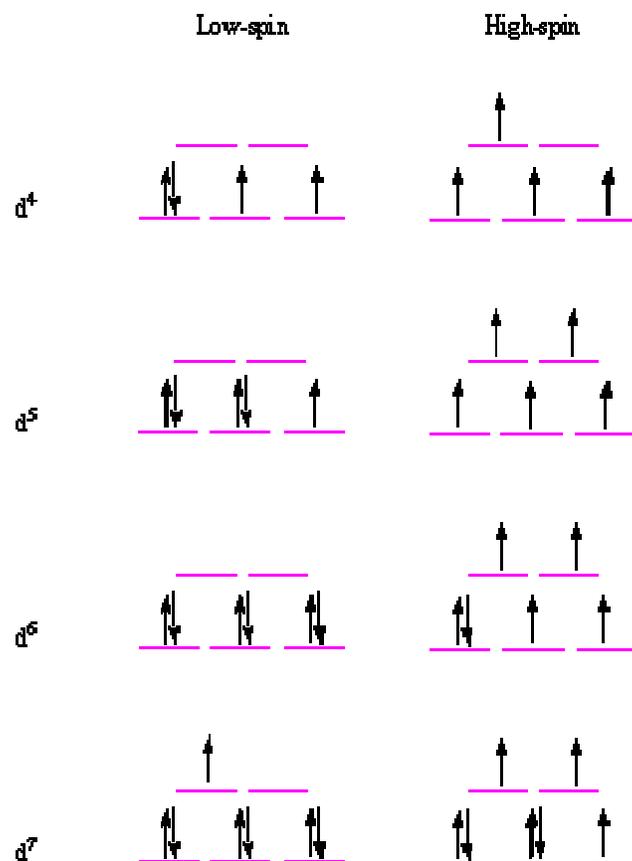
Once we know the relative energies of the d orbitals in a transition-metal complex, we have to worry about how these orbitals are filled. Degenerate orbitals are filled according to Hund's rules.

- One electron is added to each of the degenerate orbitals in a subshell before a second electron is added to any orbital in the subshell.
- Electrons are added to a subshell with the same value of the spin quantum number until each orbital in the subshell has at least one electron.

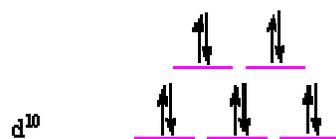
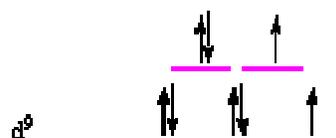
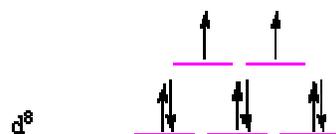
Octahedral transition-metal ions with d^1 , d^2 , or d^3 configurations can therefore be described by the following diagrams.



When we try to add a fourth electron, we are faced with a problem. This electron could be used to pair one of the electrons in the lower energy (t_{2g}) set of orbitals or it could be placed in one of the higher energy (e_g) orbitals. One of these configurations is called high-spin because it contains four unpaired electrons with the same spin. The other is called low-spin because it contains only two unpaired electrons. The same problem occurs with octahedral d^5 , d^6 , and d^7 complexes.



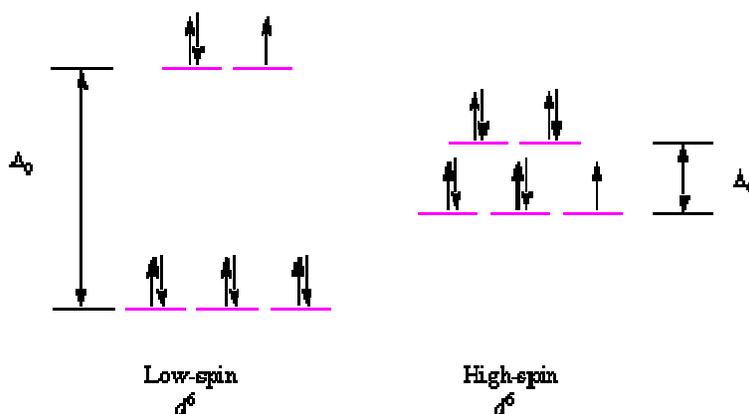
For octahedral d^8 , d^9 , and d^{10} complexes, there is only one way to write satisfactory configurations.



As a result, we have to worry about high-spin versus low-spin octahedral complexes only when there are four, five, six, or seven electrons in the d orbitals.

The choice between high-spin and low-spin configurations for octahedral d^4 , d^5 , d^6 , or d^7 complexes is easy. All we have to do is compare the energy it takes to pair electrons with the energy it takes to excite an electron to the higher energy (e_g) orbitals. If it takes less energy to pair the electrons, the complex is low-spin. If it takes less energy to excite the electron, the complex is high-spin.

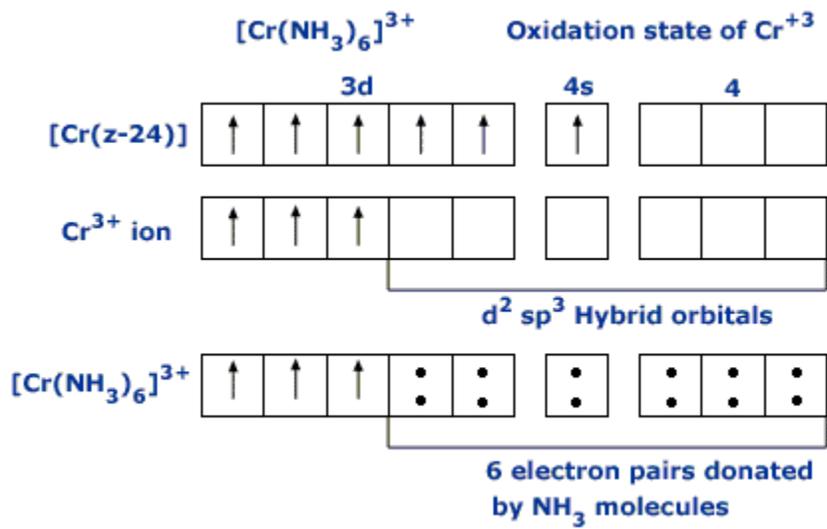
The amount of energy required to pair electrons in the t_{2g} orbitals of an octahedral complex is more or less constant. The amount of energy needed to excite an electron into the higher energy (e_g) orbitals, however, depends on the value of Δ_o for the complex. As a result, we expect to find low-spin complexes among metal ions and ligands that lie toward the high-field end of the spectrochemical series. High-spin complexes are expected among metal ions and ligands that lie toward the low-field end of these series.



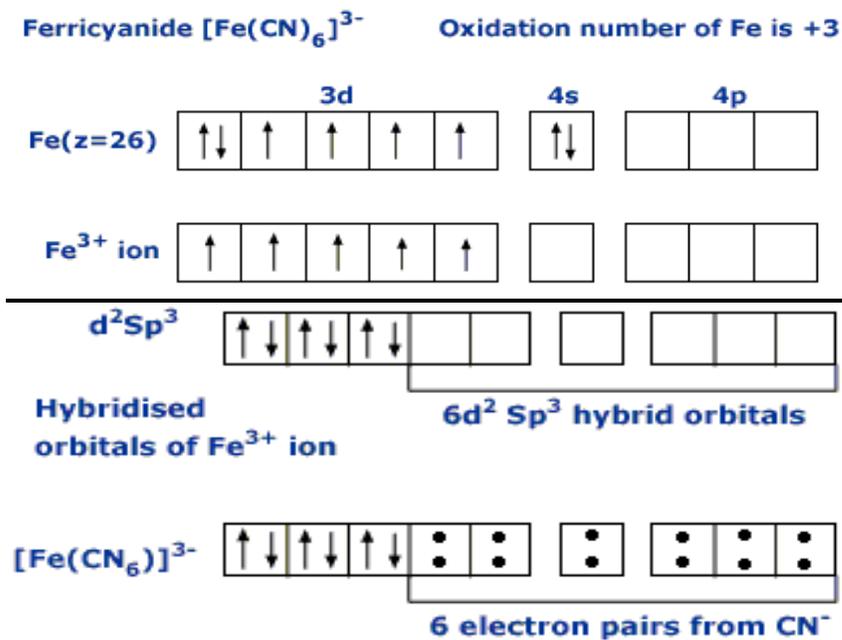
Compounds in which all of the electrons are paired are diamagnetic — they are repelled by both poles of a magnet. Compounds that contain one or more unpaired electrons are paramagnetic — they are attracted to the poles of a magnet. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of unpaired electrons in the complex. We can therefore determine whether a complex is high-spin or low-spin by measuring the strength of the interaction between the complex and a magnetic field.

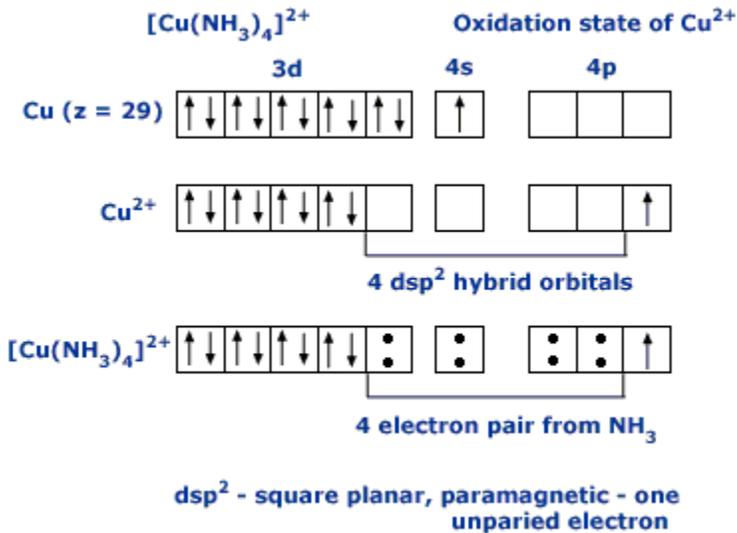
VALENCE BOND THEORY

Paramagnetic and octahedral

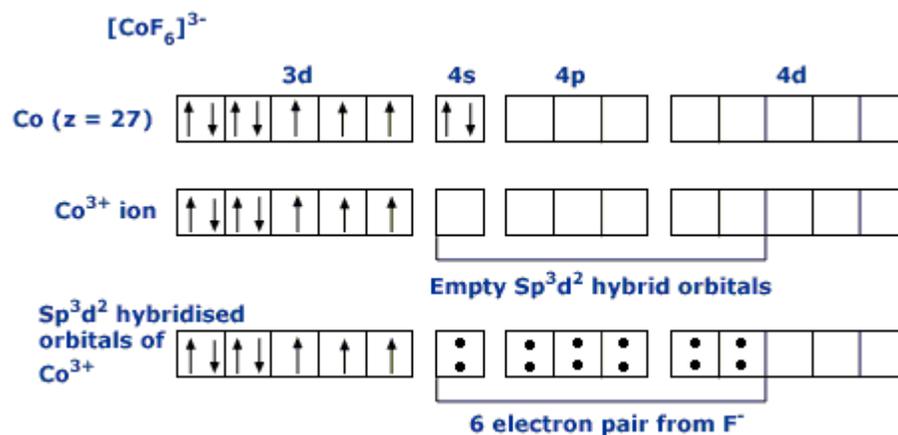


Diamagnetic and octahedral





Paramagnetic and octahedral



SOME DISPROPORTIONATION REACTIONS

1. 3 HNO₂ -----→ HNO₃ + H₂O + 2 NO
2. 4 H₃PO₃ -----→ 3 H₃PO₄ + PH₃
3. 2 Se₂Cl₂ -----→ SeCl₄ + 3 Se
4. 3 Cl₂ + 6 NaOH -----→ 5 NaCl + NaClO₃ + 3 H₂O
5. 6 XeF₄ + 12 H₂O -----→ 4 Xe + 2 XeO₃ + 24 HF + 3O₂
6. 3 [MnO₄]²⁻ + 4 H⁺ -----→ 2 [MnO₄]⁻ + MnO₂ + 2 H₂O

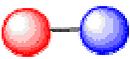
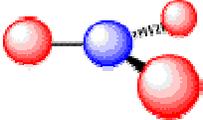
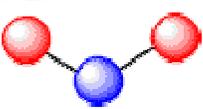
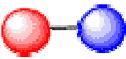
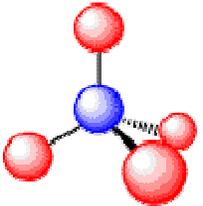
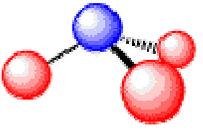
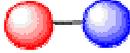
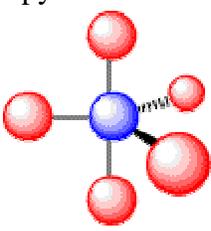
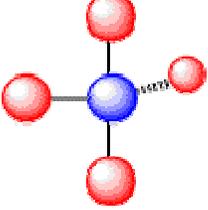
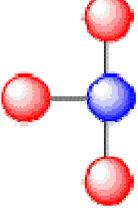
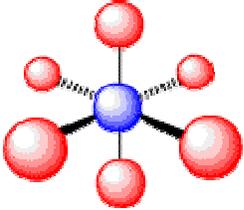
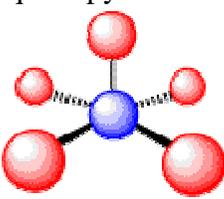
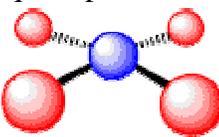
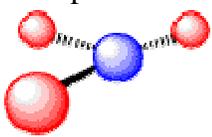
SOME QUESTIONS BASED ON HIGHER ORDER THINKING SKILLS

1. Give an example of oxidation of one halide by another halogen. Why is such a reaction feasible?
2. Comment on the nature of S—O bonds formed in SO₂ molecule.
3. Give one test to detect the presence of SO₂ gas.
4. The increasing order of acidity of oxoacids of chlorine is: HOCl < HOClO < HOClO₂ < HOClO₃
5. SO₂ is a better reducing agent in alkaline medium as compared to that in acidic medium.
6. Oxides of nitrogen have open chain structures while those of phosphorus have closed chain or cage structures. Why is it so?
7. Knowing that the second electron gain enthalpy value of oxygen is more than the first electron gain enthalpy value, account for the formation of a large number of oxides having O²⁻ species and not O⁻.
8. Give reason:
 - a) H₃PO₃ disproportionates while H₃PO₄ does not.
 - b) H₂S acts only as a reducing agent while SO₂ can act both as reducing agent and an oxidizing agent.
9. In the titration of FeSO₄ with KMnO₄ in acidic medium, why is dilute sulphuric acid used instead of HCl?
10. The lowest oxidation state of Mn is basic while the highest is acidic. Explain.
11. Calculate the magnetic moment of Mn in K₄ [Mn (NCS)₆].
12. Eu (II) (Z= 63) is more stable than Pr (II) (Z= 59). Explain.
13. Why the two complexes PtCl₄. 2 NH₃ and PtCl₄. 2 KCl do not give precipitate of AgCl with AgNO₃ solution?

14. Give the electronic configuration of the d orbitals of Ti in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion in an octahedral crystal field.

Coordination Geometry

Both bonding and non-bonding electron pairs determine the structure but we name the **geometry of molecules** according to the arrangement of atoms.

Electron Pairs	0 lone pairs	1 lone pair	2 lone pairs	3 lone pairs
2 e ⁻ pairs	linear 	linear 		
3 e ⁻ pairs	trigonal 	bent 	linear 	
4 e ⁻ pairs	tetrahedral 	trigonal pyramidal 	bent 	linear 
5 e ⁻ pairs	trigonal bipyramidal 	disphenoidal 	T-shaped 	linear 
6 e ⁻ pairs	octahedral 	square pyramidal 	square planar 	T-shaped 

SOME- HOTS- QUESTIONS SOLVED

1. A compound known before Werner's time was Magnus' green salt, having the **empirical** formula $\text{PtCl}_2 \cdot 2\text{NH}_3$. It is actually a coordination compound comprised of a complex cation with 2+ charge and a complex anion with a 2- charge. Propose a formula which describes the coordination for the Magnus' salt and assign the corresponding systematic name.

Magnus's salt is composed of two complex ions, thus, we probably need, at least, 2 Pt in its molecular formula:

Let us try $\text{Pt}_2\text{Cl}_4 \cdot 4\text{NH}_3$:

Since the chloride ligand has a charge of -1, each Pt should be in an oxidation state of 2+. Thus, the cation can be $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and the anion can be $[\text{PtCl}_4]^{2-}$. An acceptable formula for Magnus' salt is: $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, tetraammineplatinum (II) tetrachloroplatinate (II).

2. Give the systematic name for the following:

(a) $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2]$ **tetraaquadihydroxonickel (II)**

(b) $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ **ammonium diamminetetrakisothiocyanatochromate (III)**

(c) $\text{K}_3[\text{Cr}(\text{ox})_3]$ **potassium trioxalatochromium (III)**

(d) $[\text{Cr}(\text{en})_3]^{3+}[\text{Co}(\text{CN})_6]^{3-}$ **tris(ethylenediamine) chromium (III) hexacyanocobaltate (III)**

Please note that the complex ion is always ONE word, do not put spaces between the name of the ligands and the name of the metal ion.

3. Give the chemical formula for the following (use brackets to indicate the coordination sphere):

(a) Hexapyridinecobalt (III) chloride **$[\text{Co}(\text{C}_5\text{H}_5\text{N})_6]\text{Cl}_3$**

(b) Dichlorobis(ethylenediamine) platinum (IV) bromide **$[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Br}_2$ or $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Br}_2$**

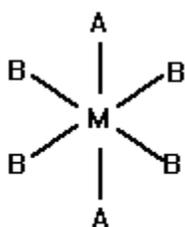
(c) Hexaamminenickel (II) tri (oxalato) chromate (II) $[\text{Ni}(\text{NH}_3)_6]_2[\text{Cr}(\text{C}_2\text{O}_4)_3]$ or $[\text{Ni}(\text{NH}_3)_6]_2[\text{Cr}(\text{ox})_3]$

(d) Tetraamminedichloroplatinum (IV) tetrachloroplatinate (II) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$

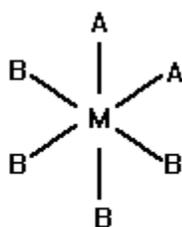
4.

(a) Draw all the geometric isomers for an MA_2B_4 complex.

For complexes that have six ligands, we will assume octahedral geometry.

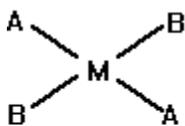


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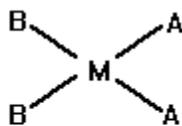


cis

(b) Draw all the geometric isomers for an MA_2B_2 complex in a planar arrangement. For a tetrahedral arrangement, are geometric isomers possible?



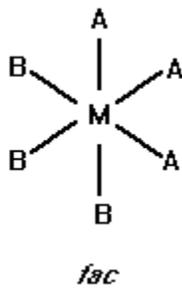
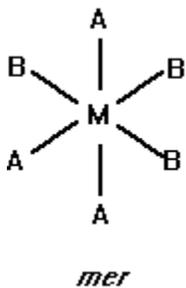
trans



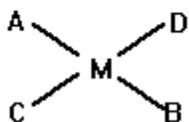
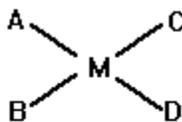
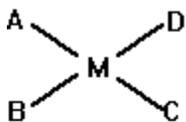
cis

Geometric isomers are not possible in a tetrahedral arrangement because all of the corners of a tetrahedron are adjacent to one another.

(c) Draw all the geometric isomers for an MA_3B_3 complex.

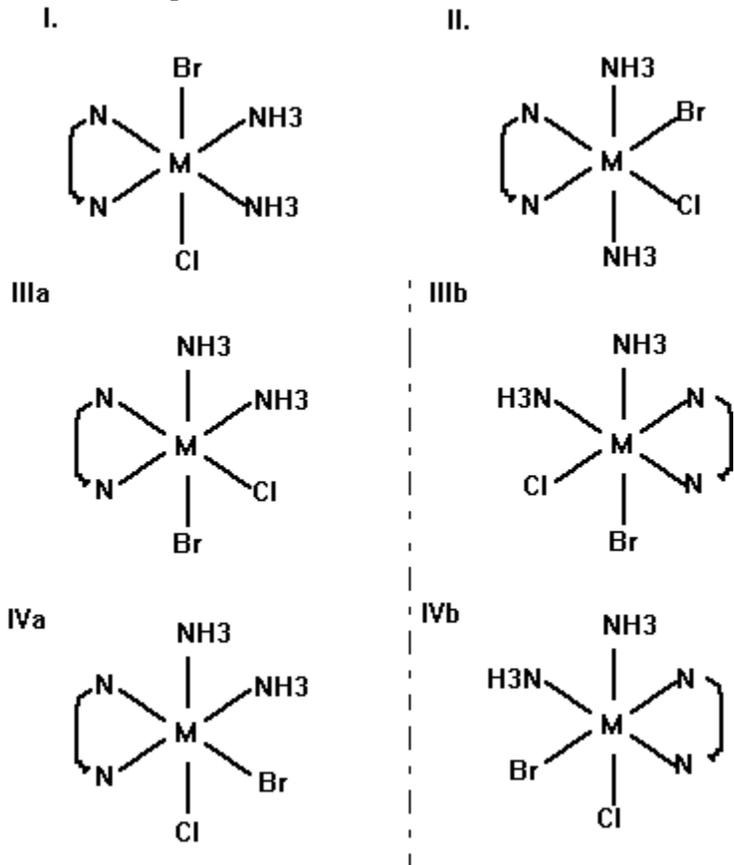


(d) Draw all the geometric isomers for an $MABCD$ complex in a planar arrangement. Are optical isomers possible?



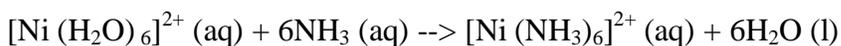
Optical isomers are not possible for square planar complexes because any planar compound will have a mirror plane containing all the atoms and a dissymmetric molecule cannot have a mirror plane of symmetry.

(e) Draw all the geometric isomers of $[\text{Cr}(\text{en})(\text{NH}_3)_2\text{BrCl}]^+$. Which of these isomers also has an optical isomer? Draw the various isomers.

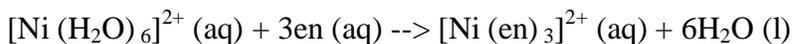


I, II, IIIa and IVa are geometric isomers; I and II have mirror planes, thus, they do not have optical isomers. IIIa/IIIb and IVa/IVb are the pairs of optical isomers.

5. The equilibrium constants (formation constants) for two nickel complexes are shown below:



$$K_f = 4 \times 10^8$$



$$K_f = 2 \times 10^{18}$$

Although the donor atom is nitrogen in both instances, the formation constants are very different. With (en), it is ten orders of magnitude bigger. The generally larger formation constants for polydentate ligands are called the **chelate effect**. Explain this effect using concepts you have seen earlier in this course.

When a solvent is bound as a ligand to a transition metal ion, it loses a great degree of freedom. The degree of randomness or entropy depends heavily on the number of free molecules. When a chelating agent binds to a metal ion, it liberates more than one ligand thereby increasing the number of free molecules and, consequently, the entropy of the system.

6. The following reduction potentials are known for various 3+ first-row transition metal ions in aqueous solution:



Explain why the reduction potential for Fe^{3+} is abnormally low.

H_2O is a weak-field ligand, thus, in all the hexaqua octahedral species of the above ions, the metal is in a high-spin state. Mn^{3+} is d^4 , Fe^{3+} is d^5 , Co^{3+} is d^6 . Only Fe^{3+} has all its d orbitals half-filled which are a relatively stable electronic configuration. Thus, the reduction potential of the Fe (III) ion is less than its neighbors in the periodic table.

7. For each of the following ions, show the d orbital occupancies in both weak and strong octahedral fields. Indicate the total number of unpaired electrons in each case.

(a) Mn^{2+} (b) Zn^{2+} (c) Cr^{3+} (d) Mn^{3+} (e) Co^{3+}

(a) $\text{Mn}^{2+} d^5$

Weak field ($t_{2g}^3 e_g^2$) 5 unpaired electrons

Strong field ($t_{2g}^5 e_g^0$) 1 unpaired electron

(b) $\text{Zn}^{2+} d^{10}$

Weak and strong field ($t_{2g}^6 e_g^4$) 0 unpaired electrons

(c) $\text{Cr}^{3+} d^3$

Weak and strong field ($t_{2g}^3 e_g^0$) 3 unpaired electrons

(d) $\text{Mn}^{3+} d^4$

Weak field ($t_{2g}^3 e_g^1$) 4 unpaired electrons

Strong field ($t_{2g}^4 e_g^0$) 2 unpaired electrons

(e) $\text{Co}^{3+} d^6$

Weak field ($t_{2g}^4 e_g^2$) 4 unpaired electrons

Strong field ($t_{2g}^6 e_g^0$) 0 unpaired electrons

8. What properties of the ligand determine the size of the splitting of the d -orbital energies in the presence of an octahedral arrangement of ligands about a central transition metal ion? Explain.

In the crystal-field theory, it is the negative charge of the ligand which forces the d electrons not to occupy the d orbitals (the e_g orbitals) which are in the direct approach of the ligand. The splitting of the d orbitals would therefore depend on the charge. Thus, the charge of the ligand will affect the size of the splitting of the d orbital energies.

In addition, the shape of the ligand is likewise important. If the ligand looks more like a rod rather than a football, it will have a greater directionality or anisotropy. A ligand that looks more like a cigarette will tend to increase more the energy of the d orbitals in its line of approach.

Crystal field theory cannot explain why some of the ligands that are neutral also lead to stronger fields. One needs a more sophisticated theory which makes use of molecular orbitals on the ligands. If a ligand has empty anti-bonding orbitals which are of the same symmetry as the d orbitals, additional bonding occurs lowering further the energies of the t_{2g} orbitals. On the other hand, if the ligands have filled orbitals such as the halides, additional overlap occurs leading to an increase in the energy of the t_{2g} orbitals.

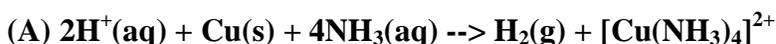
9. $[\text{NiCl}_4]^{2-}$ is more likely to be tetrahedral while $[\text{Ni}(\text{CN})_4]^{2-}$ is more likely to be square planar. Explain.

One advantage a tetrahedral arrangement has over a square planar one is space. For this reason, most first row transition metals prefer tetrahedral while the second and third-row transition metals prefer square planar. Square planar is preferred because of the higher splitting of the d orbitals which is advantageous when the

metal ion does not have filled d orbitals. The Crystal Field Stabilization Energy (CFSE) derived from the splitting of the d orbital energies is greater for square planar arrangement. In a tetrahedral arrangement, no pair of ligands is pointing at one specific d orbital. Thus, for first-row atoms such as Ni^{2+} (a d^8 species), tetrahedral arrangement will be preferred if the ligands are large and weak-field. If the ligands are small (more rod-like) and are strong-field, the planar arrangement will be preferred. The chloride ion is large and it is a weak-field ligand so tetrachloronickelate (II) is tetrahedral. The cyanide ion is small and it is a strong-field ligand so tetracyanonickelate (II) will probably be square planar.

10. A Cu electrode is immersed in a solution that is 1.00 M in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and 1.00M in NH_3 . When the cathode is a standard hydrogen electrode, the emf of the cell is found to be 0.08 V. What is the formation constant for $[\text{Cu}(\text{NH}_3)_4]^{2+}$?

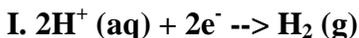
The process is:



$$E = E^0 - \frac{RT}{nF} (\ln Q)$$

$$Q = 1; E = E^0 = 0.08 \text{ V}$$

The above process (A) can be written as (I+II+III):



The reduction potentials relate to each other:

$$E_A = E_I + E_{II} + E_{III}$$

E_A is known from the experiment, 0.08 V.

E_I is 0.00 V (hydrogen reference)

E_{II} is -0.337 V (the negative of the standard reduction potential of Cu (II))

Thus, E_{III} should be 0.417 V.

$$E^0 = (0.0592/2) \log K_f$$

$$\log K_f = 2 (0.417)/0.0592$$

$$K_f = 1.2 \times 10^{14}$$

SOME MORE –HOTS- QUESTIONS SOLVED

1. Werner also studied the electrical conductance of aqueous solutions containing a series of platinum (IV) complexes having the general formula $\text{Pt}(\text{NH}_3)_x\text{Cl}_4$, where x is an integer that varied from 2 to 6. His results can be summarized as:

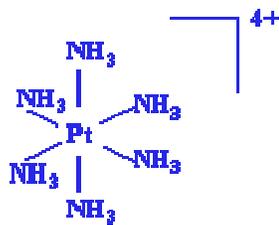
<i>Formula of Complex</i>	<i>Number of ions produced upon complete dissociation</i>
$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$	5
$\text{Pt}(\text{NH}_3)_5\text{Cl}_4$	4
$\text{Pt}(\text{NH}_3)_4\text{Cl}_4$	3
$\text{Pt}(\text{NH}_3)_3\text{Cl}_4$	2
$\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	0

Assuming that Pt(IV) forms octahedral complexes, (a) write the formulas for the five compounds based on the dissociation results, (b) draw three-dimensional sketches of the complexes, (include isomers that are possible), and (c) name each compound.

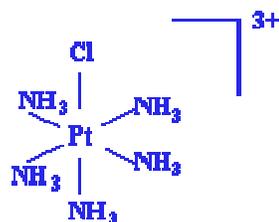
(a)

<i>Formula of Complex</i>	<i>Rewritten Formula (showing the coordinating ligands)</i>
$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$
$\text{Pt}(\text{NH}_3)_5\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$
$\text{Pt}(\text{NH}_3)_4\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
$\text{Pt}(\text{NH}_3)_3\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$
$\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$

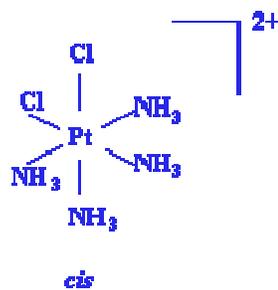
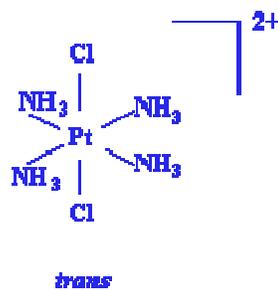
(b) and (c):



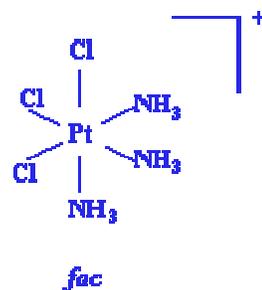
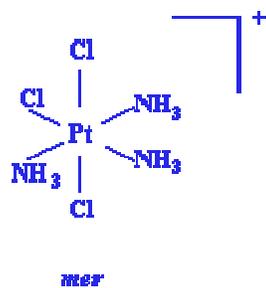
With 4 Cl⁻ as counter ions, hexaammineplatinum (IV) chloride



With 3 Cl⁻ as counter ions, pentaamminechloroplatinum (IV) chloride



With 2 Cl⁻ as counter ions, tetraamminedichloroplatinum (IV) chloride



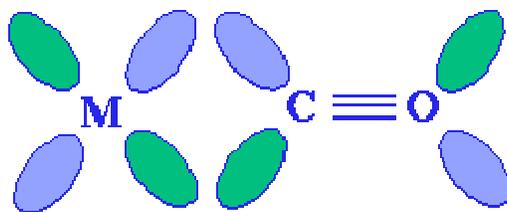
with 1 Cl⁻ as counter ion, triamminetrichloroplatinum(IV) chloride



Diamminetetrachloroplatinum (IV)

2. Crystal Field Theory fails in explaining why a neutral ligand such as CO can cause a very large crystal field splitting. Use Molecular Orbital Theory to explain why the CO ligand leads to a higher crystal field splitting.

In Molecular Orbital Theory, the crystal field splitting is related to the difference between the energy of the t_{2g} and e_g orbitals. The t_{2g} orbitals are essentially nonbonding and are composed of the d_{xz} , d_{yz} and d_{xy} orbitals. The CO molecule contains empty antibonding π^* orbitals. These antibonding orbitals have the same symmetry as the t_{2g} orbitals and since they are empty, these additional overlap (see figure below) will lead to a lowering in energy of the t_{2g} orbitals:



The t_{2g} orbitals lower in energy but the e_g orbitals (since they do not overlap with the π^* orbital) remain the same in energy, thus, leading to an increase in the energy separation between the t_{2g} and e_g orbitals.

4. When Pt has a coordination number of 6, an octahedral geometry is normally assumed. On the other hand, when Pt has a coordination number of 4, a square planar geometry is observed. A coordination compound has the empirical formula $\text{PtBr}(\text{en})(\text{SCN})_2$ and is diamagnetic. In aqueous solution, each unit of this compound produces two complex ions. The ligand ethylenediamine (en) is present only in the cation while Br is present only in the anion. (a) What is the molecular formula of this compound (b) What is the formula of the complex cation? (c) The complex anion? (d) Give the d -electron configuration (using Crystal Field Theory) of the Pt in each of the complex ions.

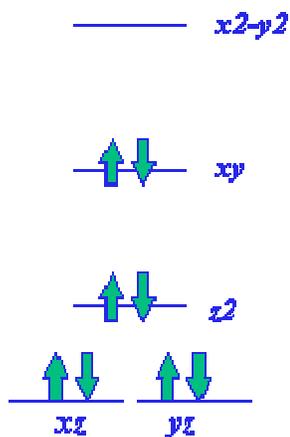
(a) Both Br^- and SCN^- have a charge of negative 1, thus, for the molecule to be neutral, Pt needs a +3 charge. However, this will not be correct since the molecule is diamagnetic. Pt (III) has an odd number of electrons so Pt cannot be diamagnetic if it has a charge of +3. Thus, we will need at least 2 Pt's per molecule. This automatically agrees with the observation that two complex ions are produced. One Pt will be +4, the other +2 (average is then 3). The molecular formula is then $\text{Pt}_2\text{Br}_2(\text{en})_2(\text{SCN})_4$.

In the molecular formula above, from the number of ligands, one can count the number of coordination available for the 2 Pt's. Remember, en is bidentate so each one counts twice. 2 (from the 2Br) + 4 (from 2en) + 4 (from 4SCN) = 10 . With 2 Pt's, this may be 5 for each Pt. A coordination number of 5, however, are not popular among Pt complexes. The more likely solution is that one Pt has a coordination of 4 (therefore, square planar) and the other Pt having a coordination of 6 (octahedral). To solve this problem further, we need to apply Crystal Field Theory. A coordination number of 4 and a square planar geometry (due to the nature of the splitting of the d orbitals in a square planar field) will be preferred by a d^8 central atom. A coordination number of 6 and an octahedral geometry will be preferred by a d^6 central atom (provided that the ligands are strong field ligands). Pt (II) is d^8 and, thus, will be square planar, Pt (IV) is d^6 and, thus, will be octahedral. Pt (II) will be in the complex anion and Pt (IV) will be in the complex cation.

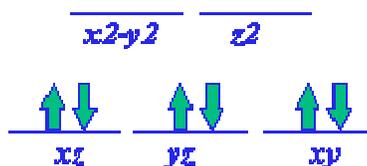
Cation: $[\text{Pt}(\text{en})_2(\text{SCN})_2]^{2+}$

Anion: $[\text{Pt}(\text{Br})_2(\text{SCN})_2]^{2-}$ (cis- and trans- isomers possible)

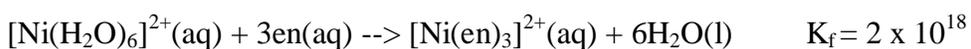
Pt(II) d⁸



Pt(IV) d⁶



6. The equilibrium constants (formation constants) for two nickel complexes are shown below:



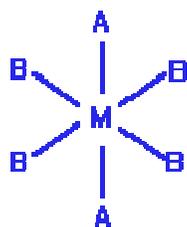
Although the donor atom is nitrogen in both instances, the formation constants are very different. With (en), it is ten orders of magnitude bigger. The generally larger formation constants for polydentate ligands are called the chelate effect. Explain this effect using a concept you have seen earlier in this course.

When a solvent is bound as a ligand to a transition metal ion, it loses a great degree of freedom. The degree of randomness or entropy depends heavily on the number of free molecules. When a chelating agent binds to a metal ion, it liberates more than one ligand thereby increasing the number of free molecules and, consequently, the entropy of the system.

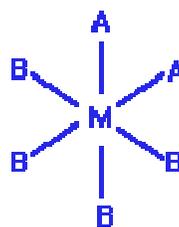
7.

(a) Draw all the geometric isomers for an MA_2B_4 complex.

For complexes that have six ligands, we will assume octahedral geometry.

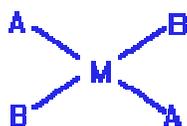


trans

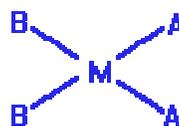


cis

(b) Draw all the geometric isomers for an MA_2B_2 complex in a planar arrangement. For a tetrahedral arrangement, are geometric isomers possible?



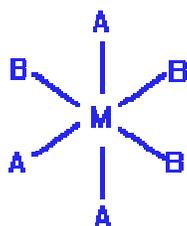
trans



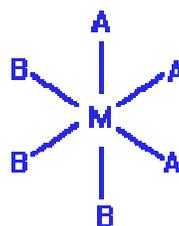
cis

Geometric isomers are not possible in a tetrahedral arrangement because all of the corners of a tetrahedron are adjacent to one another.

(c) Draw all the geometric isomers for an MA_3B_3 complex.

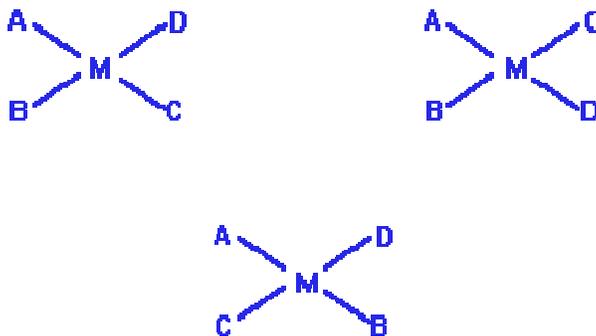


mer



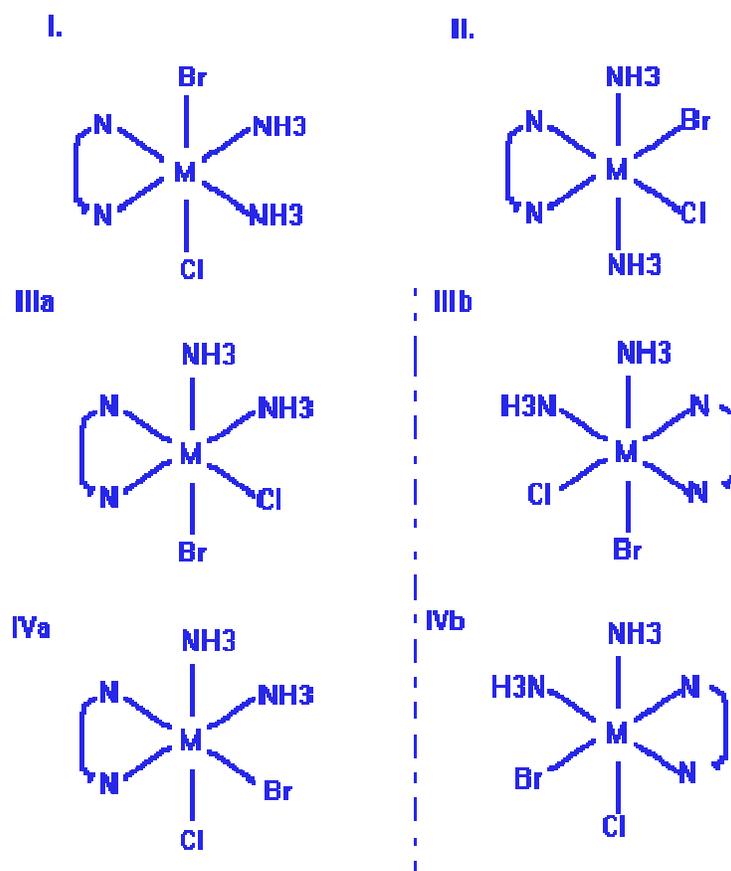
fac

(d) Draw all the geometric isomers for an MABCD complex in a planar arrangement. Are optical isomers possible?



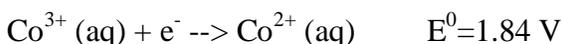
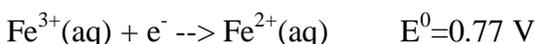
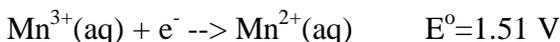
Optical isomers are not possible for square planar complexes because any planar compound will have a mirror plane containing all the atoms and a dissymmetric molecule cannot have a mirror plane of symmetry.

(e) Draw all the geometric isomers of $[\text{Cr}(\text{en})(\text{NH}_3)_2\text{BrCl}]^+$. Which of these isomers also has an optical isomer? Draw the various isomers.



**I, II, IIIa and IVa are geometric isomers;
I and II have mirror planes, thus, they do not have optical isomers.
IIIa/IIIb and IVa/IVb are the pairs of optical isomers.**

8. The following reduction potentials are known for various 3+ first-row transition metal ions in aqueous solution:



Explain why the reduction potential for Fe^{3+} is abnormally low.

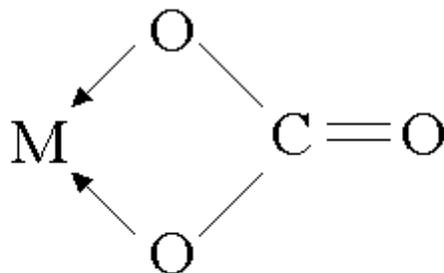
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9. $[\text{NiCl}_4]^{2-}$ is more likely to be tetrahedral while $[\text{Ni}(\text{CN})_4]^{2-}$ is more likely to be square planar. Explain.

One advantage a tetrahedral arrangement has over a square planar one is space. For this reason, most first row transition metals prefer tetrahedral while the second and third-row transition metals prefer square planar. Square planar is preferred because of the higher splitting of the d orbitals which is advantageous when the metal ion does not have filled d orbitals. The Crystal Field Stabilization Energy (CFSE) derived from the splitting of the d orbital energies is greater for square planar arrangement. In a tetrahedral arrangement, no pair of ligands is pointing at one specific d orbital. Thus, for first-row atoms such as Ni^{2+} (a d^8 species), tetrahedral arrangement will be preferred if the ligands are large and weak-field. If the ligands are small (more rod-like) and are strong-field, the planar arrangement will be preferred. The chloride ion is large and it is a weak-field ligand so tetrachloronickelate (II) is tetrahedral. The cyanide ion is small and it is a strong-field ligand so tetracyanonickelate (II) will probably be square planar.

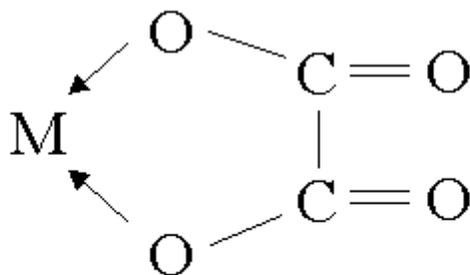
Chelation

In some cases, the ligand has two or more atoms capable of donating a pair of electrons for forming a coordinate covalent bond to a metal atom. If the spatial distance between such atoms is not too close or too far, these atoms may coordinate to the same atom. The first example is the carbonate ion. This ion is an example of a case in which the distance between the two potential donors is too short.



carbonato complex
unstable

The carbonato complex is not stable since a **4-membered ring is highly strained**. **5-membered and 6-membered rings are less strained** as illustrated by the example below.

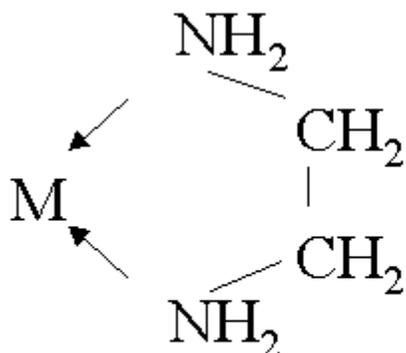


oxalato complex
stable

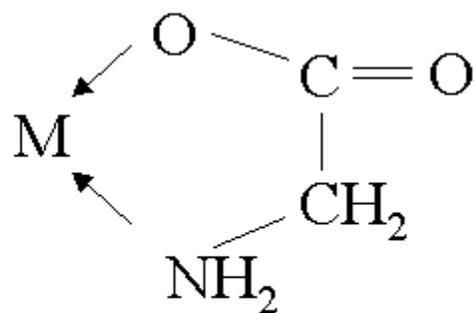
The phenomenon of ring formation by a ligand in a complex is called chelation.

Other examples of chelating agents

Forming 5-membered rings:

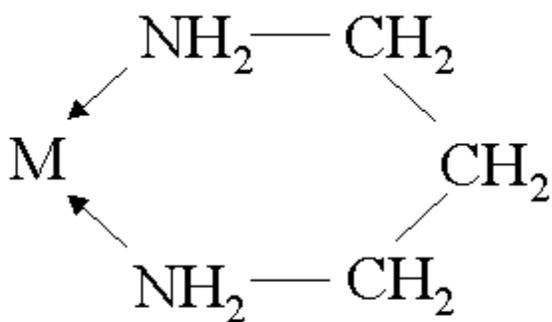


ethylenediamine

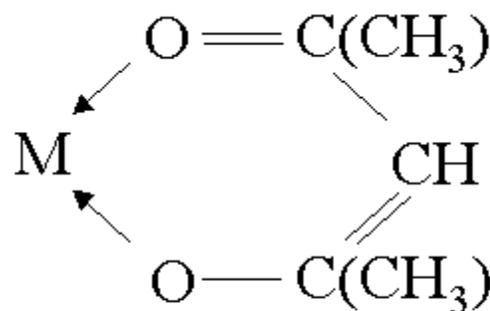


glycinato

Forming 6-membered rings:

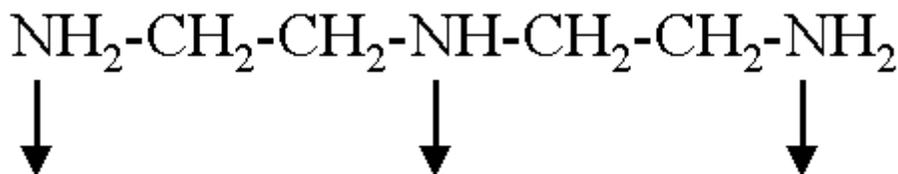


trimethylenediamine

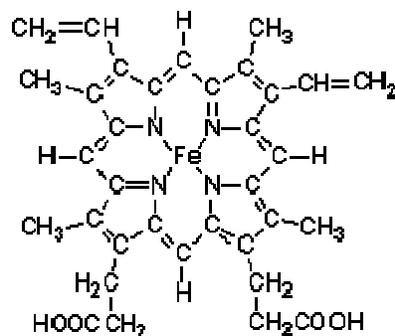


acetylacetonato (acac)

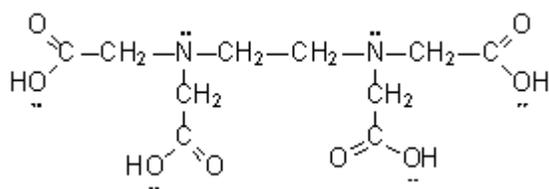
The above examples are all **bidentate** ligands. There are ligands that are capable of attaching to a metal atom via more than two atoms.



diethylenetriamine is an example of a tridentate ligand



Porphyrin (found in heme) is a tetradentate ligand

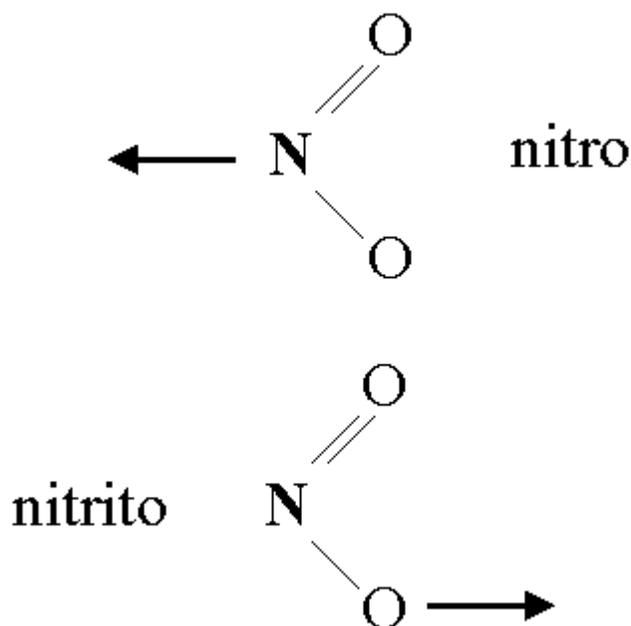


ethylenediaminetetracetate ion (EDTA) is a hexadentate ligand

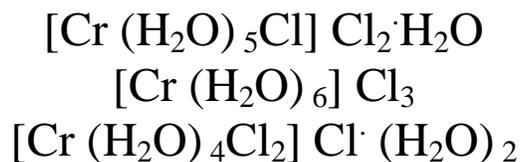
Molecular Geometry and Isomerism

Linkage Isomerism - This happens when a particular ligand is capable of coordinating to a metal

in two different and distinct ways. Here is an example:



Coordination - Sphere Isomers - Examples:



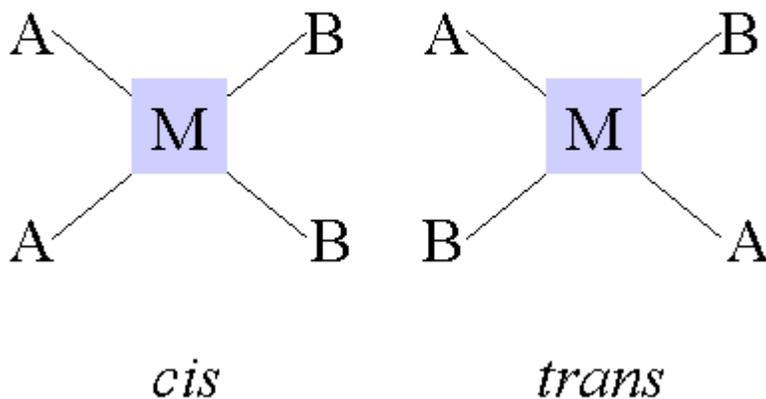
Stereoisomers (Same chemical bonds but different three dimensional arrangements)

Geometrical isomers

Enantiomers (nonsuperimposable mirror images)

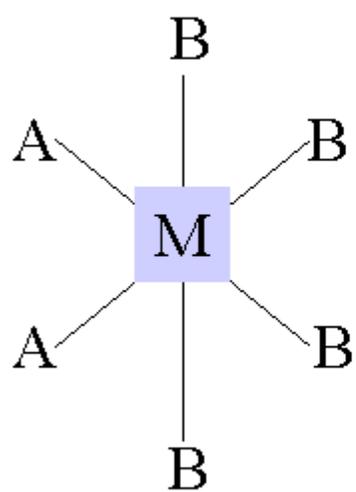
Molecular geometry and stereoisomerism are intimately related

Square planar - Since this arrangement is planar (there is a mirror plane of symmetry), these complexes do not have enantiomers. Geometric isomerism, however, is possible. Here is an example.

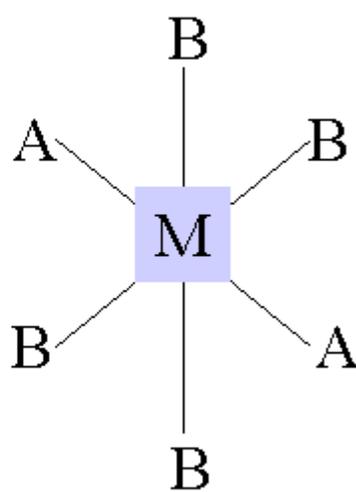


Tetrahedral - In a tetrahedral arrangement, ligands occupy corners of a tetrahedron. These corners are all adjacent to each other, therefore, **tetrahedral complexes are not capable of geometric isomerism**. Enantiomers, however, are possible, when all four ligands are different.

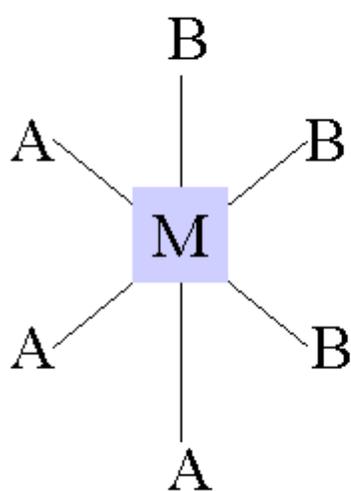
Octahedral - Both geometric isomers and enantiomers are possible. Below are some examples.



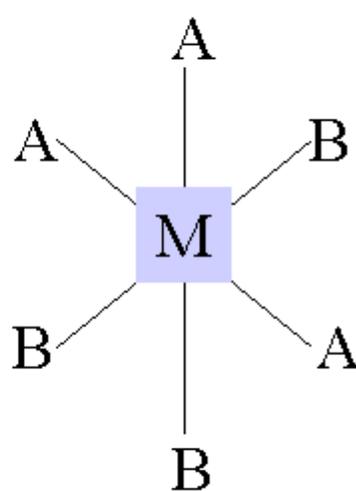
cis



trans

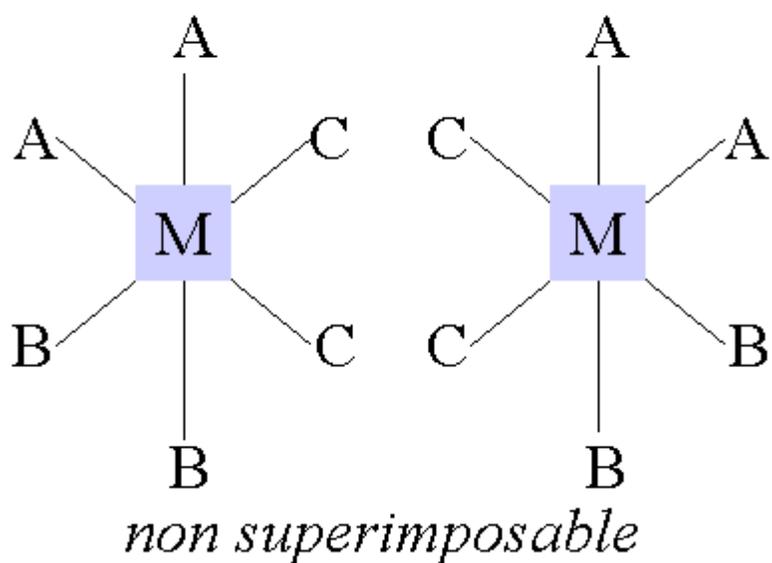


facial

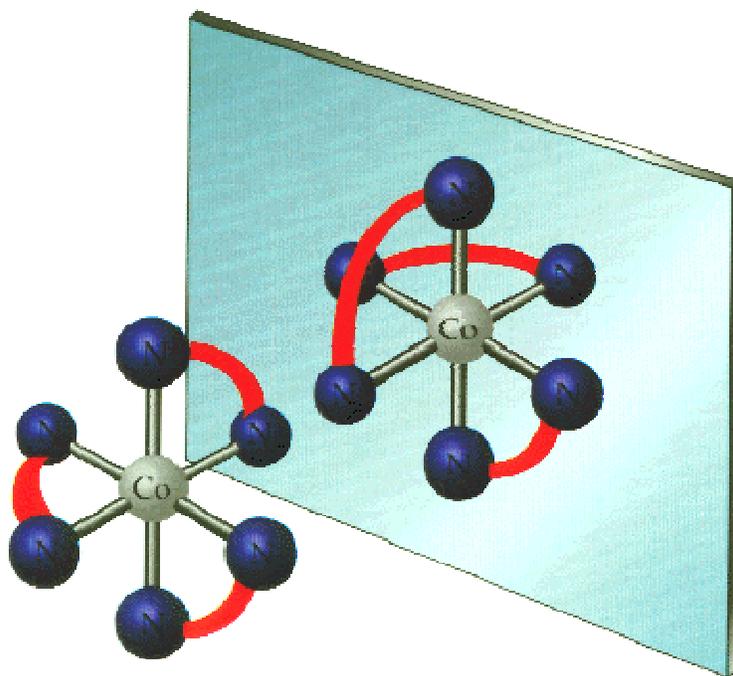


meridional

$MA_2B_2C_2$ (like ligands are *cis*)



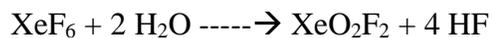
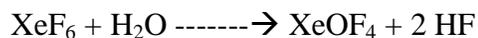
The above is true only if the like ligands are all *cis* to one another. If two like ligands are *trans* then there will be a mirror plane of symmetry normal to the line connecting the ligands that are *trans* to each other.



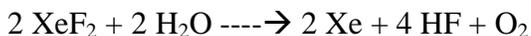
The above is an example of stereoisomerism with chelating ligand.

SOME MORE IMPORTANT CHEMICAL REACTIONS

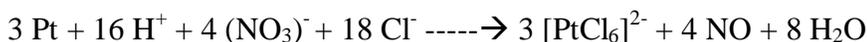
1. Partial hydrolysis of XeF₆:



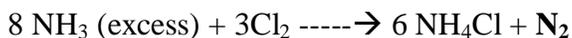
2. XeF₂ is a fluorinating agent:



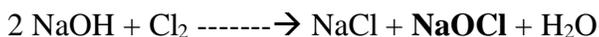
3. Au and Pt dissolve in Aqua regia:



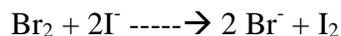
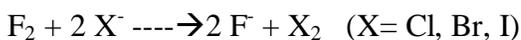
4. Reaction of Cl₂ with NH₃:



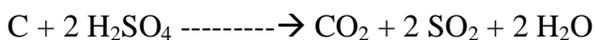
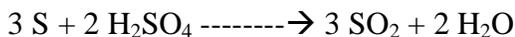
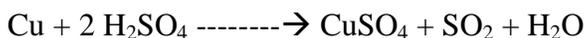
5. Reaction of Cl₂ with NaOH:



6. A halogen oxidizes halide ions of higher atomic number:



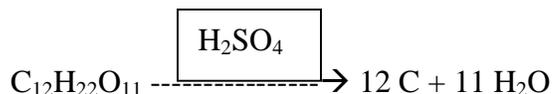
7. Hot conc. H₂SO₄ is a moderately strong oxidizing acid:



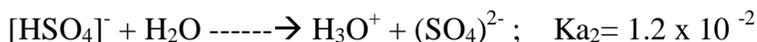
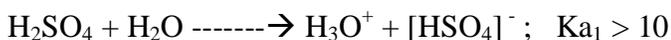
8. H₂SO₄, because of its low volatility can be used to manufacture more volatile acids



8. Conc. H₂SO₄ is a dehydrating agent:



9. K_{a2} << K_{a1} for sulphuric acid in water:



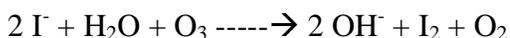
The larger value of K_{a1} means that sulphuric acid is largely dissociated into H⁺ and [HSO₄]⁻.

10. When moist SO₂ behaves as a reducing agent:

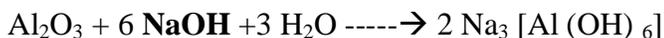


SO₂ decolorizes acidified KMnO₄ solution.

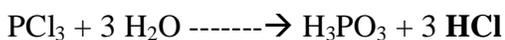
11. O₃, a powerful oxidizing agent:



12. Al₂O₃ is an amphoteric oxide:



13. PCl₃ fumes in moisture:



14. Oxidizing action of KMnO₄ in neutral/faintly alkaline medium:

