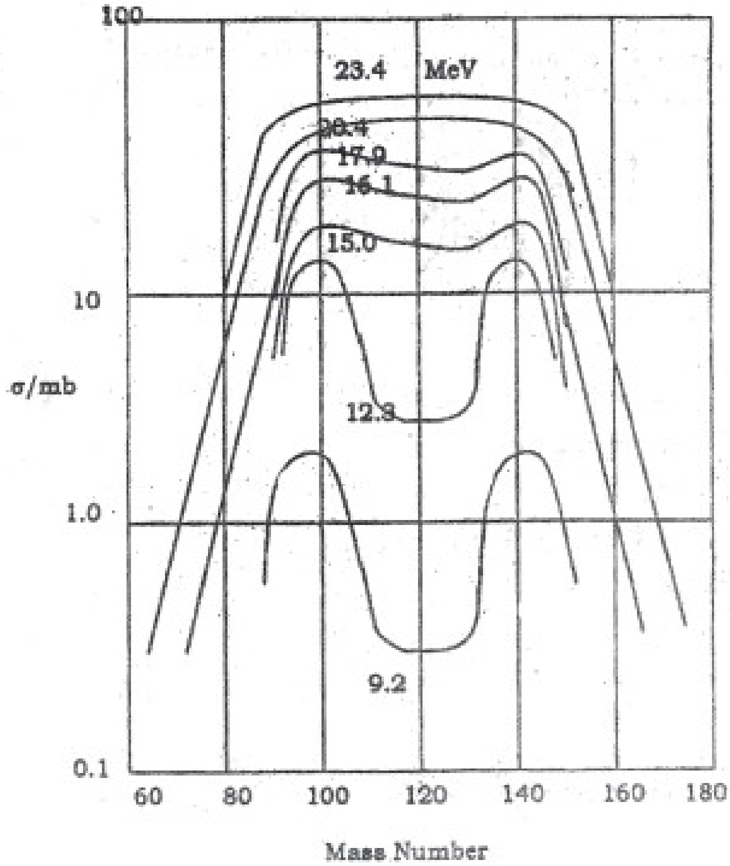
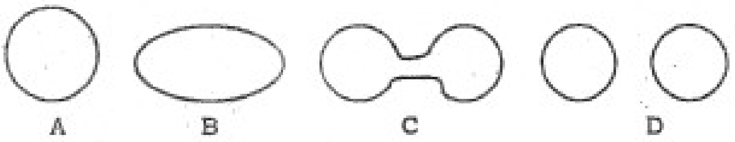


Fission fragment yield as a function of mass number in the fission of ^{239}Pu by deuterons of increasing energy

V. Liquid Drop Model

A useful approach to the understanding of the mechanism of fission is by means of the liquid – drop model of the nucleus. Because the binding energies and volumes of atomic nuclei and approximately proportional to the number of constituent nucleus has been compared in its behaviour to a drop of liquid since the strong nuclear forces which hold the nucleons together in the nucleus may be postulated as causing the nucleus to assume a spherical shape in a manner similar to the cohesive forces within a liquid drop. This analogy led Bohr (in 1936) to propose the liquid drop model of the nucleus. It was postulated that just as the forces of surface tension tend to maintain a liquid drop in a spherical form which restricts its distortion, so also the nuclear forces serve to keep the nucleus in a stable state. For a drop of liquid to be broken up into two smaller drops, or for a nucleus to undergo to undergo fission, there must be considerable distortion, which will be possible only if additional energy is available. This was the basis of the interpretation of fission, which was suggested by Meitner and Frisch and developed Bohr (in 1939), first in a qualitative manner and later quantitatively in conjunction with Wheeler.

The general idea of the proposed mechanism for fission may be understood by considering a drop of liquid, which breaks up into two smaller droplets by passing through a series of stages, as represented, on the application of a suitable force.



Liquid-drop model of nuclear fission

The drop is at first spherical (A), then elongated into an ellipsoid (B) and if sufficient energy is available the liquid crop acquires a dump – bell shape (C) and finally splits into two smaller droplets. The situation in a nuclear fission is regarded as being analogous. A target nucleus combines with a neutron to form a compound nucleus; the energy gained by the latter is equal to the binding energy of the additional neutron plus the kinetic energy, which the incident neutron may have possessed. The excitation energy may then be emitted as gamma radiation or the compound nucleus could, if sufficient energy was available, expel one or more nucleons. But there is a distinct probability that, because of the excess energy, the compound nucleus, like a liquid drop to which energy is supplied, will undergo a variety of strong oscillations and in the course of these oscillations it will pass through a phase similar to that of B.

If the gain in the energy accompanying the absorption of the neutron is insufficient to cause further deformation beyond B, the internuclear forces would compel the nucleus to return to its original spherical form, the excess energy will then be removed usually with the expulsion of a particle of some kind, or by emission of gamma radiation. But if the nucleus has obtained enough energy to permit it to form the dumb-bell shape © the restoration of the initial state A becomes very improbable because electrostatic repulsion between the positive charges on the two ends of C can now overcome the relatively small portion of the nuclear binding force operative in the constricted region of C, Consequently from C the system rapidly passes to D representing fission into two separate nuclei, which move away fast in opposite directions due to strong electrostatic repulsion. It is to be understood that the series of changes of the type from A to D can occur only if this is accompanied by a net decrease of mass, that is by an emission of energy; the state D consisting of two separate nuclei is then more stable than the initial state A.

According to the liquid-drop model the two nuclei formed in fission are expected to be nearly of the same size and mass. But the fission process in most cases is highly asymmetric. One interpretation is as follows based on the experimental observation that fission fragments of mass numbers in the vicinity of 140 and 95 are produced in highest yield.

In the fission of ${}^{235}_{92}U$ nucleus the compound nucleus (${}^{236}_{92}U$) formed has 92 protons and 236 nucleons. When fission occurs there will be a tendency to form one nucleus with 50 neutrons and another with 50 protons. Suppose that the reasonable number of 32 protons is associated with the former and 78 neutrons with the latter, giving mass numbers of 82 and 128, respectively. The total number of nucleons in these two groupings is thus 210, leaving 26 nucleons to be nucleons to be shared between the two. These nucleons will be divided up in several different ways, thus giving a variety of fission fragments.

It may be shown, however, that the most probable distribution will be for an equal number, i.e., 13, to go to each part. The masses of these instantaneous fission fragments would be 82 + 13 = 95 and 128 + 13 = 141. after neutron emission the mass numbers would be about 94 and 140, which are very close to that observed in the major fission products. The less probable unequal distributions of the other fission products that are obtained in lower yield.

VI. Fissile and Fertile Nuclides

It was mentioned that uranium -235 will undergo fission by neutrons of any energy, from almost zero upward, but uranium-238 requires neutrons of at least I MeV to induce fission. This would be so was predicted by N. Bohr in February 1939, and it was verified experimentally early in 1940 by E.T. Booth, J.R. Durnning, and A.V. Grosse at Columbia University. K.H. Kingdon and H.C. Pollock secured small samples of the separate 235 and

238 isotopes, first by A.O. Nier and shortly after, by the electromagnetic method. These were subjected to bombardment by slow neutrons; the uranium – 235 isotope definitely suffered fission, but the heavier isotope, of mass number 238, did not. Fast neutrons, however, could split the later, with energies above 1MeV.

Uranium -233 and plutonium 239 are like uranium – 235 in the respect that neutrons of any energy can induce fission; such species are referred to as fissile nuclides. On the other hand, uranium-238, thorium-232, and certain other species, which have a fission threshold at about 1 MeV, are said to be fissionable nuclides.

In general, fissile nuclides have either an even number of protons and an odd number of neutrons of neutrons or odd numbers of both; of the many possibilities, only the three mentioned above have sufficiently long half-lives to be of practical interest for the release of energy in nuclear fission reactors. Fissionable nuclides have either even numbers of protons and neutrons or an odd number of protons and an even number of neutrons. Of the fissionable nuclides, only the even – even species uranium-238 and thorium-232 are of practical interest, because they can be converted into fissile species by reactions with neutrons. These are called fertile nuclides.

VII. Nuclear Fusion and Stellar Energy

Energy is also released when nuclei of light elements fuse to produce less energetic nuclei. It has been stated that the so-called hydrogen 'bomb' may gain its detonation energy from a reaction between deuterium and tritium. The equation for the reaction is

$$1^{H^2} + 1^{H^3} \rightarrow {}_2He^4 + 0^{n^1} + 17.8 \text{ MeV}$$

In terms of whole numbers this reaction involves the fusion of 5 mass units and releases 17.8 MeV energy. The efficiency of this reaction of energy conversion is approximately.

$$\frac{17.8 \text{ MeV}}{5 \text{ mass units} \times 931} \times 100 = 0.35\%$$

The calculation shows that fusion reactions is 4 times as efficient as fission reaction. Considerable interest has been focused upon fusion reaction as a source of atomic energy. Though Scientists first tried to harness a thermonuclear weapon, there is considerable evidence that fusion reactions will eventually be harnessed for industrial power.

The energy source of the stars, including our sun, is believed to be derived from a complex chain of reactions, which finally show that four hydrogen atoms fuse together to form one helium atom the possible equation for hydrogen bomb and their energy release is given below.

$${}_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1 \qquad Q = 17.8 \text{ MeV}$$

$${}_0n^1 + {}_1H^3 \longrightarrow {}_2He^4 + {}_{-1}e^0 \qquad Q = 20.7 \text{ MeV}$$

$${}_3Li^6 + {}_1H^2 \longrightarrow 2\,{}_2He^4 \qquad Q = 17.7 \text{ MeV}$$

VIII. Isotopes and Their Applications

The isotopic tracer method is based on the fact that a mixture of isotopes of an element essentially remains invariant throughout the course of physical, chemical and biological processes. Thus a radioactive isotope added to a mixture of isotopes may serve as a tracer, label or indicator in the sense that its behaviour will be the same as that of the other atoms of the same element originally present. By measurement of radiations emitted by the decay of these tracer isotopes the fate of original material can be found.

1) Solubility of sparingly soluble salt

In determining the solubility of lead sulphate, Hevsey and Paneth, 1913, added a quantity of pb^{212} radioisotope, viz radioactive $pb(NO_3)_2$ with $pbCl_2$ and lead chloride with pb^{212} was precipitated. The activity of resulting mixture was measured, so that a relationship was established as to the activity of material per mg of lead.

(Sparingly soluble salts

$Pb(NO_3)_2 + H_2SO_4$ (or) $Na_2SO_4 \rightarrow PbSO_4$

$Pb(NO_3)_2 + K_2\,CrO_4 \rightarrow PbCrO_4$)

The soluble mixture of lead ions was precipitated as lead sulphate and held at constant temperature until a saturated solution of fairly insoluble material and reached equilibrium. After ascertaining the total volume of supernatant liquid, a sample of definite volume was withdrawn and evaporated to dryness. The activity of minute residue was determined in the same fashion as upon the initial mixture before precipitation of lead sulphate. From the activity of the residue it was possible to establish the amount of lead sulphate. From the activity of the residue it was possible to establish the amount of lead sulpate dissolved in the known quanity of solution by using the relationship;

$$\text{Amount} = \frac{S_2}{S_1} \times \frac{10}{M} \text{ moles of lead sulphate per litre}$$

Where S_1 = initial activity, S_2 = final activity and

M = molecular weight of lead sulphate

2) Isotopic dilution method

It is used in determining the volume of blood in an animal or human being. The procedure is that in a donor, a tracer is injected into and allowing sufficient time for incorporation (some times weeks) of the tracer into the circulating red cells. A tracer used for this purpose is ^{59}Fe. A sample is withdrawn from the donor and the activity per milliliter of blood is determined and then an aliquot portion of the sample introduced into the recipient subject. After a proper elapse of time, a sample from recipient is assayed for radioactivity. From the dilution of activity it is possible to calculate the volume of blood in the recipient.

The solubility of benzene or other hydrocarbons is too small to be measured by ordinary physical or chemical methods. If however, a definite quantity of $^3H_1$ tritium in the form of tritium oxide is added to a given amount of water, the resulting mixture has an activity that can be measured in the minute amounts that may dissolve organic solvents. Thus using dilution methods one has to know the amount of labeled tracer added, the weight of the mixture and the labeled content of a purified sample from the combined mixture.

3) Neutron activation analysis

When a sample is subjected to nuclear bombardment and then analysed for its radioactive content is called 'activation analysis'. Most elements give rise to radioactive isotopes with characteristic radiations, when bombarded with neutrons from a reactor or neutron generator. This permits qualitative identification and also quantitative analysis by comparative method.

The sample to be analysed is exposed to thermal neutrons from a reactor for a sufficiently long time to produce measurable amount of desired radioisotope. The capture rate is proportional to the neutron flux f (neutrons cm^{-2}) sec^{-1}) and to the number of target nuclei N available and the induced activity is represented as;

$A = f n\sigma (1 - e^{-0.693t/T_{1/2}})$

Where A = induced activity

F = neutron flux

N = number of target nuclei

$$= \frac{\text{Weight of target material} \times 6.023 \times 10^{23}}{\text{Atomic Weight}}$$

σ = nuclear cross section in barns

t = period of irradiation in seconds

$T_{1/2}$ = half-life, seconds

This is the most sensitive method to determine the trace elements like gallium in iron, copper in nickel and hafnium in zirconium.

Hair accumulates arsenic at the bottom end of hair and hair grows normally 0.5 mm per day. If a person is dead, the arsenic in hair can be neutron irradiated and the distribution of ^{76}As along the length compared, the pattern and schedule of arsenic poisoning may be determined. In normal hair ^{76}As content is lower and remains almost constant all along the length except towards the tip, while the pattern in case of arsenic poisoning reveals distinct peaks corresponding to days of poisoning each day corresponding to 0.5 mm length of hair. The technique was used in 1962 in the examination of Napoleon's hair and revealed abnormal amount of arsenic. However this evidence was not considered conclusively.

4) Structure of Thiosulphate ion

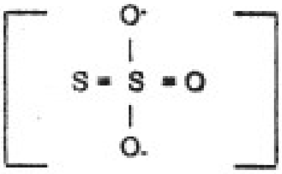
One of the applications of tracer chemistry to structural problems was the establishment of thiosulphate ion. If sulphur is heated with labeled sulphite ion, the thiosulphate ion is produced as follows;

$$S + \overset{*}{S}O_3 \longrightarrow \overset{*}{S}_2O_3$$

When the thiosulphate containing a labeled sulphur atom is broken down in acid solution, the products are

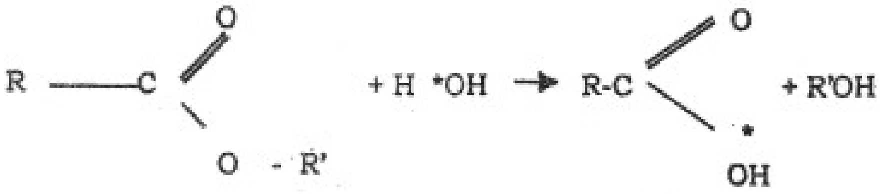
$$\overset{*}{S}_2O_3^{--} \rightleftharpoons S + \overset{*}{S}O_3^{--}$$

After decomposition of the thiosulphate the labeled sulphur is linked to the oxygen atoms in the sulphate ion. This clearly indicates that the labeled sulphur is not affected in the synthesis and decomposition of the thiosulphate and also it shows that both S atoms in the thiosulphate ion are not equivalent. Otherwise, the labeled isotope would have been distributed between the products of decomposition. This led to the conclusion that thiosulphate ion has the structure.



5) Reaction Mechanism

The course of certain organic reactions can be traced with lablelled atoms. In ester hydrolysis since oxygen does not have a radioisotope sufficiently long lived for tracer studies, it was necessary to use O^{18} the stable isotope as a tracer. The hydrolysis of an ester by water enriched with heavy oxygen is indicated as



The fact that the labeled oxygen is in the acid proves that the OR' group has been substituted by the O*H in the hydrolytic reaction. The acyl – oxygen bond breaks.

6) Radioistopes in Medicine

There are uses of tracers in diagnostic methods for localizing bodily disorders and as therapeutic agents in the treatment of certain abnormal conditions in the body.

Radioactive P is used in treatment of certain blood dis-orders. When p^{32} is orally ingested it controls the over formation of red blood cells in the bone marrow (the disease is called Polycythemia) due to the emission of beta particles. This treatment fails in 'leukemia' where white cells are over produced.

Blood circulation is checked with labeled Na^{24} . Na*C1 is injected and the blood circulation is verified with the help of GM counter following the tracer. Normally blood reaches foot in 30 minutes. If the subject has impaired circulation the period of time be longer. It is possible to locate the general area of restriction. Radiocobalt (Co^{60}) is used for treatment of cancer.

7) Radioisotopes in Biological fields

The most successful investigation with tracer methods have been achieved in four areas (i) study of dynamics of steady state (ii) an analysis of transport of ions across the cell membranes (iii) study of metabolic interconversions and (iv) study of mineral metabolism.

i) Earlier it was thought that food alone gives energy for work and replaces worn-out tissue. Further more, it was at one time thought that proteins, carbohydrates, fat etc, are all stored in body and utilized only when needed. With the use of isotopic tracers all the above notions were proved wrong. The substances of cells and tissues are constantly built up and broken down. Many balanced chemical reactions, which are dynamic in nature, occur in out body.

(ii) The use of radioisotopes enabled scientists to understand how ions move across cellular membranes. The fact that ordinary osmotic pressures do not apply here is well illustrated by the ability of the cell to maintain a high internal K^+ ion concentration in the presence of a low concentration in the external fluids. Also it appears that the cell excludes Na^+ ions even when the extra cellular concentration is quite high.

(iii) The understanding of protein metabolism has been greatly advanced by tracer methods. The synthesis and breakdown of proteins (into amino acids) is controlled by enzymes. These processes are part of metabolic pool of the body. The protein synthesis can be assayed by addition of a labeled aminoacid like glycine to the protein extract. Any synthesis, which may take place will include the tracer compound and after a period of time the protein may be removed and assayed for transfer content.

iv) Mineral metabolism using tracer isotopes in the study of

a. the movement of ions across cell membranes
b. the metabolism of bone tissues
c. the metabolism of trace elements
d. the metabolism of hemoglobin and
e. toxicology of heavy elements have been made.

Among these the calcium metabolism and the part played by the intestine in the absorption and excretion of this element are worth mentioning.

8) Ratio isotopes in Agriculture

Radioautography established the established the movement of nutrients from roots to various parts of the plants, which is a form of tracer study taking photography producing the exposure of sensitized plate to radioactive emanation from parts or whole of the plant. Thus S^{35} supplied as sulphate in sugar beet plants helped the scientists to know the distribution of sulphate.

Utilization of phosphates in soil and other fertilizers are also studied with tracer analysis. Addition of P^{32} to phosphate fertilizer helped in understanding how much plants utilize phosphates. Fungicides containing S are treated with S^{35} and sprayed over fruits which help in understanding their use. Tracer technique showed that the sulphur dusted on lemon fruit will penetrate the peel to cause sufficient injury to the fruit.

9) Industrial applications

The radiation effect of radioactive isotopes is utilized for such purposes as destruction of bacteria in food, the activation of chemical reactions, polymerization of organic monomers etc. If a β – emitter is floated in a storage tank, the level of liquid can be easily measured using GM counter. The movements of oil through pipes in oil refineries use the same idea.

Using β – emitter isotopes, the thickness of films can be controlled. As a film emerges from rollers, it passes between a beta source and detector. Any change in thickness will produce a corresponding change in radioactivity transmitted between the beta source and its detector. The beta gauge activates an automatic mechanism for resetting the rollers to a predetermined level for uniform film thickness. Studies involving the mechanism of friction and the effectiveness of lubrication have been studied through the use of tracers.

The use of radioisotopes in the metallurgy is numerous. By incorporating radioactive isotopes it is possible to gain an insight as to what is taking place when a metal is subjected to annealing, quenching cold rolling etc and uniform production of materials. Radio C^{14} is used in alkylation, polymerization, catalytic cracking, catalytic synthesis as well as many industrial applications.

10) Age of materials $C1^{4}$ - Carbon Dating

W. F. Libby developed the technique of dating with C14 of archeological and historical organic samples in 1960 and he was awarded Nobel prize. Living plants produce food for themselves by photosynthesis of sugars from water and carbon dioxide of the atmosphere. Since the mass ratios of $^{14}CO_2/^{12}CO_2$ of the atmosphere appears to have remained sensibly constant over the ages (around 1.6×10^{-12} for living being and the disintegration of ^{14}C was found to be 16.1 ± 0.3 disintegration $min^{-1}g^{-1}$ of total carbon). If a plant dies, the photosynthesis stops. This results in a continuous decay of whatever ^{14}C is left at the time of death of the plant at an exponential rate corresponding to half-life of ^{14}C, namely, 5730 years. Hence a determination of the actual count rate due to ^{14}C in a given sample of once living but now dead matter would permit a computation of the age of the sample.

Using the equation $\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t}$

where N_0 is the disintegration of ^{14}C at the time of plant living (16.1 disintegration $min^{-1} g^{-1}$), N_t = disintegration of ^{14}C at the time of investigation and t = period of living (to be determined).

Decay constant $\lambda = \frac{0.693}{T_{\frac{1}{2}}} = \frac{0.693}{5730 \times 365 \times 24 \times 60} min^{-1}$

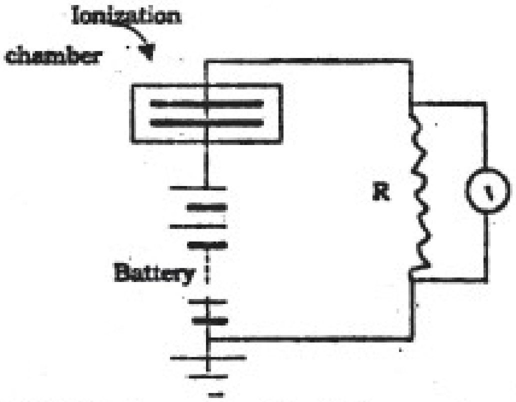
IX. Counting Techniques

Some of the most useful procedures for detection and measurement of a and β – particles and also γ - ray photons are based on the discovery that gases are ionized. The intensity of ionization produced by a moving charged particle in its path of a gas is expressed by specific ionization and this is the number of ion-pairs formed per cm of path. Usually α - particles produce 50 thousand to 1 lakh ion pairs whereas the fast moving β – particles produce a few hundred-ion pairs per cm.

Quantitative measurements are based on the counting of individual particle and the total radiation received in a given interval of time is determined. By applying voltage under various conditions, the ionizing radiations are driven to collecting electrodes in the instrument containing an inert gas or air. The magnitude of charge collected and hence the quantity of current pulse depends on (i) the number of ion-pairs produced and (ii) the applied voltage. This principle is used in proportional counters and Geiger – Muller (G.M) counter. The G.M. counter is more effective than proportional counters. Using phosphors, which produce light on irradiation with ion-pairs and the light produces scintillations as a photomultiplier tube, is used in scintillation counters.

One the simplest and generally useful device of the electrostatic type of ionization chamber is the quartz-fiber electroscope invented by C.C. Lauritsen and T. Lauritsen in the United Stated in 1937. it consists of a very fine metal-coated, quartz fiber, about 6mm in length, parallel to a very fine metal – coated, quartz fiber, about 6 mm in length, parallel to a rigid horizontal metal wire to which it is connected. This is mounted within, but insulated from, a cylindrical aluminum case, which acts both as the ionization chamber and one of the electrodes.

The system of fiber and wire, which represents the other electrode, is charged with respect to the metal case by connecting for a short time to a battery of 100 to 200 volts. As a result of the repulsion between the rigid metal wire and the flexible fiber, the latter, which acts as the indicator, is displaced from its normal position. When the electroscope is exposed to ionizing radiations, the charged wire and attached fiber collect ions. Which reduce the charge; hence the mutual repulsion decreases and the fiber gradually returns to its original position.



Simplified schematic circuit (current measuring) for integrading type of ionization chamber

In the second type of integrating ionization chamber, which has found extensive use in the atomic energy field, the circuit is based on that. In this instrument the steady production of ion-pairs in the chamber results in a very weak, but continuous, flow of current through the resistance R. The magnitude of this ion current, as it is called, can be determined with the aid suitable voltmeter V connected across the resistance. Alternatively, the current can be measured directly by means of a sensitive instrument. The current strength is directly proportional to the rate at which ionizing (alpha, beta, gamma etc.) radiation is entering the ionizing chamber.

It it is required to determine beta radiation in the presence of alpha particles, the rays are permitted to enter the ionization chamber through a "window" made of a thin sheet of aluminum. This is sufficient to prevent the passage of alpha particles without appreciably hindering the beta radiation. Allowance must be made, however, for gamma rays if they are present. Ionization chambers for gamma rays usually contain a heavy gas, such as argon or difluorodichloromethane, (Freon – 12), often at high pressure, so as to facilitate the liberation, by each gamma – ray photon, of an electron capable of producing ionization. If alpha or beta particles are present, as they frequently are they may be removed by means of a thin sheet of lead which stops these particles but has little influence on the gamma rays.

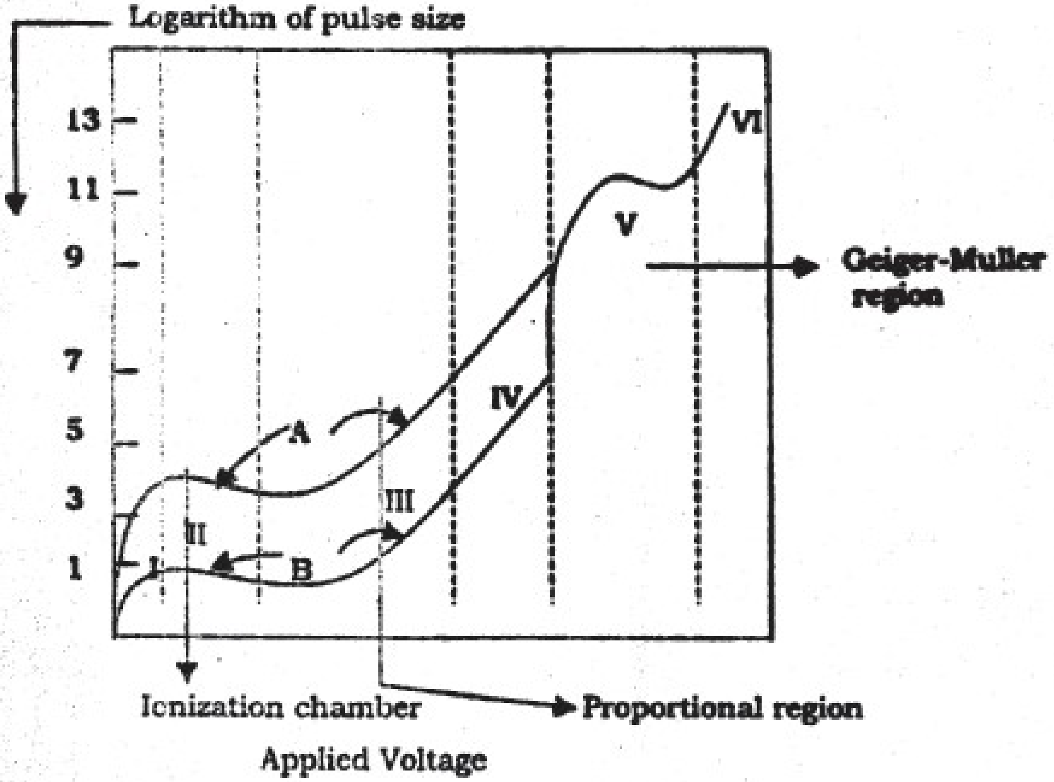
Although the ionization chamber method of measuring nuclear radiations is very simple and convenient, it has the disadvantage of often requiring the use of a very sensitive electrometer or of a powerful amplifier. Other ionization instruments have therefore been devised in which there is a considerable degree of internal amplification. It can be seen that, for a given number of initial ion-pairs, the pulse size in region III is greater than in region II.

In other words, there is a certain amount of internal amplification of the pulse in region III and this amplification increases with the applied voltage. However, for a given voltage, the size of the current pulse is proportional to the initial number of ion-pairs produced between the electrodes. For this reason, region III is called the proportional region. It is chamber, which acts as the negative electrode (cathode), with a central wire as the positive electrode (anode). When the voltage is high enough the potential gradient (or electric field strength) near the central wire becomes so large that the electrons, produced in the primary ionization of the gas by an alpha or beta particle, will move towards it with a very high speed.

In region III the speed becomes great enough for the electrons to cause the ionization of other atoms and molecules in the gas; the electrons so produced may cause further ionization and so on. This multiplication effect is often referred to as a Townsend avalanche or Townsend cascade, in honor of its discoverer J.S. Townsen.

An electron from each original (or primary) ion-pair may consequently lead to the formation of a large number of secondary ion-pairs. The total number of ion-pairs produced by a single primary ion-pair is called the gas – amplification factc This factor is unity in the ionization chamber (region II), but it may become as large as 104 or more in region III. The size of the pulse produced by a single particle is thus increased enormously, so that considerably less external amplification is required. In principle, the proportional region could be used in an integrating instrument in which the ion current is measured. But this would require such exact control of the potential difference between the electrodes as to be quite impractical. Consequently, pulse counting is always employed, and this is the reason for the name proportional counter.

A type of instrument that has been widely used in radioactive counting is the Geiger – Muller counter; a name abbreviated to Geiger counter or to G-M tube is frequently used. These instruments operate in region V of the curve, the variation of current pulse size with the applied potential. The conditions in region IV, which lies between the proportional and Geiger-Muller ranges, have found no application in nuclear radiation studies, and in region VI the potential is so high that once ionization takes place in the gas there is a continuous discharge of electricity, so that it cannot be used for counting purposes.

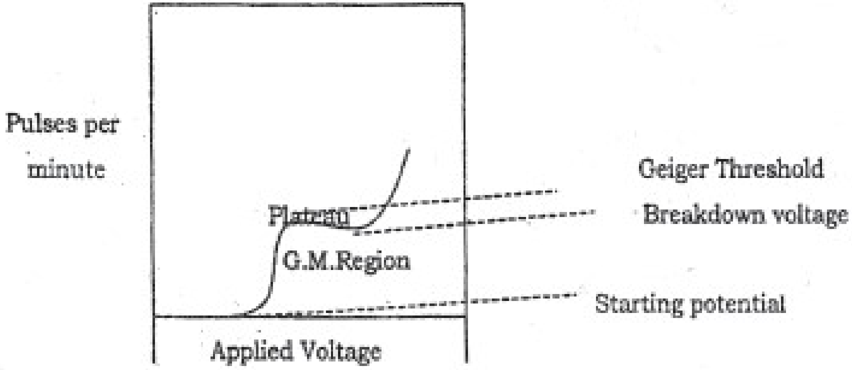


Variation with applied voltage of size of current pulse due to an ionizing particle.

Although Geiger made some improvement in the design of particle counters, leading to operation in region V, in 1913, the modern highly sensitive G- M counter is essentially that developed by Geiger in collaboration with W.Muller in Germany in 1928. it should not be overlooked, however, that the wide sphere of usefulness of the G-M tube as well as the ionization chamber and proportional counter, owes much to the developments in electronic circuits which have taken place in recent years. In this connection, mention may be made of the Swiss physicist, H. Greinacher who, in 1924, introduced the use of vacuum tubes to amplify the pulses produced by ionizing particles.

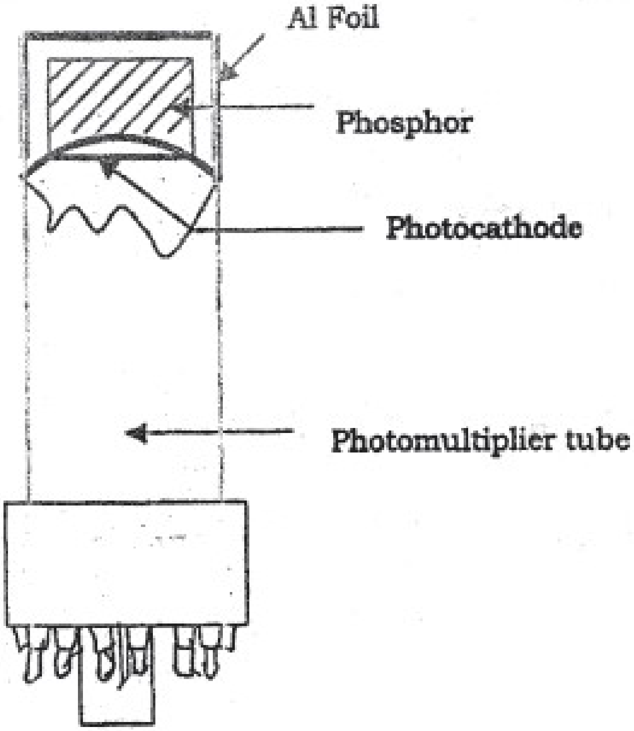
The characteristics of the Geiger region can be considered from another point of view. Imagine a weak source of ionizing (alpha, beta, or gamma) radiation placed near an instrument, similar to a proportional counter; consisting of a cylindrical cathode with a central wire as the anode. This instrument is connected with a device capable of indicating small ones. As the potential applied between the electrodes is increased the number of pulses recorded per minute will be observed to change in the manner depicted. Until the voltage reaches the value indicated as the starting potential, the pulses are too small to be detected. But with rising potential the gas amplification increases, and pulses are recorded in increasing numbers.

Eventually, when the Geiger threshold potential is reached, corresponding to the beginning of region V, the number of pulses per minute becomes essentially constant, as indicated by horizontal portion of the curve. The range of potential over which this occurs is call the Geiger plateau. Beyond the plateau, continuous discharge takes place (region VI), and counting is not possible.



Variation with applied voltage of number of current pulses received per minute due to ionizing radiation.

Since the year 1947, there have been important developments in one of the oldest methods of counting particles namely that based on the small flashes (or scintillations, which accompany the exposure of certain materials to nuclear readiations. The mechanism of production of these scintillation is very complex, but essentially it involves the initial formation of a higher-energy (or excited) electronic state of the molecules (or atoms), or in certain inorganic solids, of a small region of a crystal. The excess energy, which has been derived directly or indirectly from the nuclear radiation, is then emitted within a very short time as a flash of light.



Schematic representation of a simple scintillation counter

A simple form of the system is shown diagrammatically; the crystal of the phosphor, surrounded by thin aluminum foil, is attached to the top, close to the cathode, of the photomultiplier tube. The purpose of the foil is to reflect the light flashes on to the cathode. A particle of nuclear radiation (or a gamma-ray photon) entering the phosphor causes a flash of light, which falls on the photo cathode. As a result, electrons are emitted and these subsequently multiplied to produce a relatively large electrical pulse at the output of the tube.

X. Problems

1.Find the half-life of a radioactive element which had lost 75% of its activity in 20 days.

$N_0 = 100\ \%$, $N_t = 100 - 75 = 25\%$ and $t = 20$ days

$$2.303\ \log\frac{N_0}{N_t} = \lambda t$$

$$\therefore \lambda = \frac{2.303}{t}\log\frac{N_0}{N_t} = \frac{2.303}{20}\ \log(\frac{100}{25})$$

$$= \frac{2.303 \times 0.6021}{20} = 0.06933\ \text{day}^{-1}$$

$$T_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.06933} = 10\ \text{days}$$

2. Calculate the weight of 1 millicurie of Ra^{226} whose half-life is 1620 yrs.

Half life of Ra^{226} = 1620 yrs and 1 year = 3.156×10^7 sec

$$\therefore \lambda = \frac{0.693}{1620 \times 3.156 \times 10^7} = 1.356 \times 10^{-11}\ \text{sec}^{-1}$$

$$\frac{dN}{dt} = \lambda N = \lambda \times \frac{W}{226} \times 6.023 \times 10^{23}$$

$$= \frac{1.356 \times 10^{-11} \times W \times 6.023 \times 10^{23}}{226}$$

$$\frac{dN}{dt} = W \times 3.613 \times 10^{10}\ \text{sec}^{-1}$$

But $\frac{dN}{dt} = 1\,mc_i = 3.7 \times 10^7\,\text{sec}^{-1}$

$$\therefore 3.7 \times 10^7 = W \times 3.613 \times 10^{10}$$

$$\therefore W = \frac{3.7 \times 10^7}{3.613 \times 10^{10}} = 1.024 \times 10^{-3}\,g$$

3. Calculate the weight of 1 mc_i of C^{14} whose half – life is 5730 yrs

$$\lambda = \frac{0.693}{5730 \times 3.156 \times 10^7} = 3.82 \times 10^{-12}\,\text{sec}^{-1}$$

$$\frac{dN}{dt} = \lambda N = X = \frac{W}{14} \times 6.0230 \times 10^{23} = 1.65 \times 10^{11} \times W\ \text{sec}^{-1}$$

$$\frac{dN}{dt} = 1mc_i = 3.7x10^7 sec^{-1}$$

$$\therefore W = \frac{3.7 \times 10^7}{1.65 \times 10^{11}} = 2.2 \times 10^{-4} g.$$

4. **Uranium mineral contains 1 atom of Ra to every 2.8 x 10⁶ atoms of U and these two are in secular equilibrium. If the half-life of Ra is** 1620 **yrs** determine the half life of U **and decay constant of U.**

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A}$$ where, N_A = 2.8 x 10^6 atoms of u

N_B = 1 atom of Ra and λ_A = ?

$$\lambda_B = \frac{0.693}{1620} = 4.277 \ x10^{-4} yr^{-1}$$

$$\frac{2.8x10^6}{1} = \frac{4.277x10^{-4}}{\lambda^A}$$

$$\therefore \lambda_A = \frac{4.277 \times 10^{-4}}{2.8 \ \times 10^6} = 1.5275 \times 10^{-10} yr^{-1}$$

$$\therefore T_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{1.5275 \times 10^{-10}} = 4.537 \times 10^9 yrs$$

Decay constant of U = 1.5275 x 10^{-10} yr^{-1}

Half life of U = 4.537 x 10^9 vrs

5. **The Al isotope $_{13}Al^{27}$ has a mass of 26.9815 amu and that of neutron is 1.009 amu. Calculate the binding energy per nucleon of the Al nucleus (1 amu = 931 MeV).**

Mass of Al,	M	=	26.9815 amu
Mass of protons	M_H	=	1.0081 amu
Mass of neutron	M_n	=	1.0090 amu
Mass number	A	=	27
Atomic number	Z	=	13
Binding energy		=	[ZM_H + (A-Z) M_n-M]
		=	93[13 x 1.0081 + 14 x 1.009 – 26.9815]
		=	[13.1053 + 14.1260 – 26.9815] 93
		=	0.2498 x 931 = 232.5638 MeV

Binding energy per nucleon = $\frac{232.5638}{27}$ = 8.6135 MeV

6. A sample of Th230 weighing 0.1 mg was found to undergo 4.32 x 106 dis-integration per minute. What is the half-life of the nucleus?

$$\frac{dN}{dt} = 4.32\text{x}10^{6}\,\text{min}-1 \qquad \frac{dN}{dt} = \lambda N$$

$$N = \frac{0.1}{1000 \text{ x } 230} \text{ x } 6.023 \text{ x } 10^{23}$$

$$\therefore \lambda = \frac{4.32 \text{ x } 10^{6} \text{ x } 1000 \text{ x } 230}{0.1 \text{ x } 6.023 \text{ x} 10^{23}}$$

$$\lambda = 1.6497 \text{ x } 10^{-11}\,\text{min}^{-1}$$

$$\therefore T_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{1.6497 \text{ x} 10^{-11}} = 4.2008 \text{ x} 10^{10}\,\text{min}$$

$$= \frac{4.2008 \text{ x} 10^{10}}{365 \text{ x } 24 \text{ x } 60} \text{ x } \frac{0.693}{1.6497 \text{ x} 10^{-11}} = 4.2008\text{x}10^{10}\,\text{min}$$

(1 yr = $5.256 \text{ x } 10^{5}$ min)

∴ Half – life period of Th^{230} = $7.99 \text{ x } 10^{4}$ yrs.

Questions

1. Describe the features observed in beta emissions of different types.
2. Describe the different types of transmutation reactions brought out by neutrons, deutrons and protons.
3. Describe the working of Geiger –Muller Counter.
4. Write short notes on (i) Scintillation Counters (ii) ionization chamber and (iii) Coulomb barrier
5. What is a compound nucleus? What is its importance in transmutation reactions?
6. Define nuclear cross section. How are they determined?
7. Discuss the liquid drop model of nuclear fission.
8. Write short notes on (i) stripping and pickup reaction (ii) Fragmentation reactions (iii) Fusion reaction and stellar energy (iv) K – Electron capture.
9. If a radioactive substance loses its activity by 25% in 10 days. Calculate its half – life.
10. Account for the release of enormous amount of energy in the nuclear fission reaction.
11. Describe the different modes of decay in artificial radioisotopes.
12. Discuss the application of radioisotopes in the field of study or reaction mechanism, agriculture, industries and carbon dating.
13. Discuss the use of radioisotopes in medicine
14. Write short notes on trace elements in (i) solubility of sparingly soluble salt (ii) Isotopic dilution method (iii) Neutron Activation Analysis and (iv) Structure of thiosulphate ion.

* * * *

UNIT – IV

COORDINATION CHEMISTRY AND MAGNETISM

Syllabus

Bonding in Coordination Compound – Nature of metal – ligand bond: V.B.Theory – Electroneutrality principle and back bonding – crystal field effects for octahedral, tetragonal, square planar and tetrahedral symmetries -applications of CFT – Site preferences – Spectrochemical series and Nephelauxetic effect - M.O Theory for octahedral complexes – pi bonding and M.O.T – Static and Dynamic Jahn – Teller behaviour.

Magnetic behaviour – dia, para, ferro, ferri and antiferro magnetism – Magnetic moment determination by Guoy and Faraday methods; spin only value and its deviation - Quenching of orbital angular moment and spin – orbit coupling - Determination of geometry of Co and Ni complexes from magnetic data - spin crossover phenomenon; magnetic properties of lanthanides and actinides.

I. Introduction

Coordination chemistry field is grown in a half-century from a readily defined and limited area into what is now the most active research field of Inorganic Chemistry.

For over one hundred years the study of inorganic, metal containing, compounds was largely descriptive as indeed was much of the whole field of Chemistry. From the discovery of electrons in 1897 and latter the development of electronic theory of valency in 1920 the theoretical inorganic chemistry made a rapid progress. This has been mainly due to Lewis, Kossel, Langmuir, Sidgwick, Fajans, Pauling and many others.

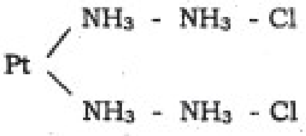
The modern study of coordination compounds comprises of theoretical, synthetic and bioinorganic fields. Alfred Werner (who was awarded Nobel prize in 1913 for his pioneering work in coordination chemistry) and Sophus Mads Jorgensen differed fundamentally in their interpretations about the various compounds they synthesized.

Many elements have fixed valencies. For example Na = +1, Cl = -1, H = +1, O = -2, N = + 3 and some exhibited two or three stable valencies. For example Cu = +1, +2 (cuprous and cupric) P = -3, +3 and +5. Some metals exhibited combining powers that were hard to reconcile with this simple picture.

The standard valency of chromium is +3 and those of platinum are +2 and +4. Yet chlorides of these metals will react with ammonia (in which the valencies of nitrogen and hydrogen are satisfied)

$$CrCl_3 + 6NH_3 \longrightarrow CrCl_3 \,.\, 6NH_3$$
$$PtCl_2 + 4\,NH_3 \longrightarrow PtCl_2 \,.\, 4NH_3$$

Jorgensen attempted to formulate these compounds by analogy to organic compounds by analogy to organic compounds such as



Werner in formulating his ideas about the structure of Coordination compounds had before him facts such as the following. Four ammonia complexes of cobalt (III) chloride had been discovered and named according to their colours.

$CoCl_3$. 6 NH_3 –Yellow – Luteo complexes
$CoCl_3$. 5 NH_3 –Purple – Purpureo complexes
$CoCl_3$. 4NH_3 - Green – Praseo complex
$CoCl_3$. 4NH_3 - Violet – Violeo complex

One of the interesting facts about this series is the presence of two compounds of identical empirical formula $CoCl_3$. 4NH_3 but have distinct properties the noticeable being the difference in colour. Further more Werner noted that the reactivities of the chloride ions in these 4 compounds differed considerably. Addition of silver nitrate resulted in different amounts of precipitated silver chloride.

$$CoCl_3.6NH_3 + \text{Excess of } Ag^+ \rightarrow 3AgCl\downarrow$$
$$CoCl_3.5NH_3 + \text{Excess of } Ag^+ \rightarrow 2AgCl\downarrow$$
$$CoCl_3.4NH_3 + \text{Excess of } Ag^+ \rightarrow AgCl\downarrow \text{(for either praseo or violeo)}$$

The correlation given by Werner postulated that in all these, cobalt has constant coordination number 6 and that as ammonia molecules are removed, chloride atoms are covalently bonded to the cobalt, rather than as free chloride ion. To describe the complex chemistry, therefore one must consider not only the oxidation states of the metal but also its coordination number. Werner thus formulated these four salts as $[CO(NH_3)_6]Cl_3$, $CO(NH_3)_5Cl]Cl_2$ and $CO(NH_3)_4Cl_2]Cl$ (cis and trans forms).

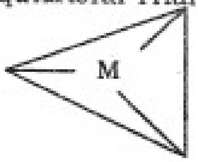
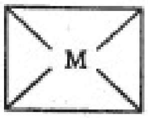
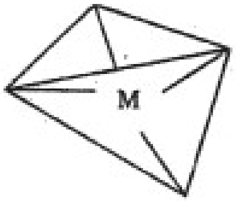
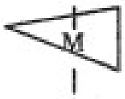
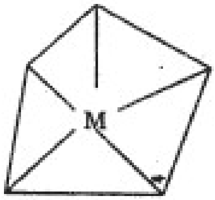
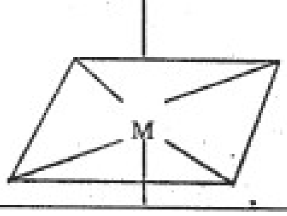
1] Coordinated Complexes

According to Werner, atoms possess two types of valencies called primary and secondary or residual or auxiliary valency. While ordinary molecules result from the satisfaction of primary valencies, utilization of the auxiliary valencies leads to the formation of Coordination compounds. Thus primary valencies of platinum and chlorine are fully satisfied in the formation of PtCl4. but the platinum still possesses auxiliary valency which enables it to combine with two ammonia or even two chloride ions to form $[Pt(NH_3)_2Cl_4]$ or $[PtCl_6]^{2-}$, respectively. Thus primary valencies can bind ionizable atoms or radicals and the secondary valencies can bind both ions and neutral molecules. But within the coordination zone both primary and secondary valencies become indistinguishable.

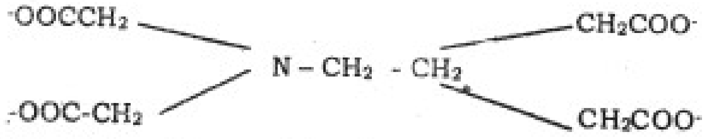
Werner introduced a new measure for the binding power of the atom, which was also expressed in integral units, to which the coordination number was given. This represents the total number of anions, group or molecules which may be directly associated with a cation giving rise to a distinct entity to which coordination complex was given. The groups of molecule or ions thus held around the central atom were said to be coordinated with it.

A complex ion will be understood to be a more or less stable, charged aggregate formed when an atom or ion most commonly from a metal, becomes directly attached to a group of neutral molecules or ions. The attached groups called ligands or donor-groups and they are complexed to the central ion or acceptor in a first coordination sphere. This leads to the general conclusion that all central ions are Lewis acids, which accept pairs of electrons and the ligands are Lewis bases, which donate a pair of electrons from each ligand.

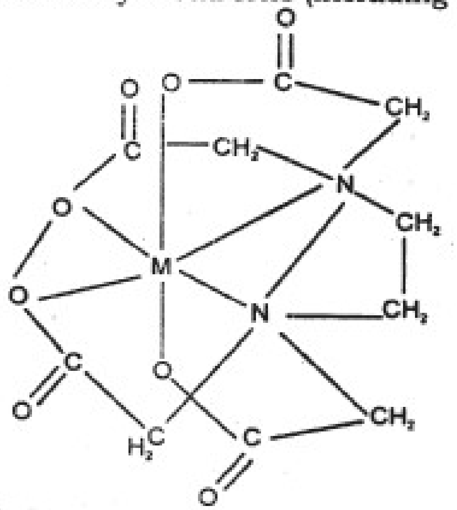
Enclosing the formula for the ion in square brackets, indicates the first coordination sphere of the complex ions $[Cu(NH_3)_4]$, SO_4, $[CO(NH_3)_4F_2]^+$ etc. The ligand atoms are arranged in a definite geometry and directly bonded to a central cation and the number of these ligands is called the coordination number of that cation. The ligands are arranged symmetrically around the central atom viz. tetrahedrally, octahedrally, cubically or in a square planar form. Transition metal ions are found to be particularly active informing coordination complexes. Though coordination numbers 2,3,4,5,6,7,8,9 and 10 are known to exist, 4 and 6 coordinated complexes are most commonly encountered.

Coord.No.	Shape	Example	Hybridization
2	Linear	$(Ag(NH_3)_2)^+$	sp
3	Equilateral Triangle 	$(Cu(SPMe_3)_3)^+$ Clo_4 $HgI_3(\varphi P)_3Pt)^0$	sp^2
4	Square planar 	$[NiCN_4)^{2-}$ $(Cu(NH_3)_4)^{2+}$	dsp^2
	Tetrahedral 	$(NiCl_4)^{2-}$ $(Ni(CO)_4)$	sp^3
5	Trigonal bipyramid 	PF_5, $(CuCl_5)^{3-}$	dsp^3
	Square pyramidal 	$(Ni(CN)_5)^{3-}$	d^2sp^3
6	Octahedral 	$(PtCl^6)^{2-}$ $(Co(NH_3)_6)^{3+}$ $(Ni(H_2O)_6)^{2+}$	sp^3d^2

A group that can attach to the same metal ion through more than one of its atoms is termed as a chelate or multidentate ligand. Chelating agents are known, which can attach to a metal ion through 2,3,4,5 or 6 or even more donor atoms with two being the most common. The terms applied to such ligands are bidentate, terdentate, quadridentate, quinquidentate and sexidentate respectively.



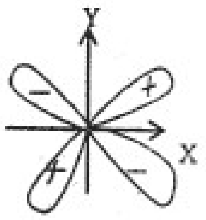
EDTA is a hexadentate ligand, which occupies all the 6 positions forming the octahedral complex with many metal ions (including Ca and Mg).



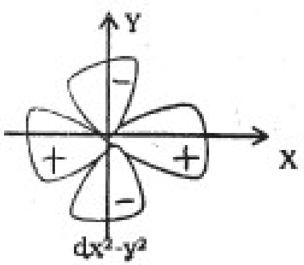
If the complex has more magnetic moments due to the presence of more unpaired electrons they are called high spin complexes (paramagnetic). The species with paired electrons are called low spin complexes (diamagnetic).

2] Bonding in Coordination Compounds

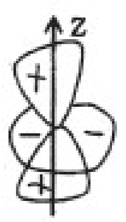
The five orbitals of transition metals are having 3 orbitals with lobes between the axes (lying in the planes) dxy, dyz, dxz, and the other two orbitals are directed along the same axes of the orbitals dx^2-y^2 and dz^2



dxy, dyz, dxz



dx^2-y^2



dz^2

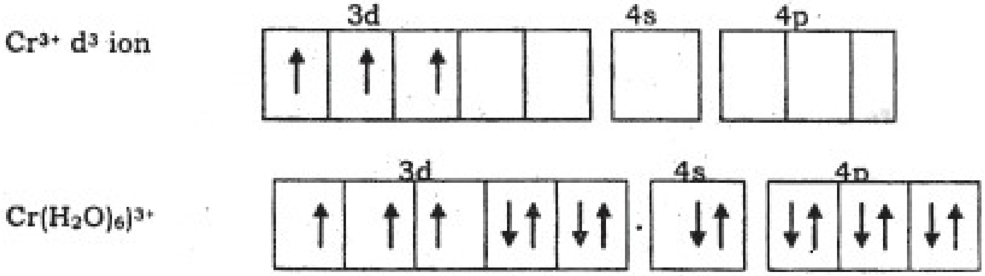
As a consequence of these differences the d-orbitals in the presence of ligands are split into groups of different energies, the type of splitting and the magnitude of the energy differences depending on the geometrical distribution and nature of the ligands. The p-orbitals are not splitting into group of different energies. This is because it is very rare for the p-orbitals to be unequally populated in stable species, so the possibility of their having different energies in different geometrical environments is of little practical significance. In f-orbitals though splitting is observed, the energies of different groups of them in different coordinations are almost the same and in this case also the splitting has no important chemical consequences.

Theories applied to coordination chemistry are the valence bond theory, the crystal field theory, the ligand field theory and the molecular orbital theory.

II. Valence Bond Theory

When valence bond theory is applied to polyatomic molecules as in the octahedral Sp^3d^2 hybridisation (s, px, py, pz, dx^2-y^2, dz^2 orbitals). The central idea of valence bond theory as applied to transition metal complexes is that empty hybrid orbitals of the metal atom or ion having the required orientation in space accept pairs of e^-s from the ligands to form ó bands.

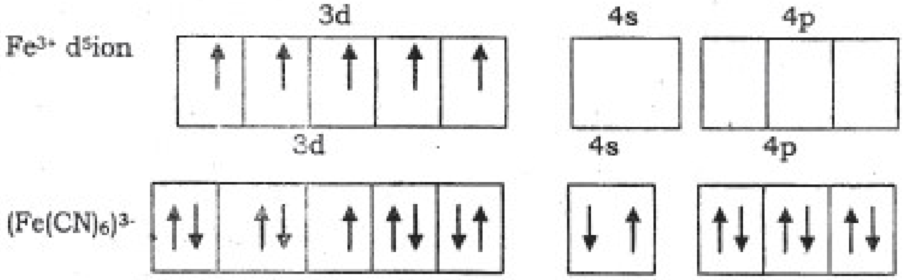
We can consider the V.B. theory as applied to Cr(III) and Fe(III) complexes. Cr^{3+} ion has the electronic configuration $3d^3$ with 3 unpaired electrons. These are placed in 3dxy, 3dyz, 3dxz orbitals which have their lobes between the ligands then six pairs of e^-s from the ligands occupy $3dx^2$-y^2, $3dz^2$, 4s, 4px, 4py and $4p_z$ orbitals as shown below.



Octahedral high spin d^2sp^3 hybridisation

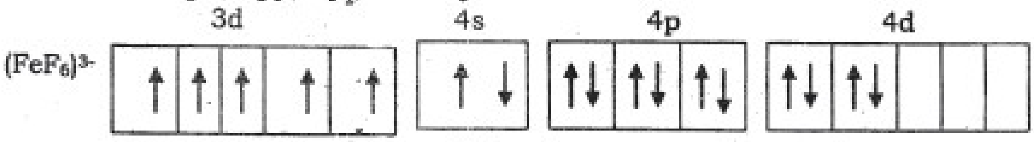
This diagram represents all octahedral Cr(III) complexes, since the 3d e^- always occupy different orbitals. For octahedral Fe(III), d^5 ion complexes, however, the five 3d e^-s can be paired as completely as possible to give a low spin complex or be all unpaired to give a high spin complex.

For a low spin complex such as $(Fe(CN)_6)^{3-}$ we can represent the electronic configuration by means of the diagram;



(Inner orbital complex) Octahedral low spin d^2sp^3 hybridization

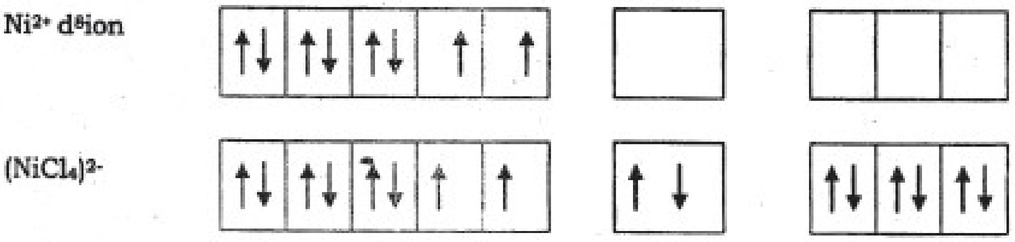
For an octahedral high spin complex of the type $(Fe(H_2O)_6)^{3+}$ or $(FeF_6)^{3-}$ the five unpaired e^-s occupy all the 3d orbitals singly and in order to maintain octahedral geometry we have to suggest that the pairs of e^-s from the ligands go into the 4s, 4px, 4py, $4p_z$, $4dx^2-y^2$ and $4dz^2$ orbitals.



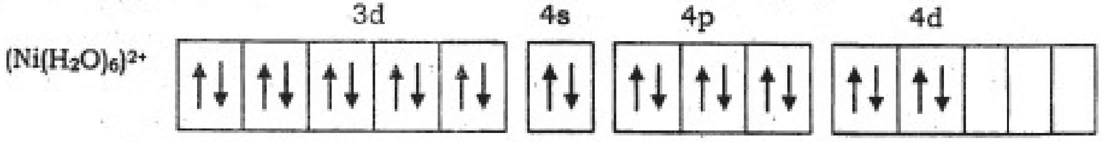
Outer orbital complex – high spin sp^3d^2 hybridisation

The complexes in which the two of the 3d orbitals are occupied by the electrons of the ligands are called inner orbital complexes and are low spin in nature. Those in which 4d orbitals are occupied are known as outer orbital complexes and are high spin in nature.

Valence bond theory can cope with other geometries and its application to Ni(II) complexes is worth discussing here. Tetrahedral and Octahedral Ni(II)d^8 complexes are all paramagnetic, the configuration of Ni(II) ion may be represented as

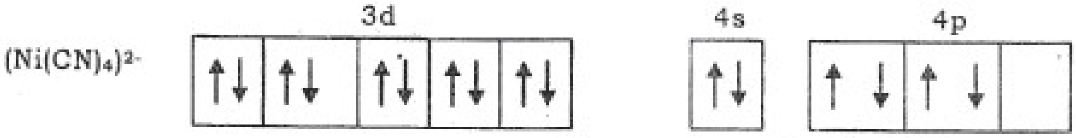


Tetrahedral sp^3 hybridisation



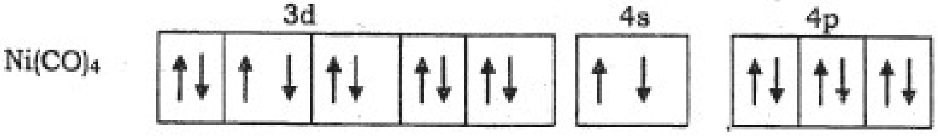
sp^3d^2 hybridisation

In tetrahedral complexes the ligand e-s occupy $4s4p^3$ orbitals and in octahedral complexes $4^54P^34D^2$ orbitals are occupied by the ligand e-s. However square planar complexes of Ni(II) eg.$(Ni(CN)_4)^{2-}$ are diamagnetic however and the electronic configuration is then shown as;



Square planar dsp^2 hybridisation

Here the ligand electrons occupying 3d,4s $4p^2$ hybrid orbitals. $Ni(CO)_4$ is tetrahedral but it is a derivative of Ni(o) for which the valence state is $3d^{10}$, the 4 pairs of e-s from the four CO molecules occupy the four 4s,$4p^3$ hybrid orbitals.



$Ni^0(3d^{10})$ SP^3 hybridisation

Tetrahedral complex

We see that V.B. theory is able to deal satisfactorily with many sterochemical and magnetic properties. Pauling suggested that complexes would be most stable when the electronegativity of the ligand was such that the metal achieved an essentially neutral condition. This rule of thumb is known as

Electro neutrality principle

In the case of carbonyls and nitrosyls the σ bonds formed by donation of e-s from the ligands to the metal atom greatly increases the e^- density on the metal atom. These complexes could not be stable if the metal did not have a second way of decreasing its e^- density. Pauling suggested that such a mechanism for delocalization of metal electron density could be found in 'back bonding' or partial double bond resonance.

$$Ni - C \equiv O \leftrightarrow N_{i}^{+} = C =_{o}$$

V.B theory uses one of the p-orbitals of C atom (making it unavailable for π bond to the O atom) whereas MO theory would speak in terms of overlap of the metal orbital with the π * orbital of CO. In either case the e^- density is shifted via a π -bond from the metal atom to the carbonyl group and the bond order of the C-O bond is reduced. The metal already in a lower oxidation state is prevented from excessively negative.

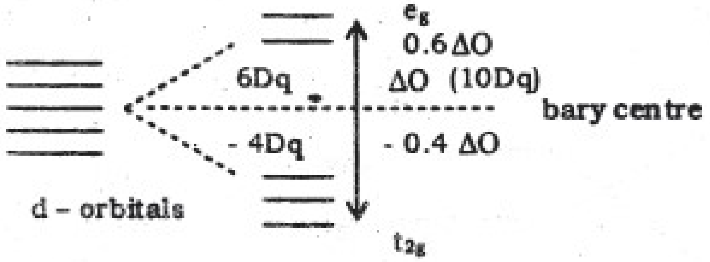
III. Crystal Field Theory

The crystal field theory was developed by Bethe and VanVleck at about the same time as V.B.theory was developed by Pauling. It is a purely electrostatic theory and it takes no account of ligand electrons except in so far as they have different energies.

Let us first consider the case of a cation surrounded octahedrally by six ligands placed on the X,Y and Z axes. There is a large net electrostatic attraction and the energy of the system is substantially lowered. If there is an e^- in each of the d orbital, there is a local increase of the energy in all these orbitals as the negative ends of the ligands are brought up to the cation.

Since the dx^2-y^2 and dz^2 orbitals lie directly in the path of the approaching ligands their energies are raised more than those of the dxy, dyz and dxz orbitals , which are directed between X,Y and Z axes. These three low energy orbitals are collectively known as t_{2g} orbitals and the two orbitals of higher energy as the e_g orbitals. t_{2g} represents triply degenerate orbitals g means gerade; the orbitals are Centro symmetric and u means ungerade (German) not Centro symmetric.

The extent to which the e_g and t_{2g} orbitals are separated is denoted by a quantity 10Dq or Δo. The pattern of splitting for octahedral geometry is said to preserve bary centre of symmetry.

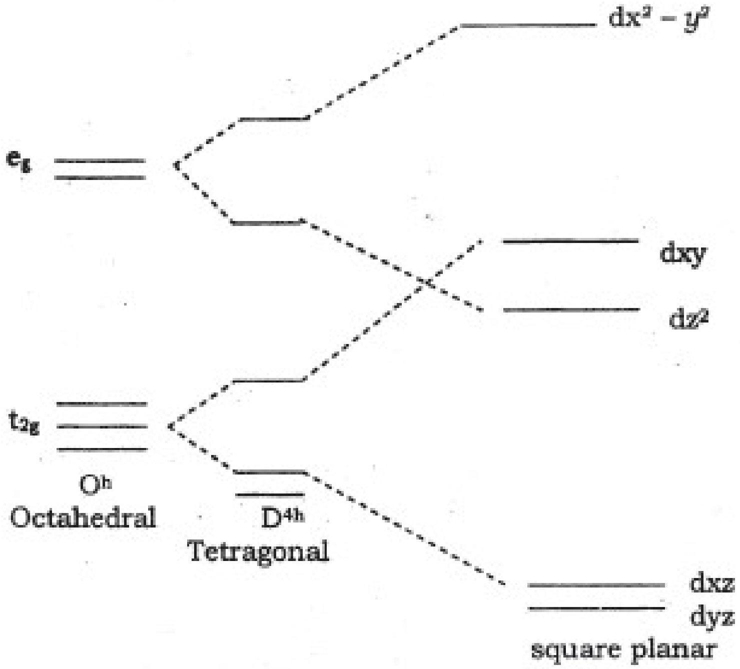


To maintain the barycentre the e_g orbitals are repelled to 6Dq to stabilize the three t_{2g} orbitals to the extent to 4Dq. For a d^{10} ion in which $t_{2g}^6 e_g^4$ configuration exists,

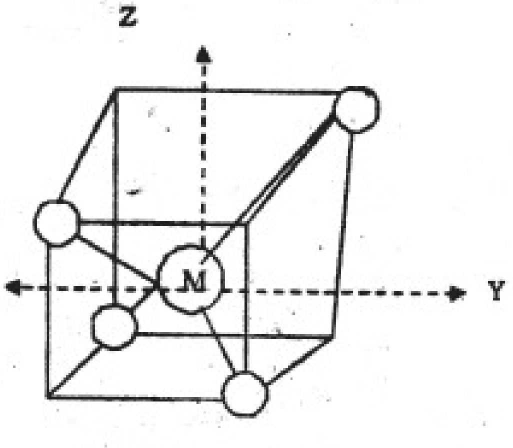
$$6(-4Dq) + 4(6Dq) = -24\ Dq + 24\ Dq = 0$$

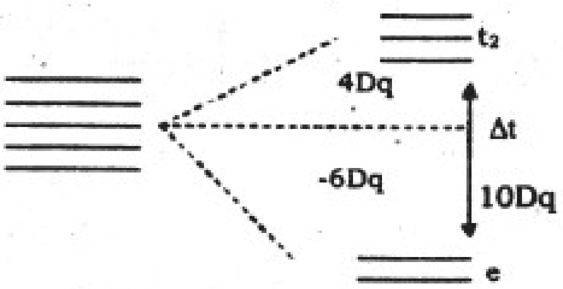
When the octahedral and square planar complexes are tetrahedrally distorted (i.e) the ligands on the Z-axis are moved out so that the metal ligand distance is slightly greater than it is for the 4 ligands in the XY plane; the result is a tetragonal structure. This permits the ligands in the XY plane to approach the central metal ion more closely and consequently d orbitals in XY plane experiences more repulsion and the energy of dx^2-y^2 and dxy orbitals increases. At the same time the d- orbitals along the Z-axis or in the XZ and YZ planes experience a similar repulsion from the ligands, which are now removed to solve distance along the Z-axis. This results in sizeable decrease in energy for the dz^2 and a light decrease for dxz and dyz orbitals relative to octahedral arrangement.

Due to the tetragonal distortion the degeneracies of e_g and t_{2g} orbitals are lifted. dz^2 orbitals and dxz and dyz orbitals becoming more stable than dxy orbital. The complete removal of two ligands along z – axis gives a square planar structure. This is accompanied by further increase in energy of dx^2-y^2 and dxy orbitals as well as the decrease of dz^2, dx^2 and dy^2 orbitals. The dz^2 orbital drops below the dxy orbital. If the energy difference between dx^2-y^2 and dz^2 is very large enough, a d^8 complex (e_g of Ni[II]) will be diamagnetic with electronic configuration $(dxy)^2$ $(dz^2)^2$ $(dx^2)^2$ $(dy^2)^2$. In the limit of tetragonal distortion, two of the ligands are removed to infinity and a square planar complex results.



Similarly trigonal bipyramid and tetrahedral splitting can be viewed in tetrahedral, d-orbital splitting for 4 coordination complexes.





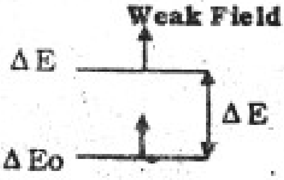
Thus the crystal field splitting for tetrahedral complex is quite reverse that of octahedral complex and energy separation between e and t_2 orbitals (here, g is omitted because the tetrahedral geometry has no centre of symmetry) is only one half to Δo. It is found that 10Dq (cubic) ≈ 8/9 (10Dq) octahedral and 10Dq (tetrahedral) ≈ 4/9 (10Dq) octahedral.

1] Crystal Field Stabilisation Energy (CFSE)

The energy associated with the metal d-orbital electrons due to their orientation in the crystal field between the two sets of t_{2g} and e_g orbitals is called crystal field stabilization energy (CFSE).

Weak Field case

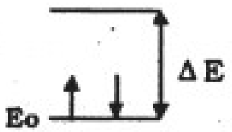
(a)



$E = Eo + Eo + \Delta E$

$= 2Eo + \Delta E$

(b)

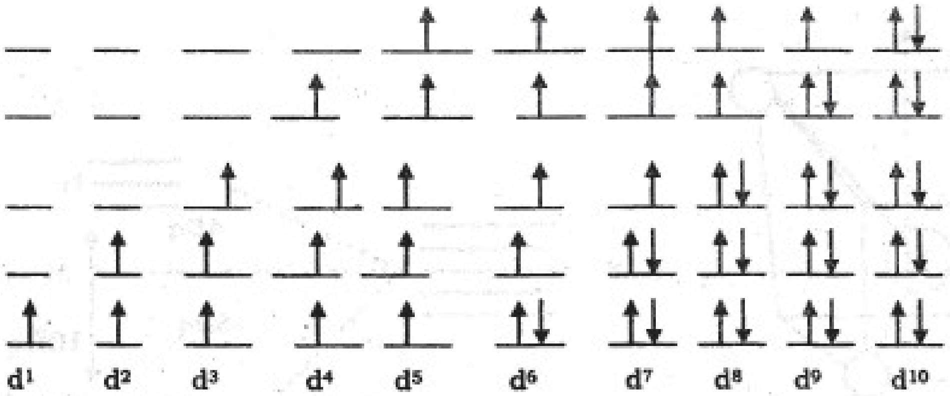


$E = Eo + Eo + P$

$= 2Eo + P$ (P = pairing energy)

Let us suppose 2 electrons occupy two orbitals separated by energy difference ΔE. If the 2 electrons are placed in two orbitals and their spins will remain uncoupled then the combined energy is (2Eo + ΔE). If the two electrons are placed in the same orbital then the energy is (2Eo + P) where P is the pairing energy required for pairing the electrons in the same orbital. Whether electrons will be distributed or paired depends on the fact that whether ΔE is greater than or less than P. If ΔE < P then the triplet state (Fig a) will be more stable. If ΔE > P then the singlet state (b) will be more stable.

The energy difference between t_{2g} and e_g orbital is defined as 10Dq and the t_{2g} orbital level relative to the barycentre of unperturbed d orbital is -4Dq. In the d^1 case CFSE is – 4Dq and for d^2 it is -8 Dq.



Here $d^1 = t_{2g}^1e_g^0 = (-4 \times 1) = -4$ Dq

$d^2 = t_{2g}^2e_g^0 = (-4 \times 2) = -8$ Dq

$d^3 = t_{2g}^3e_g^0 = (-4 \times 3) = -12$ Dq

$d^4 = t_{2g}^3e_g^1 = (-4 \times 3) + (1 \times 6) = -6$ Dq

$d^5 = t_{2g}^3e_g^2 = (-4 \times 3) + (2 \times 6) = 0$ Dq

$d^6 = t_{2g}^4e_g^2 = (-4 \times 4) + (2 \times 6) = -4$ Dq

$d^7 = t_{2g}^5e_g^2 = (-4 \times 5) + (2 \times 6) = -8$ Dq

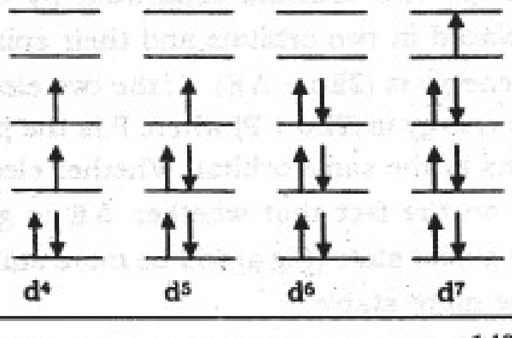
$d^8 = t_{2g}^6e_g^2 = (-4 \times 6) + (2 \times 6) = -12$ Dq

$d^9 = t_{2g}^6e_g^3 = (-4 \times 6) + (3 \times 6) = -6$ Dq

$d^{10} = t_{2g}^6e_g^4 = (-4 \times 6) + (4 \times 6) = 0$ Dq

In all these cases the electrons obey Hund's rule upon reaching d^3 configuration the t_{2g} level is half filled and if one more electron is added either it has to pair or move to the e_g level. Since P > 10 Dq, the further electron enters one of the e_g level instead of the t_{2g} level. Here it loses a small amount of energy CFSE = (3 x – 4 Dq) + (1 x 6 Dq) = - 6 Dq. Similarly for the entire configuration CFSE is calculated.

Strong Field Case



$d^4 = (4 \times -4Dq) + P = -16Dq+P$

$d^5 = (5 \times -4Dq) + 2P = -20Dq+2P$

$d^6 = (6 \times -4Dq) + 2P = -24Dq+2P$

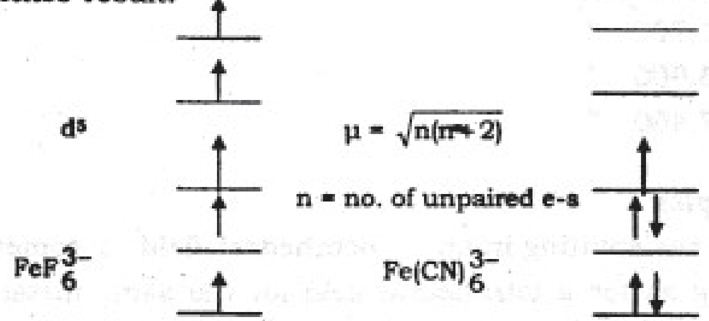
$d^7 = (6 \times -4Dq) + (1 \times 6Dq) + P$

$= -18 Dq + P$

If pairing energy is less than the splitting energy (10Dq > P) pairing in the t_{2g} level takes place instead of going into the e_g level is favoured. The situation is known as strong field case. For d^4, it is $t_{2g}^4 e_g^0$ and pairing occurs in one of the t_{2g} levels. For t_{2g}^4, CFSE = (4 x -4Dq) +P = -16Dq + P. Similarly d^5 and d^6 have 2P in the strong field case.

d^n	Weak field		Strong field		Tetrahedral	
	Confign	CFSE	Confign	CFSE	Confign	CFSE
d^1	t_{2g}^1	-4Dq	t_{2g}^1	-4Dq	e^1	-6Dq
d^2	t_{2g}^2	-8Dq	t_{2g}^2	-8Dq	e^2	-12q
d^3	t_{2g}^3	-12Dq	t_{2g}^3	-12Dq	$e^2t_2^1$	-8Dq
d^4	$t_{2g}^3e_g^1$	-6Dq	$t_{2g}^4e_g^0$	-16Dq+P	$e^2t_2^2$	-4Dq
d^5	$t_{2g}^3\ e_g^2$	0	$t_{2g}^5\ e_g^0$	-20Dq+2P	$e^2t_2^3$	0
d^6	$t_{2g}^4\ e_g^2$	-4Dq	$t_{2g}^6\ e_g^0$	-24Dq+2P	$e^3t_2^3$	-6Dq
d^7	$t_{2g}^5\ e_g^2$	-8Dq	$t_{2g}^6\ e_g^1$	-18Dq+P	$e^4t_2^3$	-12Dq
d^8	$t_{2g}^6\ e_g^2$	-12Dq	$t_{2g}^6\ e_g^2$	-12Dq	$e^4t_2^4$	-8Dq
d^9	$t_{2g}^6\ e_g^3$	-6Dq	$t_{2g}^6\ e_g^3$	-6Dq	$e^4t_2^5$	-4Dq
d^{10}	$t_{2g}^6\ e_g^4$	0	$t_{2g}^6\ e_g^4$	0	$e^4t_2^6$	0

In strong field cases, d^1,d^2,d^3,d^8 and d^9 have the same number of unpaired electrons as in the free ion irrespective of how strong the field may become for d^4,d^5,d^6, d^7 two possibilities are existing (low spin and high spin or strong field and weak field, respectively) and the ground state quantum can be answered by comparing Δo and P. If Δo > P then strong field (low spin) complexes arise and if Δo < P (high spin) weak field complexes result.

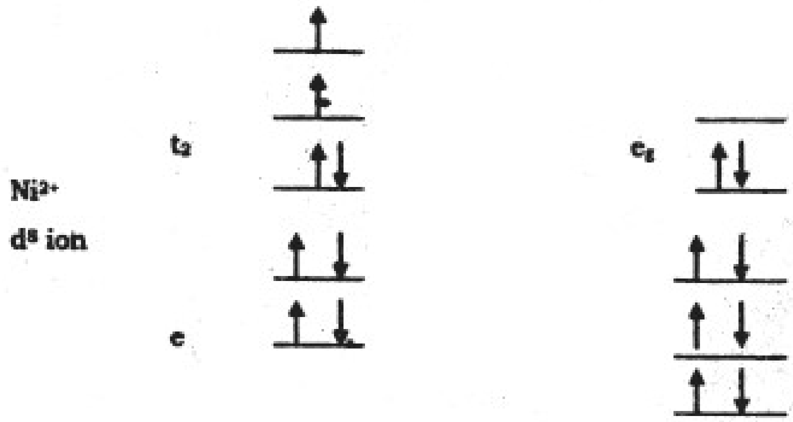


Weak field (μ = 5.8 B.M)
(5 unpaired electrons)

Strong field (μ = 1.4 B.M)
(one unpaired electron)

The low and high spin complexes can be explained by CFT. Similarly CFT can explain tetrahedral field and square field complexes.

For eg. Ni(II) d^8 ion



Tetrahedral Paramagnetic
[high spin]
(Two unpaired electrons)

Square field Diamagnetic
(low spin)
(All paired electrons)

2] Factors Affecting Magnitude of 10Dq

(i) Charge on the ion

The increased charge on the metal ion tends to pull the negatively charged ligand closer to half, which will have a greater effect in perturbing the metal d orbitals. This is reflected in the increased 10Dq values. Theoretically the change from 2+ to 3+ ionic charge would increase 10Dq by 50%.

Ionic charge	10Dq($6H_2O$)
V^{2+}	12,600 cm^{-1}
V^{3+}	17,700 "
Cr^{2+}	13,900 "
Cr^{3+}	17,400 "

(ii) Geometry of the Complex

As discussed earlier the splitting in an octahedral field is somewhat more than twice as strong as for a tetrahedral field for the same metal ion. Further in the tetrahedral complex, the ligands are less efficiently directed than in the octahedral (O_h) complexes.

(iii) Nature of the Ligands: Spectrochemcial series

The nature of the ligand also affects the degree of splitting. There is steady progression in frequency of the absorption maxima as the ligands change with the linking atoms progressing $Cl \longrightarrow S \longrightarrow O \longrightarrow N \longrightarrow C$ corresponding to an increase in the value of 10Dq. A spectrochemical series is constructed from overlapping sequences each illustrating a portion of series.

Weak field

$I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < OX^{-2} < H_2O < NCS^- < CH_3CN$

Strong field

$< NH_3 < en < dipy < phen < NO_2^- < Cp < CN^- < CO$

The spectrochemical series for ligands arranges them in order of their ability to cause increasing Dq value in complexes with any metal ion. It is not an absolute ordering under all circumstances but it is a good approximation and flexible in its applications.

(iv)Nature of the Metal ion

Within a given transition series the differences in the Dq values are not great, but noticeable changes occur between the congeners in a group, the orbital splitting (10Dq) are in the order 3d < 4d < 5d. Moving from Co to Rh the Dq value increases by 60%. Likewise the values for Ir complexes are 25% greater than for Rh complexes.

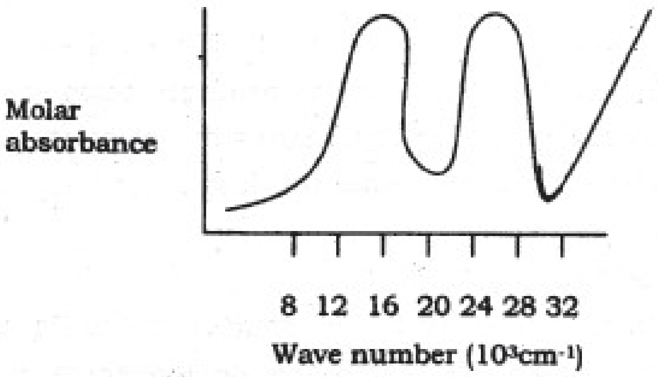
Complex	10Dq(6NH3)cm-1
Co^{3+} $(3d^6)$	22,900 "
Rh^{3+} $(4d^6)$	34,100 "
Ir^{3+} $(5d^6)$	41,000 "

4] Limitations of the CFT

Although CFT adequately accounts for a surprisingly large amount of data it has serious defects. It was soon realized that the assumption of a point charge model was a drastic over simplification. There are several experimental and semitheroetical arguments that can be presented against the assumption that the splitting of the d-orbital is a result solely of electrostatic effects and that the bonding is "ionic" with no covalent character. We have seen that the interpretation of spectrochemical series in terms of point – charge model is extremely tenuous. The ligand exerting the strongest field and thus lying at the head of the series is the carbonyl CO group with no ionic charge and almost no dipole moment $\left(\mu = 0.374 \times 10^{-30} \text{cm}\right)$. Evidences for CFSE are obtained from lattice energies of ionic compounds, the enthalpy of hydration and from the ionic radii.

IV. Nephelauxetic Effect

When the spectrum of $(Cr(H_2O)_6)^{3+}$ complex is interpreted experimentally by assigning transitions to the observed peaks and using the theoretical quantities Dq and B as parameters to be established by fitting them to the spectrum. The significance of Dq quantity can only be established by comparing various ligands and various metals.



The B parameter, however, we can immediately compare with the value for the free ion, which is $10^3 cm^{-1}$. In the complex the value of B has been reduced to only about 65% of the free ion value. Remembering that B represents the magnitude of d-electron/d-electron repulsion, this result implies that the repulsion was significantly reduced when the complex is formed. This has been interpreted as an expansion of the d-electron cloud out onto the ligand atoms (oxygen in this case). If the electron cloud is larger, more diffuse, the repulsion is less.

The d-electrons are thus delocalized into at least partially covalent bonds with the ligand atoms. The cloud-expanding effect is called nephelauxetic effect (nephelaux – cloud expanding - Greek). The ligands are arranged in the nephelauxetic series in which electron delocalization increases and B becomes smaller.

$$\text{(Large B)} \; F^- > H_2O > \text{urea} > NH_3 > \text{en}$$

$$\cong C_2O_4^{2-} > NCS^- > Cl^- \cong CN^- > Br^- > I^- \; \text{(small B)}$$

The ligands lie to a reasonable approximation in the order of decreasing electronegativity of the donor atom F,O,N, Cl, C, Br, S. That is the less electronegative a donor atom, the more it reduces the repulsion between d electrons already present on the metal. The increase in the molecular orbital size results from the combination of orbitals on the metal and ligand and ligands that can delocalize the metal electrons over a large space (those containing larger atoms with d orbitals for π – bonding) are most effective in this manner. Nephelauxetic series is entirely different from spectrochemical series.

V. Molecular Orbital Theory

The essential feature of this theory is that overlap of atomic orbitals of the metal ion and ligands will occur to some degree whenever symmetry permits.

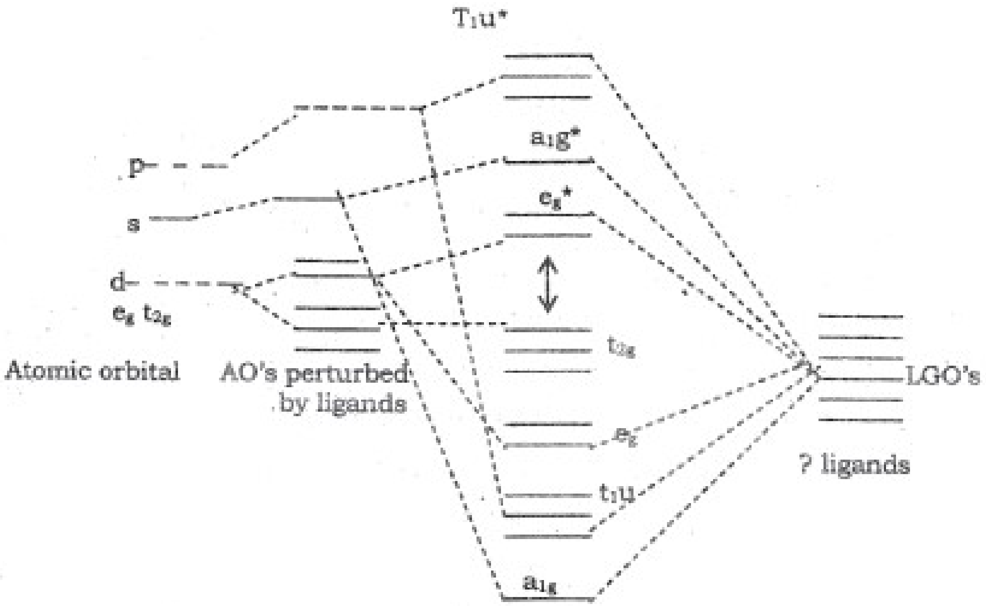
1.There are 9 valence shell orbitals (s, p^3, d^5) of the metal ion to be considered. The dz^2, dx^2-y^2 s, px, py, pz are lying along the axes (direction of σ bonding); dxy , dyz and dxz are suitable for π bonding. These 9 orbitals lie in 4 symmetry classes. (a) Totally symmetric a_{1g} (s orbital) (b) triply degenerate T_1u (p orbitals), (c) doubly degenerate e_g and (d) triply degenerate t_{2g} orbitals.

2. The six σ – orbitals of the metal overlap with σ orbitals of the ligand group orbitals (LGO).

3. By effective orbital overlapping of the metal and ligand orbitals, the bonding and antibonding orbitals are formed.

The ion $(Co(NH_3)_6)^{3+}$ is a low spin complex with $18e^-$ (6 from Co^3+ 12 from ligands) are accommodated with a,g,t,u,e_g, t_{2g} molecular orbitals. For a high spin Co[III] complex such as $(CoF_6)^{3-}$. On the other hand there are only 4 electrons in the t_{2g} orbitals and other 2 in the e_g* orbital with 4 unpaired e^-s in all. (The overlap of metal s and p orbitals with Ligand group orbitals (LGO's) is extensive] There are large differences in energy between the resulting a_{1g} and a_{1g}*, t_1u and t_1u* bonding and antibonding orbitals.

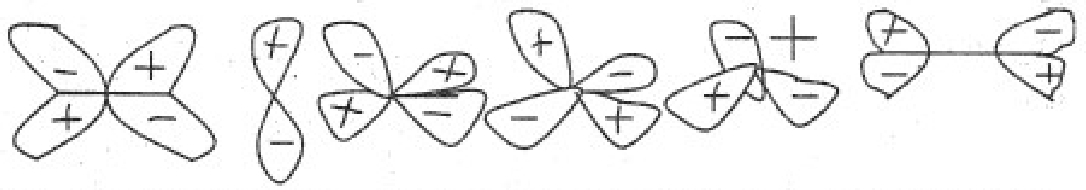
Thus the a_1g and t_1u are the lowest Molecular orbitals and a_1g* and t_1u* are the highest antibonding Molecular orbitals. The e_g and e_g* orbitals are less widely separated because of the poorer overlap between dx^2-y^2 and dz^2 orbitals and the LGO's. Even so, the better the overlap, the bigger the separation will be. If no π – bonding takes place, t_{2g} is non-bonding and has the same energy. The t_{2g} – e_g* energy separation is Δ o (as in CFT) .



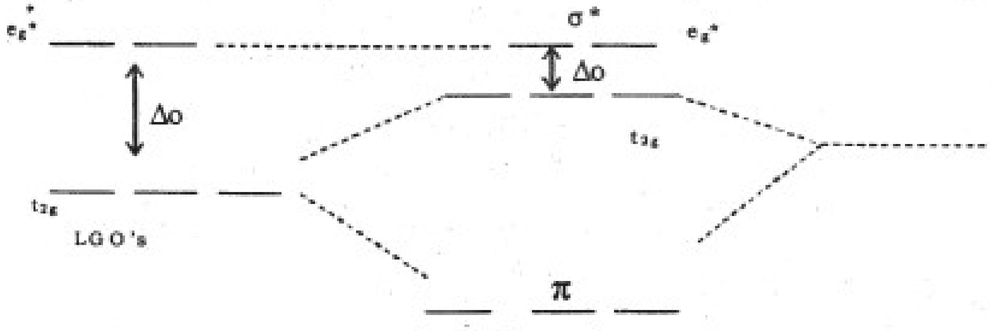
σ – Complex

Molecular orbital without π - bonding

For π – bonding in octahedral complexes the metal t_{2g} orbitals are directed between the ligands and non-bonding in a complex in which only σ – bonding is present can readily overlap with LGO having the same symmetry and these can be formed from p-orbials perpendicular to σ – bond axes; d-orbitals lying in a plane that includes the metal atom or π*



(a) p – orbital overlapping (b) d-orbital overlapping π* - orbital overlapping



π - bonded complex

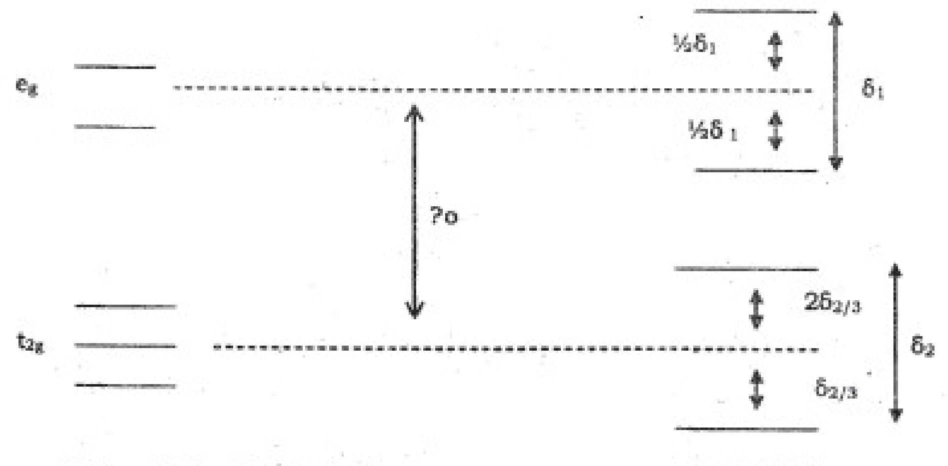
If the LGO's lie at a lower energy than the metal t_{2g} orbital, then π – bonding involves only t_{2g} of the metal and not the e_g^*. The Δo when the π – bonding is absent. Further e_g^* orbitals will be more strongly antibonding and will therefore less likely to be occupied. Thus octahedral complexes involving π – bonding ligands are very unlikely to be high spin complexes, only low spin complexes are formed. Here the ligands may be C1 phosphine, CO respectively.

VI. Jahn – Teller Distortions

An interesting theorem proved by Jahn and Teller in 1937 although only qualitative has important stereochemical significance. It states, "Any non-linear molecular system in a degenerate electronic state will be unstable and will lower its symmetry and split the degenerate state". This simple theorem has great practical importance in understanding the structural chemistry of certain transition metal ions.

The general theory is best illustrated with specific example of Cu^{2+}, which is d^9 ion with $t_{2g}^6\ e_g^3$ configuration. The e_g^3 electrons occupy $(dz^2)^2\ (dx^2\text{-}y^2)$ or it may be $(dz^2)\ (dx^2\text{-}y^2)^2$ the Cu^{2+} ion is now placed in an already set up regular octahedron environment of ligands. The dz^2 orbital, which is filled and points at the ligands as the Z-axis now offers greater shielding of the Cu^{2+} nucleus than the half - filled $dx^2\text{-}y^2$ orbital, which points towards the ligands in the XY plane. The latter which see a higher effective nuclear change are drawn in closer to the Cu^{2+} nucleus whereas the ligands on the Z – axis move further out since they experience a lower effective nuclear charge.

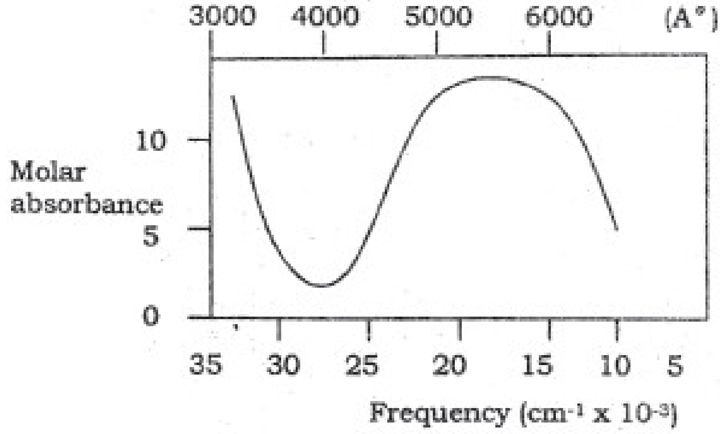
Naturally the 4 ligands in the XY plane will be drawn more closely to the cation than will the other two in the Z – axis (i.e) 4 shorter and 2 longer bonds. If conversely $(dx^2\text{-}y^2)$ is doubly occupied and (dz^2) is singly occupied the two ligands will be drawn somewhat more closely than the other four. It may be noted that if there is centre of symmetry in the undistorted molecule, then the distorted equilibrium configuration will also have centre of symmetry. The effect of distortion is shown in the Figure. Due to distortion, e_g orbitals are separated equally up and down the e_g level (i.e.) each orbital moving $\delta_{1/2}$ approximately. The triply degenerate t_{2g} is distorted in δ_2 (δ_2 is smaller than δ_1). The two orbitals are separated $\delta_{2/3}$ for dxz and dyz and $2\delta_{2/3}$ for dxy. The stabilization of $\delta_{1/2}$ in e_g level gives the driving force for distortion. It is observed that when e_g set of levels are occupied by odd number of electrons.



Jahn - Teller distortion is larger,

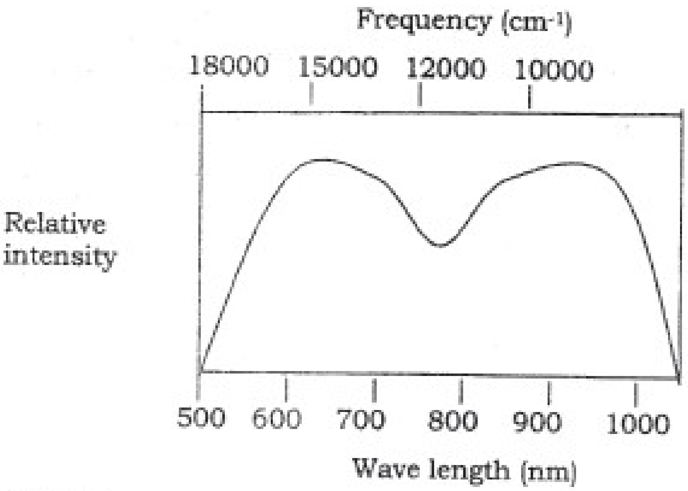
$d^4 - t_{2g}^3\, e_g^1$ high spin Cr^{2+}, Mn^{3+}
$d^7 - t_{2g}^6\, e_g^1$ low spin Co^{2+}, Ni^{3+}
$d^9 - t_{2g}^6\, e_g^3$ Cu^{2+}, Ag^{2+}

It may also be noted that Jahn – Teller theorem applied to excited states as well as ground states. To see the effect in excited state let us consider $(Ti(H_2O)_6)^{3+}$ $(Fe(H_2O)_6)^{3+}$ and $(CoF_6)^{3-}$. In $(Ti(H_2O)_6)^{3+}$ e^- is in $t_{2g}^1e_g^0$. On excitation it moves to $t_{2g}^0e_g^1$ configuration. The presence of single electron in the e_g causes the excited state to split which leads to the formation of a broad band in the spectrum.



Infact the very small number of Cu(II) complexes that do show ideal octahedral geometry, such as some chelates and the $(Cu(NO_2)_6)^{4-}$ ion in $K_2Pb(Cu(NO_2)_6$ are thought to show a "dynamic Jahn - Teller distortion" in which the molecule oscillates between the three possible tetragonally distorted shapes so rapidly that experimental techniques show only the time average geometry, which is octahedral. If the above compound is cooled a few degrees, the dynamic Jahn – Teller effect is "frozen" out. For eg. at 276 K, K_2 Pb $Cu(NO_2)_6$ has obvious distortion in Cu – N distances of 205.8, 215.3 and 216.6 pm.

In some species such as $(CoF_6)^{3-}$ in $(t_2g^4eg^2 \longrightarrow t_2g^3eg^3)$ excited state splitting of the two bonds is sufficient to cause two distinct peaks to be found in the spectrum.



VII. Magnetic Properties

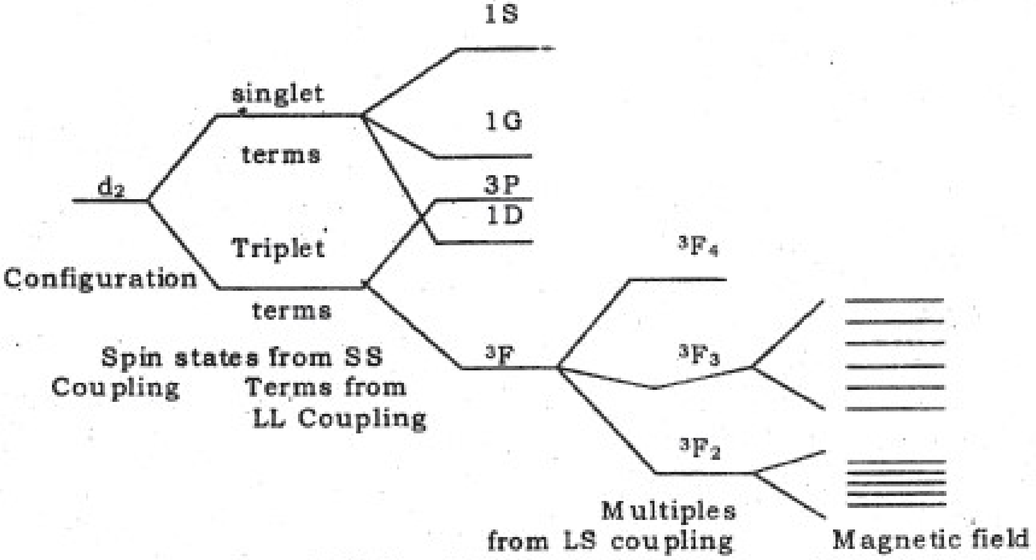
If the metal ions have no interaction with other metal ions then there is no magnetic interaction. Magnetic susceptibilities are in general very small. Interaction between the atomic dipoles in a system can very greatly increase the magnetic alignment energy by making it the property of a large number of units rather than of a single one. Under such circumstances the alignment energy may be comparable to or greater than the thermal energy.

Substances in which there is no interaction between adjacent atomic dipoles are said to be magnetically dilute. In magnetically non-dilute (magnetically concentrated) substances there is interaction between adjacent dipoles. Magnetically non-dilute substances may possess very complicated magnetic polarization effects and show the well-known phenomenon of ferromagnetism and antiferromagnetism. Two types of magnetic behaviour are found in magnetically dilute substances. In diamagnetic substances, the magnetic susceptibly χ is negative and in paramagnetic substances it is positive. In ferromagnetic materials the magnetic domains are aligned in the same direction. In antiferromagnetic the neighbouring magnetic dipoles are aligned in opposite directions.

$TiCl_3$ at ordinary temperatures has a magnetic moment, 1.3 μB instead of the expected 1.73 μB. K_2' $(OsCl_6)$ has moment of 1.4 μB but if it forms dilute solid solution with $K_2(PtCl_6)$ (which is diamagnetic) the moment rises to 1.9 μB. However $(OsCl_6)^{2-}$ is a low spin d^4 complex and this moment is still low for a species containing 2 unpaired electron (μB – dipolemoment in Bohr magneton)

Using Russell Saunder's LS coupling the ground state term is written as $(2S+1)L_J$ The energy difference of J values, J' and J'+1 is given by (J' + 1) λ where λ is the spin – orbit coupling constant. For the d^2 configuration for example spin-spin interaction separates the energy levels into a set having the spins of the same sign (S = ½ + ½ = 1) then multiplicity 2S + 1 = 3 and a set having opposite spins (S = ½ - ½ = 0) then multiplicity 2S + 1 = 1. The triplets are lower in energy than singlet state. Orbital coupling splits these levels further, for the d – electron $l = 2$ and if S = 1 the maximum value for L is 3 term letters F and the term symbol is ^3F. This is split by spin-orbit coupling into states $^3F_2$, $^3F_3$ and $^3F_4$ of which $^3F_2$ is the lowest and the difference between successive pairs are 3 λ and 4 λ, respectively.

In a magnetic field, spectroscopic states are split again to give (2J + 1) levels each separated by gβH where g is the Lande splitting factor for the system β the Bohr magneton and H the field strength for a field of 10000 gauss, gβH is about 1cm^{-1} since this corresponds to only 0.012 KJ (0.003 K cal) mol^{-1}. Magnetic field structure is like spectroscopic field structure is concerned with extremely small amounts of energy compared with energy changes in chemical process. The overall splitting pattern is given below;



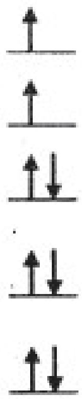
Splitting of the states of a gaseous d² ion

If the separation of energy level is large the magnetic moment can be given as;

$$M = g_J\sqrt{J(J+1)} \text{ where } g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

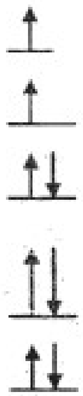
It is called Lande splitting factor, a constant. This value gives values for magnetic moments of lanthanides ions for which λ is about 1000 cm^{-1}. For many ions λ is very small and spin and orbital angular momenta of the electrons operate independently. For electron spin only L = 0, J = S and $g_J = 2$ and for orbital motion only S = 0, J = L and $g_J = 1$. Then μ is given by $\mu = \sqrt{4S(S+1)+L(L+1)}$ which, if there is no contribution from orbital motion (L = O) reduces to spin only formula; $\mu = 2\sqrt{S(S+1)}$ or $\sqrt{n(n+2)}$ where n is the number of unpaired electrons. Any ion for which L = 0, e.g. Mn^{2+}, Fe^{3+} (d^5 configuration) for which all d orbitals are occupied, singly by e^-s then m_l = 2, 1,0, -1,-2 giving L = 0 should obviously obey the spin only formula and some others also give L = 0 and in these cases the orbital angular momentum is said to be quenched.

In order for an electron to have orbital angular momentum, it must be possible to transform the orbital it occupies into an entirely equivalent and degenerate orbital by rotation; the e^- is then effectively rotating about the axis used for rotation of the orbital. In an octahedral complex the three t_{2g} orbitals can be interconverted by rotation through 90^0 so an electron in a t_{2g} orbital has orbital angular momentum, the e_g orbitals having differences in shapes cannot be interconverted, so electrons in e_g orbitals never have orbital angular momentum. If all the t_{2g} orbitals are singly occupied (t_{2g}^3) an electron, in say, dxz orbital cannot be transferred into the dxy or dyz orbital because these already contain an electron having the same spin quantum number as the incoming electron. If all the t_2g orbitals are doubly occupied the transfer is impossible. Thus only the configuration, which have t_{2g} electrons but not t_{2g}^3 or t_{2g}^6 make orbital contribution to the magnetic moments of octahedral complexes. For high spin complexes only t_{2g}^1, t_{2g}^2, $t_{2g}^4 e_g^2$, $t_{2g}^5 e_g^2$ configurations are contributing. For tetrahedral geometry, it is easily shown that the configurations giving rise to an orbital contribution are $e^2t_2^1$, $e^2t_2^2$, $e^4t_2^4$ and $e^4t_2^5$. So an octahedral d^8 has low dipolemoment than tetrahedral geometry.



$Ni^{2+}d^8$

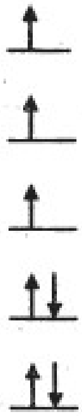
Octahedral $t_{2g}^6e_g^2$



$e^4t_2^4$

tetrahedral

In high spin d^7 complex, the magnetic moment should be greater than the spin only value of 3.87 μB but a tetrahedral d^7 complex should not.



Co^{2+} $t_{2g}^5 e_g^2$ $\mu = \sqrt{3(3+2)} = 3.87\ \mu B$

In practice $(Co(H_2O_6)^{2+}$ and $(CoCl_4)^{2-}$ both have magnetic moments above the spin only value of 5.0 and 4.4 respectively. Another factor called spin-orbit coupling leads to somewhat low magnetic moments for d^1, d^2,d^3 and d^4 ion and high magnetic moments for d^6,d^7,d^8,d^9 ions. For the first series λ is positive value and for next series it has –ve value Here, $\mu = \mu_s (1-\alpha)\frac{\lambda}{\Delta o}$ value from spin only and λ is a constant depending on the ground state.

VIII. Measurement of Magnetic Susceptibility

It can be defined as the molar susceptibility χ_M where $\chi_M = (M/d)\ \chi$ $\chi = I / H$ with I = Intensity of magnetization and H = Field strength per unit volume. The quantity χ_M which is the induced moment I per mole percent has applied field H the units cc $mole^{-1}$. For normal paramagnetic substances χ, $\chi\gamma$, $\chi\mu$ are constants independent of field strength.

The susceptibility measured for a given material will consist of contributions from paramagnetic and diamagnetic susceptibilities, the former being much greater. The diamagnetic contribution can be appreciable and the measured susceptibility becomes equal to the sum of the paramagnetic and diamagnetic susceptibility.

This formula leads to a positive correction to the measured susceptibility because the value of the diamagnetic susceptibility is negative. This takes into the direction of the diamagnetic and paramagnetic moments. From the measured paramagnetic susceptibility one can calculate the magnetic moment μ_{eff} of the compound in B.M units using the relationship μ eff = $2.84\ (\chi'_A T)^{1/2}$

Where T is the absolute temperature and χ_A is the molar susceptibility corrected for diamagnetic effects. This equation holds good for substances that obey the Curies law $\chi = C/T$ where c'is a constant. In practice it is found that for many substances the temperature variation of the susceptibility is expressed not by the Curie law but by the Curie Weiess law $C/T-\theta$ where θ is also a constant often 30^0 or less. Use of this equation introduces an error of a few tenths of a B.M. at most, which is insignificant in most applications.

Gouy Method

The magnetic susceptibility of a compound may be determined by the Gouy method. The method involves measuring the force on a thin cylindrical sample suspended over the poles of a powerful electromagnetic and gives the gram susceptibility χ_g. The molar susceptibility $\chi_m = \chi_g$ x m.wt

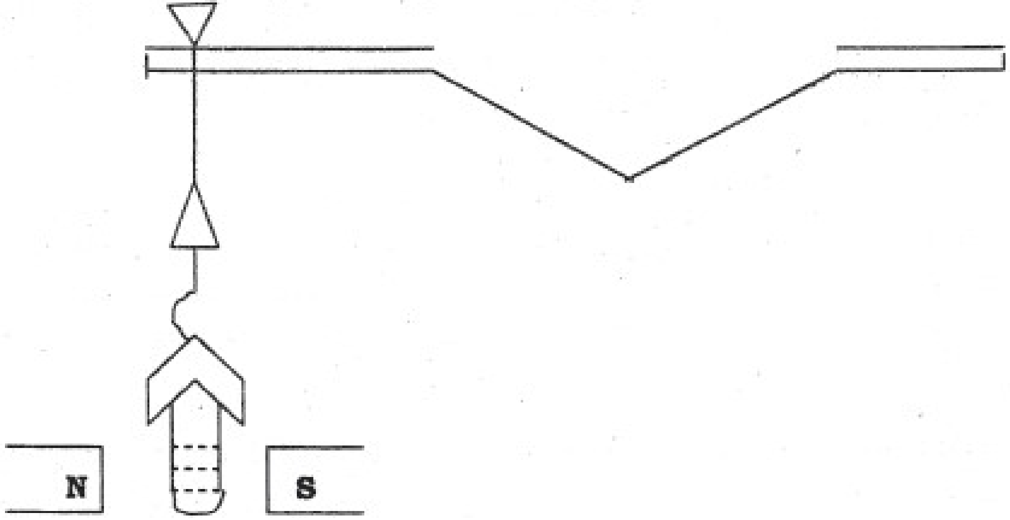
A small correction must be made to compensate for the diamagnetism of the ligands surrounding the metal atom and any other diamagnetic ions or molecules in the (lattice). Diamagnetic corrections for common groups are tabulated below. χ_Δ is always subtracted from χ_m and (corr) = $(\chi_m - \chi_\Delta)$

Constitutive corrections				Ligand corrections			
C = C	-5.5	N = N	-1.8	C – Cl	-3.1	dipyridyl	105
C = C -C = C	-10.6	C = N -R	-8.2	C – Br	-4.1	Phenanthridine	128
C = C	-0.8	Carbon in Benzene ring = -0.24		C – I	-4.1	Water	13
				Phenylene bisdimethyl carbons			194

Diamagnetic Corrections
(All values x 10^{-6}/g atom)

Cations		Anions		Elements	Pascal	Constant	
Li^+	1.0	F^-	9.1	H	2.93	P	26.3
Na^+	6.8	Cl^-	23.4	C	6.00	As(q)	43.0
K^+	14.9	Br^-	34.6	N ring	4.61	As(III)	20.9
Rb^+	22.5	I^-	50.6	N open chain	5.57	Sb(III)	74.00
Cs^+	35.0	NO_3^-	18.9	N Mono	1.54	Li	4.2
Ti^+	35.7	ClO_3^-	30.2	N diamide	2.11	Na	9.2
NH_4^+	13.3	ClO_4^-	32.0	O ether alcohol	4.61	K	18.5
Hg^{2+}	40.0	BrO_3^-	38.8	O	-1.73	Mg	10.0
Mg^{2+}	5.0	IO_3^-	51.9	O carboxyl	3.36	Ca	15.9
Zn^{2+}	15.0	IO_4^-	51.4	F	6.39	Al	13.0
Pb^{2+}	32.0	CN^-	13.0	Cl	20.1	Zn	13.5
Ca^{2+}	10.4	CNS^-	31.0	BR	30.6	Hg(II)	33.0
Fe^{2+}	12.8	SO^{2-}	40.1	I	44.6	Si	20.0
Cu^{2+}	12.8	CO_3^{2-}	29.5	S	15.0	Sn(IV)	30.0
Co^{2+}	12.8	OH^-	12.0	Se	23.0	Pb	46.0
Ni^{2+}	12.8			Te	37.3		

Magnetic susceptibilities can be determined by measuring the apparent change in weight of paramagnetic sample in a magnetic field.



The instrument is calibrated by use of a sample, such as Hg CO $(SCN)_4$ or $(NH_4)_2$ $Fe(SO_4)_2$ $6H_2O$ of known susceptibility.

Gouy Balance: for samples of constant height and area in the magnetic balance, the molar susceptibility χ_m is related to the weight W, the change in weight ΔW and the formula weight M, by $\chi_m = K\frac{\Delta W}{W} M$ where K is an instrumental constant to be determined using the calibrant.

Questions

1. Discuss the salient features of Valence Bond theory.
2. Explain the terms ligand, chelate, diamagnetic, paramagnetic and coordination number.
3. Give the differences between valence bond theory and crystal field theory.
4. Explain how crystal field stabilization energies are calculated.
5. Show that octahedral splitting is inverted to that of tetrahedral splitting.
6. Show that square planar Ni(II) complexes are diamagnetic using the crystal field theory.
7. Discuss the factors affecting the magnitude of 10Dq.
8. How the Molecular Orbital Theory explains the σ - bond formation in Co(II) complexes.
9. Discuss the M.O theory for π - bonded complexes.
10. What is Jahn Teller Theorem? How it can account for distortion in some octahedral complexes?
11. What do you mean by Dynamic Jahn – Teller theorem?
12. How spectrochemical series and Nephalauxetic effect series are differing?
13. What do you mean by magnetic dilution?
14. Write short notes on (i) Spin – orbit coupling. (ii) Spin only value (iii) Orbital contribution to magnetic moment (iv) Orbital quenching.
15. Discuss how Gouy Balance is used to measure magnetic susceptibilities.
16. Calculate the magnetic moments for $(FeF_6)^{3-}$, $(NiCl_4)^{2-}$, $(Co(NH_3)_6{}^{3+}$, $(Cu(NH_3)_4)^{2+}$

UNIT – V

METALLURGY AND INORGANIC POLYMERS

SYLLABUS

Occurrence, isolation, purification, properties and uses of the following metals and their important compounds; Zr, Ge, Pu, Th, U and Os. Silicates – Various silicate structures – property correlation – silicones – polyacids – Structure of heteropoly and Isopolyacids – polymeric sulphur nitride – borazines – phosphonitrilic compounds – boranes and carboranes.

I. Zirconium

The treatment of zircon are involves the preparation of pure zirconium compounds like basic sulphate, $42ro^{2+}$, $3SO^{3+}$, $14H^{z}O$ or zirconium oxychloride, $ZrOCI_2$, $8H_2O$, or an insoluble phosphate, or a crystalline precipitate of the sulphate $Zr(SO_4)^{2+}\ 4H_2$ or double fluorides like potassium zirconium fluoride or the preparation of alkali chlorozirconates or even zirconium tetrafluoride from the extracted mass, separation of zirconium and hafnium, and lastly production of pure metal as a reduced product of some of the compounds of zirconium.

Occurrence

The starting ore is zircon, which contains traces of hafnium also. Though it does not occur free in nature, it is found widely distributed as silicate or oxide. It is almost as abundant as carbon, constituting nearly 0.017 per cent of the earth's lithosphere. Its large workable deposits are rare.

It occurs in nature as an oxide in the mineral baddeleyite (80% ZrO_2) complex zirconates as zirkelite, (Ca, Fe) 0.2 (Zr Ti, Th)O_2; which has 50% ZrO_2 ; uhligite, $Ca(Zr.Ti)_2O_5.Al_2.\ TiO_5$ (33% ZrO_2); and wohlerite, 12R (Si, Zr) $O_3R(Cb_2O_5)$ (15.23% ZrO_2). The important important silicates of zirconium are zircon, $ZrSiO_4$(61-67% ZrO_2) and its varieties as azurite, hyacinth and jargon, and its altered forms as adelpholite, alvite, orvillite etc. it also occurs in various tantalum and columbium minerals as chalcolamprite (5%) and columbite (1.11%), fergusonite (2%), samarskite (0.4%).

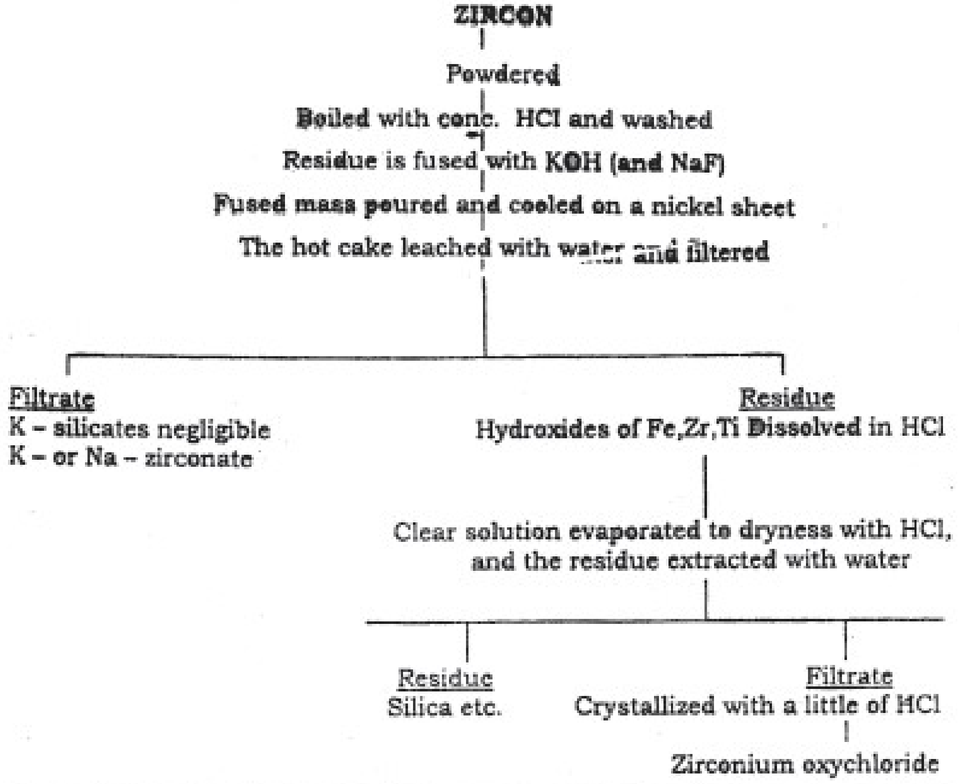
Zirconium occurs in the alluvial sands of Ceylon and Travancore in India.

1. Extraction

The process employed for extraction of zirconium form the native and impure oxides or silicates, depends on the degree of purity desired. The mineral is first pulverized to a fine state of sub – division by heating and suddenly cooling the mineral, (i) 90-95% silica can be removed by heating a mixture of the ore and carbon in an electric in an electric furnace at 222°; (ii) hot sulphuric or hydrochloric acids or equa regia will remove most of the iron. Silica from zirconium silicate cannot be removed by hydrofluoric acid. If silica is to be removed fully, it is necessary to open up the mineral by sintering or fusion with suitable fluxes.

i) Fusion with Alkali Hydroxides or Carbonates

Klaporth fused the mineral with 5 times its weight of potassium hydroxide. During such a fusion, silica, zirconia and titania change respectively to the alkali silicate, zirconate and titanate and the iron is converted to ferric oxide. Zirconia may also form a double alkali zirconium silicate. The fused mass is cooled and leached with water. The insoluble residue consists of hydroxides of iron, zirconium, and titanium (and alkali zirconium silicate). When treated with hydrochloric acid, most of it dissolves, leaving a little silica. The solution is repeatedly evaporated with hydrochloric acid hydrochloric acid to dryness; thus separates the insoluble is repeatedly evaporated with hydrochloric acid to dryness; thus separates the insoluble fluosilicic acid (silica and hydrofluoric acid). The filtrate is treated with a little hydrochloric acid and zirconium oxychloride is crys



ii) Fusion with Alkaline Earths or Lead Oxide Bayer's Method

The powdered mineral is heated with barium carbonate in a graphite crucible. The barium zirconate is extracted from the cold mass with hydrochloric acid and the acid solution is evaporated to dryness to make the silica insoluble. The residue is leached with hydrochloric acid, from which barium chloride is crystallized out; and finally, the crystals of zirconium oxychloride, $ZrOCl_2\ 8H_2O$, also separate out.

2. Preparation of the metal

The extraction processes yield zirconium oxide, oxychloride, or sulphate, together with various contaminated impurities, e.g., iron titanium, chromium, aluminum, vanadium and rate earths. It is not always easy to procure a very pure sample of the metal.

The metal obtained (i) by reducing the halogen salts with alkali metals, or (ii) by reducing the dioxide with aluminum, magnesium, calcium or carbon.

(i) Reduction of Halides by Alkali Metals (Berzelius)

A mixture of dry potassium fluozirconate and potassium is heated over a spirit lamp in an iron tube. The reduction $K_2ZrF_6 + 4K = 6KF + Zr$ proceeds quietly. The old mass is washed repeatedly with dilute hydrochloric acid and a solution of ammonium chloride and finally with alcohol.

(ii) Reduction of the oxide by calcium (Burger)

A mixture of zirconia and calcium is heated giving

$2ZrO_2 + 2Ca = CaZrO_3 + Zr + CaO$, and at 1050°, $CaZrO_3 + 2Ca = 3CaO + Zr$. The cold product is powdered and washed with water, acetic acid dilute hydrochloric acid, water and finally with acetone, and then dried at an ordinary temperature, then in vacuum at 250°, and finally in an evacuated porcelain tube at 1000° m

(iii) Reduction of Halides or Oxide by Aluminium (Troost)

(a) The vapour of zirconium tetrachloride is passed over heated aluminum: $3ZrCl_4 + 4Al \rightarrow 3Zr + 4AlCl_3$;

(b) A mixture of potassium fluozirconate, K_2ZrF_6, is heated with aluminum in a crucible to the melting point of iron; the cold mass is treated with hydrochloric id to extract the metal;

(c) By the thermite process (kuhne) $ZrO_2 + 2Al + BaO^2 \rightarrow Al_2O_3 + BaO + Zr$.

(iv) Reduction of Zirconia by Hydrogen, Calcium Cabide and Carbon, Boron or Silicon

The following reaction may be employed (Widekind):

$ZrSiO_4 + 2CAC_2 \rightarrow SiC + 2CaO + 2CO$

The reduction with carbon begins at 1400°. Moissan stated that when zircon was heated in a carbon crucible in the electric are furnace, he obtained a metal containing 5% of carbon and no nitrogen; the silica passed off as white fumes. With boron in an electric furnace, the metal thus obtained contained a small percentage of the bromide and carbide.

(v) Electrolytic Reduction (Becquerel)

A solution of zirconium tetrachloride mixed with a small proportion of ferric chloride (in the cathode compartment) is electrolysed. Zirconium collects on the platinum wire cathode.

3. Properties

Physical properties

Zirconium exists in two forms, crystalline an amorphous. The crystalline tractured substance is white, resembling cast iron. The coherent metal may even have a white colour. Amorphous zirconium has been obtained as a blue – black powder, Sp.Gr.4.15; hardness is 4.7; m pt. 1530°, sp.heat 0.660; entropy 9.5 at 25°. there is no absorption spectrum for the colourless zirconium salts. Magnetic susceptibility is $- 0.45 \times 10^{-6}$.

Chemical properties

Zirconium absorbs gases very tenaciously, but zirconium does not form hydrides, though zirconium dihydride, ZrH_2 has been reported as a gray deposit, when a current of hydrogen passes over red – hot zirconium. Amorphous zirconium and crystalline zirconium are stable in air at an ordinary temperature. The metal, however, burns to an oxide if heated below redness. Troost reports that the crystalline zirconium resists the action of air at a red heat.

Amorphous zirconium and crystalline zirconium, contaminated with aluminide, are rapidly dissolved in hydrofluoric acid. Chlorine or bromine vapour attacks the heated metal forming the tetrahalides; liquid bromine acts slowly, whereas iodine vapour is active at a high temperature only. Cold hydrochloric or sulphuric acid does not act on zirconium. Hot strong sulphuric acid evolves sulphur dioxide with metal. Hydrochloric acid vapour forms the tetrachloride.

Zirconium combines with nitrogen to form the nitride at a temperature not exceeding 800°; the metal is not attacked by hot or cold nitric acid. Zirconium is dissolved in a few minutes when heated with phosphoric acid. Zircon forms carbide with carbon; with silicon a silicide; and with boron a boride.

Very pure zirconium is not acted upon by alkali or its solution, but the ordinary zirconium evolved hydrogen. The amorphous zirconium is slowly oxidized and dissolved by the fused alkali. It is also said that when amorphous zirconium is heated with an alkali carbonate, it combines with the oxygen of the carbon dioxide with a slight explosion.

Zirconium does not appear to alloy so readily with other metals as do silicon and titanium. It alloys with copper, silver, gold magnesium, mercury and aluminium and in the latter case, such compounds as $ZrAl^2$ and Zr_3Al_4, have also been determined by the boiling point elevation method of zirconium acetylacetonate.

Valency

The hybride, ZrH_2, shows zirconium may be bivalent, though the existence of ZrO is doubtful. The vapour density of the tetrachloride, $ZrCl_4$, shows the tetravalency. Molecular weight has also been determined by the boiling point elevation method of zirconium acetylacetonate.

Atomic weight

The atomic weight is 91.22 determined on the basis of such analytical ratios; $ZrBr_4$: 4AgBr; $ZrBr_4$: 4 Ag. The atomic number is 40. the isotopes are 90, 92 and 94. The electronic structure is; $Is^2 2s^2 2p^2 3s^2 3p^6 3d^{10} 4s^2 \cdot 4p^6. 4d^2. 5s^2$.

4. Analytical Reactions

a) Zirconium salts give a white precipitate of zirconium hydroxide with such reagents as ammonia, ammonium sulphide, and alkali hydroxides (the precipitate does not dissolve in an excess of the alkali, thus differing from aluminum and beryllium).

b) Ammonium carbonate gives a white flocculent precipitate of basic carbonate, soluble in the reagent, but reappearing on boiling the solution.

c) Oxalic acid and ammonium oxalate give a crystalline precipitate of zirconium oxalate, when added to a solution of zirconium chloride (not given by A1 or Ba). The precipitate is soluble in excess of the reagent, but sparingly soluble in hydrofluoric acid.

5. Uses

Zirconium metal has been used as a construction material for chemical industry. For example (a) Zirconium plates have been employed in a pulse column operating alternatively with hydrochloric acid and sulphuric acid. (b) In the construction of a high speed generator, zirconium metal was used as the construction material operating successfully in zirconium phthalate solution. (c) The metal has been used for the construction of immersion heaters, heat exchangers, reactorsand tank linings, agitators and mixers, pumps and valves and valve fittings.

Nuclear power applications

The development of. nuclear energy and realization that zirconium was particularly suitable as a material for reactors has resulted in a complete change in the usage of zirconium. This material is particularly useful for thermal reactors.

Zirconium as a getter

Zirconium is found as an excellent getter. It absorbs or forms solid solutions with oxygen up to 40 atomic percent, and with nitrogen up to 20 atomic percent without X – ray evidence of an actual compound is formed. This means that one gram of zirconium will absorb 82 c.c of oxygen or 30.7 c.c. of nitrogen at normal temperature and pressure.

Zirconium in electronics

Zirconium will not alloy or amalgamate with mere mercury and can be used in mercury vapour or mercury are rectifier tubes. Zirconium absorbs hydrogen, nitrogen and oxygen gases (hydrogen at much lower temperature). One can use two getters placed alternately, one located at a point which will give a temperature of 900° to 1000°c and the other at a point which will give approximately 300°C.

The use of zirconium has been in power tubes and tube developments for radio, television etc. it is also used as a gird emission inhibitor. Powder in the form of zirconium hydride of fine particle size is usually employed, its suspension in xylene amyl acetate being used for the purposes of spray to the grid laterals.

II. Germanium

Germanium is one of those elements, which were predicted by Mendeleyev in the light of his Periodic Law. Clemens Winkler discovered eka – silicon, the name given by Mendeleyev to the element number 32, in 1886, who named it germanium in honour of his fatherland. At the close of the close of the year 1885, Professor Welsbach discovered a new are in a mine near Freiburg. This ore was argyrodite.

Occurrence

Argyrodite contains 4.99 – 7.05% germanium. Its formula is GeS_2. Ag_2 S or Ag_8GeS_6 (silver sulphogermanate). Other minerals are germanite, $Cu_3(Cu, Fe)_6$ $AsGeS_{12}$ and canfieldite Ag_8 $(GeSn)S_6$. Some minerals contain traces of germanium. Francheite, 5PbS. Sb_2S_5. $2SnS_2$(o.1% Ge); samarskite (1.5% Ge); tantalite (0.01% Ge).

The are of argyrodite at Freiburg is exhausted. Germanite has not been worked out. The mineral water at Vichy is a possible source. The evaporation of a quarter million of litres of water yield 0.06g. of GeO_2 per 100kg. of the residue.

1. Extraction

Germanium minerals may contain impurities as silver, copper, zinc, cadmium, gallium, titanium, tin, lead, arsenic, antimony, tantalum and columbium. Commercial recovery of germanium is from two main sources; (i) zinc ores, and (ii) germanite. It is also commercially extracted from flue dust in coals.

(i) Recovery of germanium from zinc ores

The recovery of germanium from zinc ores is economically feasible only because the germanium is concentrated in by – products during the process of recovering the zinc and cadmium; without such initial concentration of the germanium, it would not be economically possible to separate and purify it. For recovering about half –a – kilorgram of germanium, 1250 tons of the ore rock (as mined) has to be processed.

The rock is separated into zinc sulphide concentrate by the usual ore-dressing methods. Then the zinc sulphide concentrate, containing 0.01 to 0.015 percent germanium, is roasted to form a crude zinc oxide. The roasted ore is then mixed with salt and coke and sintered at a high temperature. This removes cadmium and germanium as a vapour phase, along with other volatile impurities also. The vapours are condesed and collected in an electrostatic precipitator.

This by – product fume is chemically treated to obtain crude fractions of germanium and cadmium (the sintered zinc oxide left over after the sublimation is utilized for recovering zinc.

The germanium fraction is reacted with strong hydrochloric acid. Since germanium tetrachloride has the b.pt. 86° C, it is easily distilled off. This further purified and finally distilled with chlorine (which holds arsenic back). The purified redistilled tetrachloride is then hydrolyzed to form germanium dioxide. The dioxide is then heated to 650° in an atmosphere of hydrogen, and thus the metal germanium is obtained. The metal is then powdered and heated in an inert atmosphere, and thus it is given the shape of ingots.

(ii) Recovery of Germanium from Germanite

The germanite ore is pulverized, and then treated with 50% sodium hydroxide solution and the mixture is evaporated to dryness. The dry mass is leached with hot water and the leach solution brought to pH8 with sulphuric acid. Then nitric acid is carefully added in boiling condition to raise the acidity to 5% (free-acid). The solution is filtered and the pH is brough down to 3 by adding sodium hydroxide; this now precipitates gallium which is filtered off and now germanium is precipitated. The precipitate is then filtered and washed and then dissolved in strong hydrochloric acid. Thus we get germanium tetrachloride, which is distilled off and purified further.

By hydrolyzing the tetrachloride, one can have germanium dioxide, which may then be reduced to germanium metal.

2. Preparation of the Metal

i. Heating in a current of hydrogen can reduce i) Small quantities of germanium sulphide or oxide.

ii) Powdered germanium is obtained by heating a mixture of fluogermanate and sodium (the powdered metal thus obtained is mixed with a little sodium fluoride which is difficult to be removed).

iii) A very convenient method due to Winkler is to mould – little balls from a mixture of the powdered oxide with 15 – 20 per cent of starch and a little boiling water. These are dried and carbonized at a dull red heat, and introduced in a crucible between layers of charcoal. A porous regulus of germanium is obtained by heating the crucible and contents to bright redness for an hour. The regulus is then fused under borax glass and germanium is obtained as a metallic bead.

3. Properties

Physical Properties

It is a grayish – white metal. The crystals are octahedral. Sp.gr.is 5.469 at 20.4°. atomic radius is 1.22A°. Hardness on Moh's scale is 6.25. M.pt is about 958°. Sp. Heat is 0.0737. it is diamagnetic. Its electrical resistance is between that of silicon and tin.

Chemical Properties

Germanium and hydrogen do not combine directly. Fused and crystallized germanium does not oxidize at an ordinary temperature in dry or moist air. At only an incipient red heat, the metal becomes covered with a thin film of oxide. It burns with incandescence when heated in oxygen. Hydrogen peroxide reacts with the metal at temperatures 90° - 100° forming GeO_2 which dissolves in the liquid. Germanium burns with a bluish white flame when heated in chlorine forming germanium tetrachloride. Germanium Powder catches fire spontaneously in chorine. The metal burns in bromine with a yellowish flame forming the tetrabromide. When heated to redness in iodine vapours it forms an iodide.

The metal only slightly dissolves in hot hydrofluoric acid. Hydrochloric acid solution has also no action on it, even when heated. However, when the metal is heated in a current of hydrogen chloride, hydrogen is liberated and germanium chloroform, $GeHCl_2$, is formed as $Ge + 3HCl \rightarrow GeHCl_3, + H_2$

When heated with sulphur, germanium sulph is formed at the red heat. Sulphur dioxide reacting at 510° -530° forms germanium sulphide and oxide. When heated with concentrated sulphuric acid, it evolved sulphur dioxide, and the sulphate, which is soluble in water, is formed.

The action of powdered germanium on nitric acid is violent, yielding nitric oxide and germanium dioxide. The metal dissolved in aqua regia.

When melted under borax, germanium monoxide, GeO, is formed. When fused with potassium hydroxide, the reaction is violent, hydrogen evolves and potassium germinates, K_2GeO_3 is formed. Similarly, the metal dissolves when fused with sodium peroxide. It dissolves when heated with potassium nitrate or chlorate. Winkler found that then heated with mercuric chloride or bromide germanium forms its chloride or bromide.

4. Analytical Reactions

i) When the acid solution of a germanium salt is treated with hydrogen sulphide, a white precipitate of germanium sulphide, GeS_2, is obtained.

The precipitation is complete only in the presence of a large excess of concentrated hydrochloric acid. The precipitate is soluble in water and is peptized by aqueous hydrogen sulphide. It should, therefore be washed with dilute hydrochloric acid saturated with hydrogen sulphide, with alcohol saturated with the same gas, and finally with ether.

ii) Germanium sulphide is soluble in ammonium sulphide, forming a stable sulphosalt, $(NH_4)_2$ GeS_3 On the addition of acids, the sulphide is again precipitated.

III. Plutonium

History of isotopes

Some of the neptunium isotopes show beta – activity, and after emitting a beta particle, are converted to an element with atomic number 94.

$$92^{Np^{239}} \rightarrow 94^{Pu^{239}} + -1^{e^{0}}$$

McMillan and Abelson, in their study of neptunium – 239 wee unable to detect any new activity when this nuclide decayed; and hence they concluded that the new product of atomic number 94 was an alpha – emitter of long life. This fact got condirmation in March 1941, by Kennedy, Seaborg, Segre and Wahl. This plutonium – 239 was actually an alpha – emitter with a half – life of 24,000 years. This isotope of plutonium was found to undergo fission by slow neutrons, and hence, immense importance was attached to its production in appreciable amounts for the purposes of atom bomb (bf. Uranium 235). Does this plutonium – 239 isotope occur in nature, since it has such a long half – life period? The results obtained so far indicate that the minerals pitchblende and carbotite, contain, if at all only $1/10^{14}$ of plutonium.

1. Extraction

The separation of plutonium from neptunium is based on these facts; plutonium in (IV) state is oxideized to (VI) state only with a powerful oxidizing agent, while the presence of a relatively weak reducing agent would reverse the process.

$Pu^{IV} \rightarrow Pu^{VI}$ (difficult) $U^{IV} \underset{\rightarrow}{O_2} U^{VI}$ (easy)

$Pu^{VI} \underset{\rightarrow}{2H} Pu^{IV}$ (easy) $U^{VI} \underset{\rightarrow}{2H} U^{IV}$ (difficult)

Thus the method of separation "involves a precipitation of plutonium (IV) with a certain compound as a carrier, then dissolution of the precipitate, oxidation of plutonium to the (VI) state and reprecipitation of the carrier compound, while the plutonium (VI) remains in solution". Fission compounds, which are not carried by these compounds, remain in solution when plutonium (IV) is precipitated. The fission products, which are removed from the plutonium (IV) is precipitated. The fission products, which are carried, are removed from the plutonium when it is in the (VI) state. Successive oxidation – reduction cycle are carried out until the desired decontamination is achieved. This is merely a modest description.

The actual separation of plutonium, as carried out at Hansford, entails some thirty major chemical reactions involving many hundred operations.

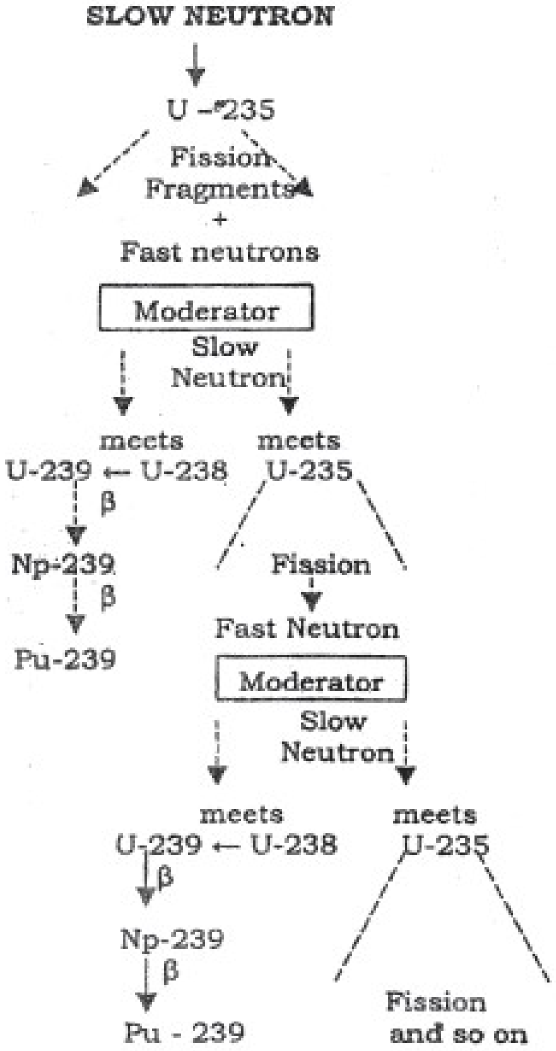
Technical Production of Plutonium

Production of plutonium on the large scale for harnessing energy depends on the following reaction, which involves interaction of slow neutrons on the abundant isotope of uranium U – 238.

$$238_{U_{92}} + 1_{n_0} \rightarrow 238_{U_{92}} \xrightarrow[23mins]{\beta} 238_{NP_{93}} \xrightarrow[23days]{\beta} 238_{Pu_{94}}$$

The neutrons necessary for these reactions are to be obtained from the nuclear fission of U - 235, which are present in natural uranium to only 7% extent. In the nuclear fission of U – 235 at least two fresh neutrons are generated for every neutron, which is to bring about the fission. If such conditions are realized, then each one of these neutrons could bring about the fission of another nucleus, the number of neutrons released would be conditions and this number would increase with rapidity. The chain – reaction would be self – accelerating, and would take place with an explosive violence. The uncontrolled chain reactions lead to explosion (as in the atom bomb), but one can have such a nuclear reactor as makes the use of a controlled chain reaction, and then it can be used for the generation of power for useful purposes.

It has been shown that 1 atom of plutonium should be produced for each atom of U – 235 that undergoes fission. The scheme of the production of plutonium is given below;



2. Preparation of Pure Plutonium

The irradiated rods, which contain neptunium and plutonium, are dropped into deep – water tanks when they are taken out from the reactors. Thus they are allowed to "cool" for a long period, until the conversion of neptunium intro plutonium has become complete.

During the long period of the "cooling", all the short – lived members amongst the fission products would also decay away. The X – ray activity is excessively high before this "cooling", and even after "Cooling" it does not disappear altogether and therefore it is necessary to carry out the entire chemical processing under heavy shields of concrete and necessary precautions.

The principle of separation takes into account two factors; (i) plutonium and uranium compounds in + 6 state are very much similar, and (ii) plutonium (IV) compounds are by far the more stable than uranium (IV) compounds. The irradiated uranium is dissolved in an acid, oxidized to uranium (VI) salts under such restriction that plutonium remains unoxidized;. Plutonium (IV) is then precipitated is then centrifuged off, re – dissolved, and oxidized so that Pu(IV) is converted to Pu(VI). The carrier is precipitated at this stage, and it carries down with it a certain proportion of the fission products. Pu(IV) is now converted to Pu(VI) state, and again precipitated. Oxidation, reduction and precipitation processes are repeated a number of times to obtain absolutely pure plutonium free from all fission products.

3. Properties

Toxicity of Plutonium

Plutonium, as well as the entire alpha emitting fission products of sufficient half – life, is extremely injurious to the tissues. They form insoluble phosphates, and get incorporated in growing bone cells. They enter the blood stream, through an injured tissue. Plutonium (IV) phosphate is so insoluble, that if once precipitated, its elimination from the system is very slow. A speck of plutonium compound is sufficient to cause injury through its alpha emissions and produce lesions lessons in the bone marrow cells, which generate red blood corpuscles. Absolute precautions are necessary for workers in the field of radioactivity, since the affects are cumulative.

IV. Thorium

Occurrence

Thorium is widely distributed in nature, though in small proportions. It is present, on the average about 0.002 per cent on the earth's crust. It occurs in small quantities with the rare earths in most of the minerals and also with many tantalum, columbium, titanium, scandium, zirconium and uranium minerals. It occurs in minerals, thorite, (SiO_2 ThO_2). nH_2O orangite (yellow mineral analysed by Krautz in 1850), uranothorite (SiO_2 ThO_2 UO_2)nH_2O, and thorianite (containing 55 – 79% ThO_2; 11 – 32% UO_2 and 1 – 8% ceria earths). Thorite contains 50 – 58% ThO_2; and orangite contains 70-72% ThO_2.

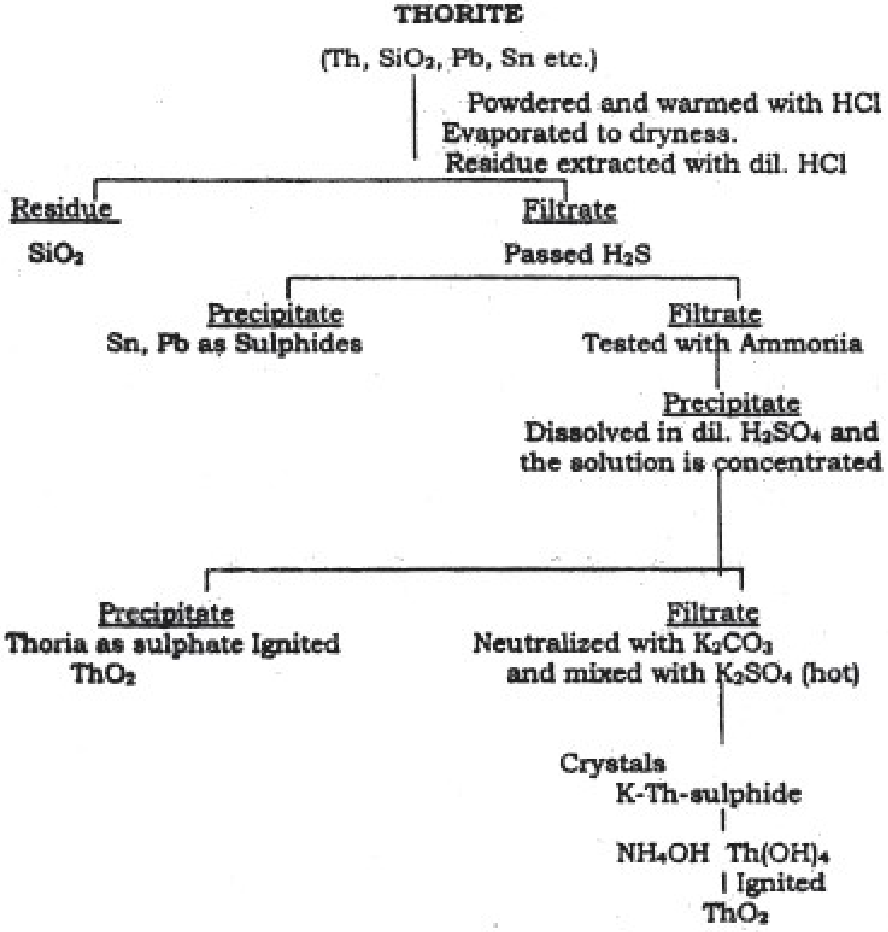
Thorium is found in Ceylon, Kanyakumari district and Travancore sands in India. Thorium minerals chiefly occur in Norway and Sweden, North and South Carolina, Brazil, Urals and Tasmania.

The radio element th^{232} is a α - emitter with half – life of 1.30×10^{10} years.

1. Extraction (Berzelius process from Thorite)

Thorite mineral contains SiO_2 (20%). ThO_2 (58%), U_2O_3 (1.5%), Fe_2O_3 (4%), pb(1%), CaO(2%) and the rest water.

The powdered mineral is warmed with hydrofluoric acid, some chlorine is evolved and the mineral gelatinized. The whole is evaporated to dryness to make the silica insoluble. The residue is leached with dilute hydrochloric acid, and lead, tin etc. removed from the filtered solution by passing hydrogen sulphide. The filtrate is treated with ammonlia; and the washed precipitate is dissolved in dilute sulphuric acid. The solution is evaporated at a gentle heat when thorium sulphate is deposited as a sparingly soluble salt from the hot solution. The precipitate is dried and ignited to furnish thoria. The mother liquor still contains some thorium; it is neutralized with potassium carbonate and mixed with a boiling saturated solution of potassium sulphate. The double sulphate (k-sulphate) separates out which is dissolved a in water and precipitated as thorium hydroxide by ammonia. This on ignition gives thoria.



2. Thorium Metal

It has not been obtained in a high degree of purity. The impure metal has, been obtained

(i) by heating a mixture of metallic potassium with potassium thorium fluoride or thorium chloride in glass tube (Berzlius).

$K_2ThF_6 + 4K \longrightarrow Th + 6KF$

(ii) by heating to redness a mixture of sodium, thorium chloride and potassium chloride in alternate layers in an iron cylinder (Nilson).

(iii) by heating to 600° thorium chloride mixed with lithium or sodium in an iron boat in a quartz tube (Chauvenet).

(iv) by heating thoria with alkali metals (60-80% purity yield is obtained); and

(v) by the electrolysis of a mixture of thorium chloride and potassium chloride in a graphite crucible using graphite electrodes (von Warternberg); the product contained 88% thorium.

Colloidal Thorium

Wedekind and Baumhauer have made it by rubbing in a mortar finely divided thorium with cold dilute acetic acid. On washing the paste, colloidal thorium passes through the filter paper.

3. Properties

Physical properties

It has been described as a dark lead – grey powder, which when passed in an agate mortar assumes an iron – grey colour. The crystals are octahedrons. Sp.gr.is 10.968 for amorphous; 11.23 for crystals. Sp Heat is 0.2757 Entropy is13.6 cals per degree at 25°; m.pt.1450°; b.pt 2800°. thorium salts are colourless and show no visible absorption spectrum. Its paramagnetic susceptibility is 0.177×10^{-6} (Honda).

Chemical Properties

Thorium hydride, Th H_2 is formed when thorium oxide is reduced by magnesium in an atmosphere of hydrogen; the hydride very much looks like the metal, The metal is stable in air at 120°, but it takes fire just below redness; it showers incandescent sparks. Water does not act on the metal, unless it contains a good percentage of carbide also.

When thorium is heated in chlorine; the two elements combine with incandescence and thorium chloride is formed. Bromine and iodine also similarly act on it. Though hydrofluoric acid has no act hydrogen evolves when hydrochloric acid acts on it.

When thorium is heated with sulphur, thorium sulphide is vigorously formed. Hydrogen sulphide when passed over red- hot thorium furnished its sulphide. Sulphuric acid attacks thorium only slowly and sulphur dioxide evolves; with the dilute acid hydrogen evolves.

When thorium is heated with nitrogen, thorium nitride is formed. Nitric acid, hot or cold, does not attack the metal. Solution of alkali hydroxides has also no perceptible action on the metal.

Radioactivity of thorium

In 1898, G.C. Schmidt and M.S. Curie independently found that thorium and its compounds and thorium minerals are radioactive. Thorium products emit α, β and y – rays.

The radioactivity of freshly prepared thorium compounds is not constant, but decreases slowly for some years, reaches a maximum and then slowly increases and finally attains a maximum value. This is due to the growth in thorium of some new radioactive substances. It is very difficult to prepare thorium free from all its decay products.

4. Analytical Reactions

The following reactions may be done with thorium nitrate or sulphate;

(i) With ammonia, or caustic soda solution, a white precipitate is obtained, which is insoluble in excess of the reagent.

(ii) Thorium hydroxide, when ignited forms thorium oxide, which is soluble in concentrated sulphuric acid only on prolonged treatment.

(iii) Thorium salts are completely precipitated by barium carbonate in the cold.

(iv) Thorium salts with potassium sulphate give a white precipitate of the double salt $K_4\ Th(SO_4)_4 \cdot 2H_2O$.

(v) A white precipitate is obtained by the addition of potassium ferrocyanide, or on treatment with sodium azide.

(vi) If the solution of thorium slats be not highly acidic, a white precipitate is obtained on the addition of oxalic acid, or ammonium oxalate.

(vii) A neutral aqueous solution of a thorium salt gives a white precipitate with m-nitrobenzoic acid, and with aniline m–nitrobenzoate.

(viii)Fumaric acid precipitates thorium completely in presence of 40 per cent alcohol.

(ix) Ammonium auric tricarboxylate (aluminon) forms a coloured chlorate complex with tetravalent thorium (Middleton, 1926, Mukherji and Dev, 1957)

Valency

The quadrivalency of thorium is seen from the isomorphism 0f thoria with stannic oxide and titanic oxide, and from the analogy between potassium thorium fluoride and potassium zirconium fluoride. It is quadrivalent in such compounds as the ferrocyanide. $ThFeCN_6$.; the double salts of mercuric cyanide with thorium trihydroxy – thiocyanate, $nHgCN_2 . Th(SO_4)_3 . nH_2O$; and sodium thorium carbonate, $3NaCO_3 . Th(CO_3)_2$.

The specific heat rule of the metal also supports the quadrivalency. Thorium chloride, $ThCl_4$, dissociates above, 1,050°, $ThCl4 \rightleftharpoons = ThCl_3 + Cl_2$ etc., and hence the vapour density of thorium chloride does not correctly indicate the molecular formula.

Atomic Weight

It has been determined on the basis of such rations as;

$ThO_2 : BaSO_4 . ThO_2 . K_4 . Th(SO_4)_2 . 2H_2O : ThO_2 . Th(CH_3COO)_4 : ThO_2$. etc.

The atomic weight is 232.4. its atomic number is 90. The electronic configuration is; $ls^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 6d^2\ 7s^2$

5. Uses

Thoria has an immense use in the propagation of incandescent mantels. Mixtures of thoria with traces of ceria have been used in the form of pastilles for searchlights and headlights of cars. Magnesium flashlight powders also often contain some thorium preparations (thorium chromate, thorium tungstate etc). the thoriferrous flash powders are said to evolve less smoke than if magnesium is used along. Thorium alloys have been used as reducing agents and thoria as a contact catalyst.

Alloys

Very few alloys of the metal have been prepared. With aluminum, it forms thorium trialuminide, $ThAl_3$, when mixture of the double fluoride of thorium and potassium, potassium silico – fluoride and aluminum is heated at 1200°.

V. Uranium

Occurrence

Uranium does not occur native, it occurs combined in a few scarce minerals. Its proportion in the earth's crust is 0.000003 per cent. Its occurrence in the sun is doubtful. Deposits in India have been reported in Bengal, Pichhli and Bane Khap in Gaya District, Rapur Taluq in Nellore district, on Abraki Pahar east of Banekhap, Central India and in Ceylon. Virtually all the pitchblende of the British Isles is from Cornwell.

The United Sates has been the greatest possessor of the pitchblende and other uranium minerals, and then comes Portugal.

The prominent uranium minerals are;

Becquerelite, (pb, UO_2)O.2H_2O Broggerite which is uraninite, 76% U_2O_5; carnotite K_2O. 2UO_3.V_2O_5 3H_2O– 65% UO_2; euxenite 4 – 16% UO_2; pitchblende also known as uraninite, U_3O_8 with some lead nitrate, 75 – 85% UO_2, uraconite containing uranium sulphate, 65% U_3O_8.

1. Extraction

Pitchblende and Carnotite are the only two uranium ores that have been processed for by – product uranium production.

(a) The ores are treated with a mineral acid to bring uranium into solution and occasional alkaline extraction of fussion must be used to disintegrate it.

(b) The uranium is converted to a soluble complex carbonate, thereby removing iron aluminum and manganese.

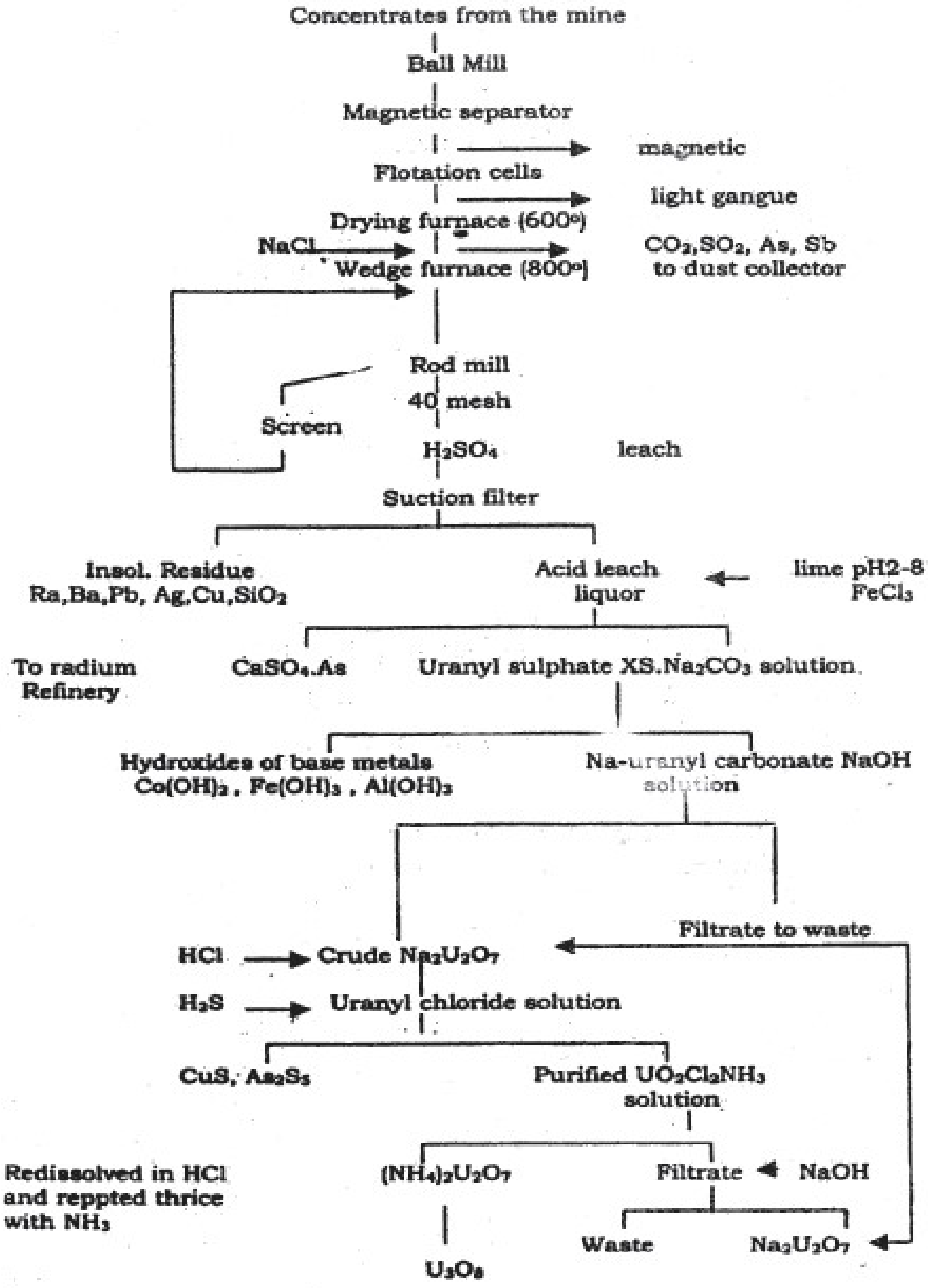
(c) Lead and copper are precipitated as sulphides from these uranyl solutions.

(d) Uranium is recovered as sodium uranate ($Na_2U_2O_7$) or Ammonium uranate $(NH_4)_2U_2O_7$.

(i) Klaproth's process: The powdered pitchblende is digested with nitric acid or aqua regia; the solution is evaporated to dryness; the soluble matter is extracted with hydrochloric acid; a current of hydrogen sulphide is passed to precipitate arsenic, lead etc; the filtrate is the treated with nitric acid and then with ammonium carbonate; the solution is then boiled to precipitate uranium, zinc and cobalt oxides. The precipitate is then digested with cold dilute hydrochloric acid, which leaves uranium oxide as an insoluble residue.

FLOWSHEET FOR THE PRODUCTION OF U_3O_8 FROM CANADIAN PITCHBLENDE

(PORT HOPE REFINERY, ONTARIO)



(ii) Pitchblende contains uranium and radium, the compounds of copper, silver, zinc, thallium, rare earths, lead arsenic, antimony, bismuth, vanadium, columbium, tantalum, molybdenum, tungsten, manganese, iron, cobalt, nickel, alumina, lime silica, sulphur and selenium.

The ore is concentrated and then roasted in a reverberate furnace to remove sulphur, arsenic and the other volatile impurities. The roasted ore is then mixed with sodium carbonate and sodium nitrate and fused in the reverberate furnace. This converts uranium, vanadium, molybdenum, tungsten and arsenic (if left) into sodium uranate, vanadate, molybdate, tungastate and arsenate. These pass into solution when the cold fused mass is extracted with hot water.

The residue left is the starting point for extracting radium and it may have retained some uranium also; and therefore, it is digested with a little dilute sulphuric acid, which takes up any uranium as uranyl sulphate. The solution is evaporated to dryness and extracted with water. The residue now left consists of silica, lead sulphate and arsenate.

The two extracts are treated with an excess of sodium carbonate to precipitate the basic carbonates of iron, aluminum, nickel and cobalt, while the uranium remains in solution as sodium uranyl carbonate. The liquid is boiled and filtered and the filtrate and the filtrate is then neutralized with dilute sulphuric acid, boiled and evaporated when sodium diuranate, $Na_2U_2O_7.6H_2O$, separates as a heavy yellow precipitate.

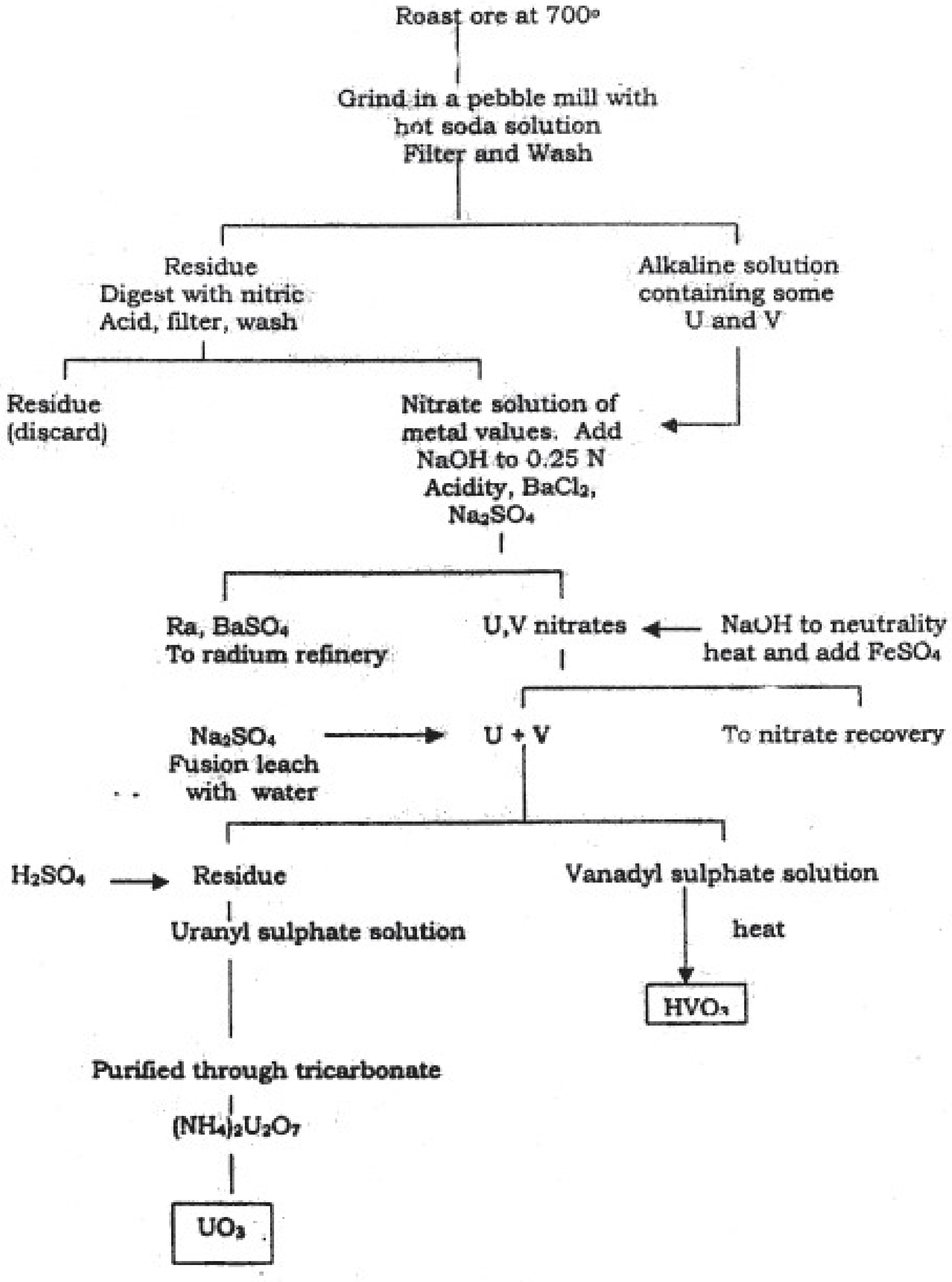
In place of sodium carbonate, one may use ammonium carbonate which will then furnish ammonium diuranate, $(NH_4)_2U_2O_7$ which on calcinations, would give uranium oxide, U_3O_8.

(iii) From Carnotite: The powdered mineral is fused with potassium hydrosulphate, and the cold product is then extracted with water. The solution on crystallization furnishes the double sulphates of vanadium and uranium. These are reduced by zinc and sulphuric acid and the vanadium precipitated from the solution by the addition of ammonia and ammonium carbonate.

When the filtrate is boiled, ammonium diuranate, $(NH_4)_2U_2O_7$ is precipitated. This on ignition furnishes the oxide, U_3O_8.

FLOWSHEET FOR PROCESSING CARNOTITE ORE

(BUREAU OF MINES, NITRIC ACID PROCESS)



2. Isolation of the metal

Up to the time of Peligot (1841), observers had mistaken uranium dioxide, UO_2, for the metal. This dioxide was obtained by reducing U_3O_8 in hydrogen or by carbon.

(i) Moissan could, however, reduce the oxide actually to the metal by carbon in the electric furnace. He mixed 500g. of the oxide, U_3O_8, with 40g of sugar charcoal in a carbon tube furnace, then reduced for 12 minutes in the electric carbon tube furnace, and got 350g. of the metal, contaminated with only a little of carbon.

(ii) Aloy found that the oxide, UO_2, could be reduced to the metal by the powdered aluminum in the thermite process. The reaction is vigorous.

(iii) Reduction with magnesium could furnish the metal of 98-99 per cent, purity. The vapour of calcium can reduce the trioxide in vacuo (Burger)

(iv) Jander and marden obtained uranium by heating uranium oxide with metallic calcium in a welded iron crucible embedded in charcoal for 40 minutes at 950° – 1,250°. The resulting mass was treated with ammonium chloride solution to remove the unchanged calcium. The uranium thus obtained still contained some oxides.

(v) Peligot reduced uranium tetrachloride mixed with potassium chloride and sodium and covered with potassium chloride in a porcelain crucible contained inside a graphite crucible, packed with dry powdered carbon and the temperature rapidly raised to redness. The cold product was lixiviated with water; there remained a metallic powder with metallic globules.

(Peligot's earlier experiments were with potassium in a platinum crucible. The metal thus obtained was contaminated with potassium).

Uranium metal may also be made by thermal decomposition of uranium halide vapours on a hot tungsten filament below 1133° the melting point of uranium. The process is similar to the one used in the preparation of zirconium, titanium, tugsten, and thorium (van Arkel), and produces a very pure metal. This method has been successfully developed by regulating the partial pressure of iodine in evacuated reaction vessel, so as to form some uranium tetraiodide, which has the necessary vapour pressure at the desired temperature. Uranium triiodide, which is substantially nonvolatile, also is used in the reaction chamber. If the conditions chosen are favourable, one gets the deposit of solid uranium metal on a hot filament (filament temperature should be 1030 – 1100^0, glass bulb temp. 520^0 – 560^0, UI_3 temp. 500^0-540^0, and iodine pressure controlled in a side tube at 7 x 10^{-3} mm. Hg. The reactions are;

$$UI_4 \rightleftharpoons UI_3 + \frac{1}{2} I_2$$

3. Properties

Physical Properties

When prepared by the Moissan's carbon – reduction process, uranium is obtained as an ingot with a bright fracture. The metal of a high degree of purity is white with a faint bluish tinge. It has a yellowish tinge when some nitride is present. Sp.gr.is 18.33 – 18-40; atomic radius for U^{IV} is 1.22A^0 (or 0.97 – 1.05A^0). The metal is very ductile, and in malleability, it is less than thorium. Its specific heat is 0.0249 or 0.0276. Its m.pt is 1,150^0 (not 1,600^0 as previously reported). It can be distilled in an electric furnace. B.pt. is 3,500^0; entropy is 11.1. It is more volatite than iron. The solid has two transition points at 662^0 and 772^0, the heats of transition being 0.680 and 2.165 K.cals. per g. atom. (Moore and Kelley, 1947). Uranium salts do not show a flame spectrum.

The absorption spectrum of uranium salt solution has been extensively studied. All uranium salts, solid or in solution, show absorption. As the temperature rises, these bands shift towards the red, e.g., in uranyl sulphate:

	20^0	40^0	60^0	80^0
(i)	4906	4909	4915	4992cm^{-1}
(ii)	4738	4741	4743	4745cm^{-1}

The absorption bands with uranyl sulphate are; 4885, 4725, 4560, 4410, 4310, 4180, 4060 and 3950 cm^{-1}.

Uranyl salts exhibit pleochroism. The centres of bands of solid uranyl nitrate are 5600/ 5350 and 4850cm^{-1}. The absorption bands in the aqueous solution of these salts are 4880, 4720, 4550, 4400, 4280, 4160 and 4040cm^{-1}. The absorption spectrum of the canary – yellow glass coloured by uranium furnishes bands between 5110 and 4860, 4760 and 4600 and at 4500 cm^{-1}.

Uranyl salts in solution exhibit a greenish fluorescence. The phosphorescent spectrum of uranyl sulphate, UO_2, SO_4, $3H_2O$, consists of eight equidistant bands.

In 1804, Gehlen observed that an ethereal solution of uranium chloride is decomposed by light. Uranyl salt solution in presence of glycerine is reduced in light. Uranyl oxalate is reduced in light. The organic acids also decompose by light in the presence of uranyl salts (J.C.Ghosh, Dhar etc.). Alloy and Rodier represent one of such reaction as;

$$UO_2Cl_2+2HCl+C_2H_5OH \rightarrow Ucl_4+CH_3CHO+2H_2O$$

Some photosyntheses have been studied in presence of uranyl salts. Uranium free from iron is also feebly paramagnetic. The subsceptibility of salts of sexivalent uranium is diamagnetic.

Chemical Properties

The metal is stable at ordinary temperatures in dry air. It ignites in oxygen at 170^0; it burns with a brilliant flame. The finely divided metal slowly decomposes cold water and more quickly at 100^0. Electrolytic uranium catches fire in fluorine and furnishes a green volatile tetrafluoride. The finely divided uranium burns in chlorine also, catching fire at 180^0. The ignition temperature in bromine is 240^0. Iodine vapour, however attacks uranium with difficulty; at 260^0, the tetraiodide is formed with incandescence. Hydrogen chloride attacks uranium at a dull red heat forming a stable chloride. Uranium is soluble in dilute hydrochloric acid forming uranous chloride. Uranium is soluble in dilute hydrochloric acid forming uranous chloride. $U+4HCl \rightarrow UCl_4+2H_2$. With the more concentrated acid, a hyacinth – red solution of the trichloride is also formed.

Boiling sulphur unites with uranium with incandescence; when it burns in sulphur vapour, the black disulphide is formed; the combination gives uranous sulphate and evolving hydrogen. Uranium has a great affinity for nitrogen; the combination to form the nitride takes place at $1,000^0$. Powdered uranium reacts with ammonia at a dull red heat with incandescence; hydrogen is evolved and a black powder formed. When it reacts with dilute nitric acid, nitric oxide is evolved and uranyl nitrate is formed. Red fuming nitric acid, nitric oxide is evolved and uranyl nitrate is formed. Red fuming nitric acid attacks the metal vigorously. When the metal is heated with carbon, uranium carbide is formed.

4. Analytical Reactions

i (a) Green solutions of quadrivalent uranium are easily oxidized to hexavalent uranyl salt by usual oxidizing agents.

(b) The yellow uranyl salts are reduced to green quadrivalent salts by zinc and sulphuric acid.

ii (a) Hydrogen sulphide does not precipitate uranium from hydrochloric acid solutions.

(b) Quadrivalent salts give a black precipitate when boiled with ammonium sulphide solution,

(c) Uranyl salts precipitate brown uranyl sulphide when treated with ammonium sulphide; the precipitate is soluble in hydrochloric acid, as well as ammonium carbonate solution.

iii (a) Quadrivalent salts give a voluminous pale green precipitate of the hydroxide when treated with caustic soda or ammonium hydroxide solutions; the precipitate rapidly oxidizes in air, (b) Uranyl salts with these reagents give yellow precipitates of the urinates; the precipitation is hindered by citrates and tartrates. The precipitates are soluble in ammonium carbonate.

Isotopes of Uranium

A number of isotopes of uranium have been reported. The important among them are mentioned below:

Ordinary uranium consists of the three isotopes of mass number 238, 235 and 233.

Uranium 238 (U-238)

This is the principal isotope of uranium. U – 238 constitutes 99.28% of the natural element. This isotope has a half – life of 4.5 x 10^9 years. It decomposes by emitting an α -particle and form Th-234. U -238 is non-fissionable, but will capture neutrons in a nuclear reactor to produce heavier unstable isotope Pu-239 which can substitute for U – 235 as a fuel or explosive.

$$92^{U^{238}} + o^{n^1} \rightarrow 92^{U^{239}} + h\gamma \;\; 92^{U} \xrightarrow{239\text{-}\beta \text{ rays}} 93^{NP^{239}} \xrightarrow{-\beta \text{ rays}} 94^{Pu^{239}}$$

Uranium 235 (U-235)

This isotope occurs to the extent of 0.71% only in natural uranium. The importance of this isotope was realized when a huge amount of nuclear energy was needed. The essential ideas relating to the production of the atom bomb was the isolation of a sufficient amount of U-235 from the natural uranium.

Uranium 233 (U-233)

It is a fission isotope of uranium produced artificially by bombarding thorium with neutrons. It can be used as an atomic fuel. This isotope of Uranium is obtained from thorium whose ore occurs in nature as monazite in India, by the following series of nuclear reactions.

$$90^{Th^{232}} + 0^{n^{1}} \longrightarrow 90^{Th^{233}} \xrightarrow{-\beta\ (23mins)}$$

$$91^{Pa^{233}} \xrightarrow{-\beta(27\ days)} 92^{U^{233}}$$

The technical production is quite simple. A mantle of thorium surrounds a uranium reactor. The slow neutrons escaping from the core of the reactor bring about the above conversion.

The production of U-233 by India is considered to be of big significance. U – 233 is successfully prepared from thorium in the Kalpakkam experimental breeder reactor. The lead given by India in this direction is a valuable contribution towards solving the energy problem.

Oxidation states

Uranium displays a number of oxidation states +2, +3, +4, +5 and +6. Green tetravalent uranium and yellow uranyl ion (UO_2++) are the only species, which are stable in solution.

Uranium Oxides

The principal oxides are UO_2, U_3O_3, U_3O_8 and UO_4 $2H_2O$, UO_2. Uranic oxide is formed when uranyl nitrate, ammonium urinate or uranyl sulphate is heated.

$$UO_2(NO_3)_2 6H_2O \xrightarrow{350^0C} UO_3 + N_2O_2 + 6H_2O + \frac{1}{2}O_2$$

$$(NH_4)_2U_2O_7 \xrightarrow{350^0C} 2UO_3 + H_2O + 2NH_3$$

The oxide is amphoteric. It dissolves in acids to form uranyl satls $UO_2(NO_3)_2$ or $UO_2SO_2H_2$. The oxide is very hygroscopic.

UO_2 uranium dioxide is prepared by reducing the higher oxides with carbon or hydrogen.

$$UO_3 + H_2 \xrightarrow{700^0C} UO_2 + H_2O$$

$$UO_3 + CO \xrightarrow{350} UO_2 + CO_2$$

It is a brown, strongly basic oxide. It is converted into uranyl nitrate $UO_2(NO_3)_2$ 6 H_2O is got. It is soluble in water, alcohol and ether. Uranium octoxide U_3O_8 is got by heating oxides of uranium in air – at 700°C.

$$6UO_2+2O_2 \xrightarrow{700^0C} 2U_3O_8$$

$$6UO_3 \xrightarrow{200^0C} 2U_3O_8+O_2\uparrow$$

The oxide U_3O_8 is the most stable oxide of uranium. The oxide is green in colour and can be sublimed at about 1600°c (with some dissociation). Yellow orange urinates are obtained when (a) uranium oxides are fused with carbonates of alkaline earth metals and (b) when uranyl acetate is thermally decomposed.

Uranium forms carbide, UC, UC_2 and U_2C_3; borides UB_2, UB_4 and UB_{12}; nitrides UN, U_2N_3 and UN_2 sillicides U_2Si, USi_3, sulphides US, U_2S_2 and US_2.

Uranium Halides

The compounds have been studied in detail. Uranium forms fluorides of the type UF_2, UF_4 and reducing the UF_4 with hydrogen or A1 forms UF_6 and UF_3.

$$2UF_4+H_2 \longrightarrow 2UF_3+2HF$$

It is a high melting, green, non- volatile solid with the hexagonal symmetry. It is insoluble in water and dil, acids. On heating to temperature above 1000°C it disproportionate;

$$4UF_4 \longrightarrow 3\ UF_3+U$$

$$U_3O_8+6\ Cl_2+8C \longrightarrow 3UCl_4+8\ CO$$

$$UO_2+2\ C+2\ Cl_2 \longrightarrow UCl_4+2\ CO$$

UCl_4 is a dark green crystalline substance. It is soluble in water and organic solvents. It is strong reducing agent and hydrolyses in water yielding uranyl chloride. UO_2Cl_2. UCl_5 is prepared by treating UCl_4 with gaseous chlorine at 500°C. It is a reddish brown solid; it is violently hydrolysed by water.

UCl_6 is a black unstable compound, obtained by the disporportionation of UCl_5 at 120-150° C in high vacuum

$$2\ UCl_5 \xrightarrow[\text{Vacuum}]{150^0C} UCl_4+UCl_6$$

UCl_3 can be isolated by sublimation. It is also hydrolysed by water to give uranyl chloride UO_2Cl_2.

UBr_3 (red), UBr_4 (brown), UI_3 (black) and UI_4 (black) are known; all of them are prepared by the direct combination of elements.

Uranyl Compounds

A large number of uranyl compounds are formed containing the bivalent uranyl UO_2^{++}. Important among the uranyl compounds are uranyl nitrate $UO_2(NO_3)_2.6H_2O$, uranyl sulphate UO_2SO_4, uranyl acetate $UO_2(CH_3COO)_2 . 2H_2O$ etc.

Uranyl nitrate

It is prepared by dissolving U_2O_3 or UO_2 in nitric acid and evaporating the solution to crystallization. It is a lemon yellow crystalline substance. It exhibits green fluorescence.

It is soluble in water and organic solvents. It causes violent combustion on ignition. Uranyl nitrate finds use in photography and medicines.

Uranyl Sulphate

$UO_2SO_4,3H_2O$ is obtained by treating U_2O_3 or UO_3 with concentrated sulphuric acid.

$$UO_3+H_2SO_4 \longrightarrow UO_2SO_4+H_2O$$

It is also obtained by treating uranyl nitrate with concentrated sulphuric acid.

Uranates

The fusion of uranium oxide with alkali or alkaline earth carbonates give orange or yellow materials, which are referred to as uranates. The examples are sodium uranate. Na_2UO_4, potassium uranate K_2UO_4, calcium uranate $CaUO_4$.

5. Uses

(1) The most significant use of uranium is in the nuclear energy field. It is used in atomic and hydrogen bombs for military purposes. It is useful in preparing trans – uranium elements.

(2) Due to this metal only, discovery of radioactivity, discovery of radium, application of radiations in medical sciences have all been made possible.

(3) Uranium salts are used in the manufacture of costly glasses and ceramic articles to give them yellow and orange glasses and emitting green fluorescence.

(4) Uranium steels are used for speed tools, range guns etc.

(5) Uranium carbide is used in automatic cigarette lighters.

(6) In medicine, the nitrate, salicylate and chloride are used for treatment of gout, diabetes and as throat spray.

(7) Uranyl nitrate is used in volumetric estimation of phosphates and arsenates.

(8) UO_2 is used in incandescent lamps, used in movie picture projection and in photography for giving a brown tint to the prints.

(9) Zinc uranyl acetate is used in the detection of sodium.

VI. Osmium

Osmium occurs in nature in association with platinum minerals. About 3 percent of Osmium present in laurite (RuOs) S_2. From 1 to 20 percent of osmium is present in osmiridium in native platinum minerals. Minerals containing under 60 percent of iridium are known as syserskite or osmiridium and those containing over and above 60 percent of iridium are known as iridosmium or nevyanskite; Iridosmium sometimes occurs along with chromite and iron ores as irite. Certain platinum residues containing a solid solution of gold, osmium and iridium is known as aurozmiridium.

1. Extraction : Vanquelin and Wollaston's Method

The extraction of osmium is fairly simple. The principle of the process is based on the fact that osmium forms the tetroxide O_sO_4, which is highly volatile. Osmium is obtained in a high degree of purity by distillation of a strongly acidified mineral whereupon the tetroxide is distilled. In practice the platinum metals are opened up with hot aqua regia in a retort when the osmium collect in the distillate as osmic acid.

From osmiridum: The crude osmium – iridium alloy is fused with alkaline oxidizing mixture such as sodium hydroxide and sodium peroxide, whereupon O_sO_4 formed. The mass is treated with further quantity of NaOH and alcohol so as to convert it into sodium osmate $Na_2O_sO_4$. The solution is now treated with suitable reducing agent such as zinc and HCl, the hydrogen evolved reduces $Na_2O_sO_4$ to metallic Os.

Osmium has the highest density of all known matter. It is brittle and non-malleable. Pure metal has a tin-white colour. It combines with oxygen readily; Osmium displays five degrees of oxidation. Osmium tetroxide, O_sO_4, is usually called osmic acid, although it does not act as an acid. It is one of the most powerful oxidizing agents known.

2. Uses

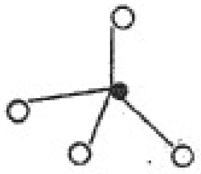
Osmium metal and the tetroxide are both powerful catalysts. Alloy of Os with Ir is used for pen points and for bearings of fine balances and other delicate instruments, O_sO_4, turns black when it comes into contact with organic matter and hence it is used in finger printing. O_sO_4 is also used in the volumetric determination of chlorates in the presence of perchlorates. O_sF_2 is one of the most powerful fluorinating agents known.

VII. Silicates

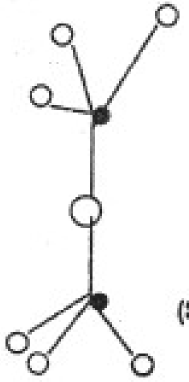
Most of the knowledge about silicate structures comes from the study of naturally occurring silicate minerals. They may have interchanging of similar sized ions like Mg, Ca, Iron (II), Si^{4+} ($r = 0.50A^0$), Al^{3+} ($r = 0.55A^0$)

1. Orthosilicates

Contain discrete $(SiO_4)^{4-}$ tetrahedral arranged in the lattice that the oxygen atoms of each are also coordinated round the metal cation so as to form a neutral structure.



$(SiO_4)^{4-}$

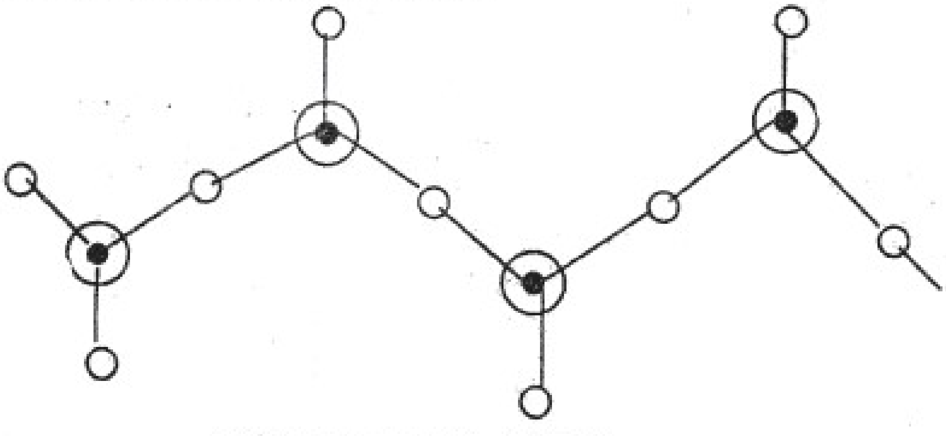


$(Si_2O_7)^{6-}$

In olivine $(Mg, Fe)_2\ SiO_4$, phenacite Be_2SiO_4, willemite Zn_2SiO_4 have the metal ions tetrahedrally coordinated. Each oxygen is then common to one SiO_4, tetrahedran and two MO_4 tetrahedra.

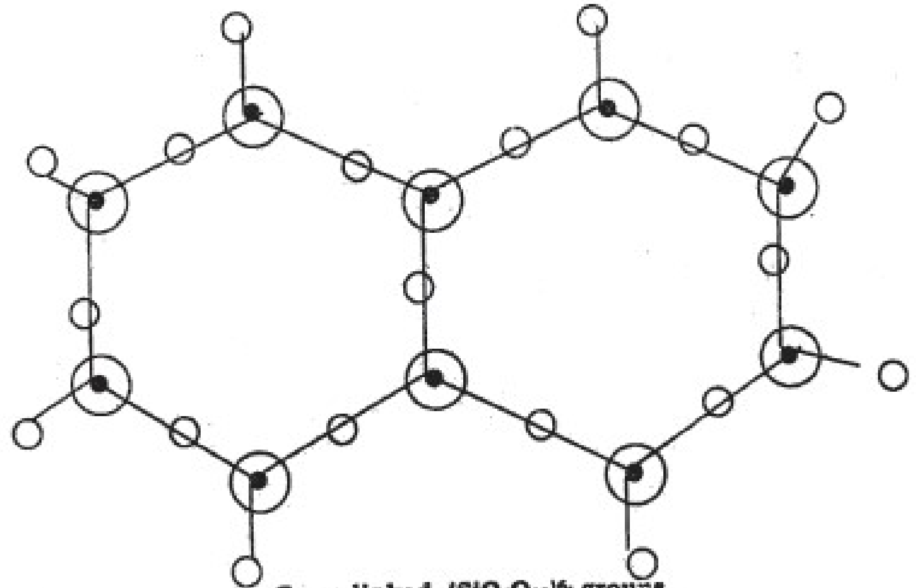
In thortveitite $(Sc_2Si_2O_7)$ in which Se^{3+} ions are octahedrally coordinated. The binding oxygen atom of the anion uses both 5 electrovalencies in joining the two tetrahedral and the charge − 6 arises from 6 free electrovalencies of other oxygen atom.

2. Metasilicates : Linear polyanion



Chain – like metasilicate $(SiO_3)^{2-}$ group

Infinite chain of $(SiO_3)^{2n-}_n$ in minerals are called matosilicate pyroxene. I diopside $CaMg(SiO_3)^{2-}$, a pyroxene type is a metasilicate with $(SIO_3)^{2n-}_n$ is formed by linking up of SiO_4 tetrahedra into infinite chains extending throughout the crystal. The amphibole mineral tremolite $Ca_2Mg_2\ (Si_4O_{11})_2\ (OH)_2$ is one of the minerals in which the anion is formed by cross linking two diopside chains by a further sharing of tetrahedran corners to give a band structure. Asbestos is a form of amphibole.

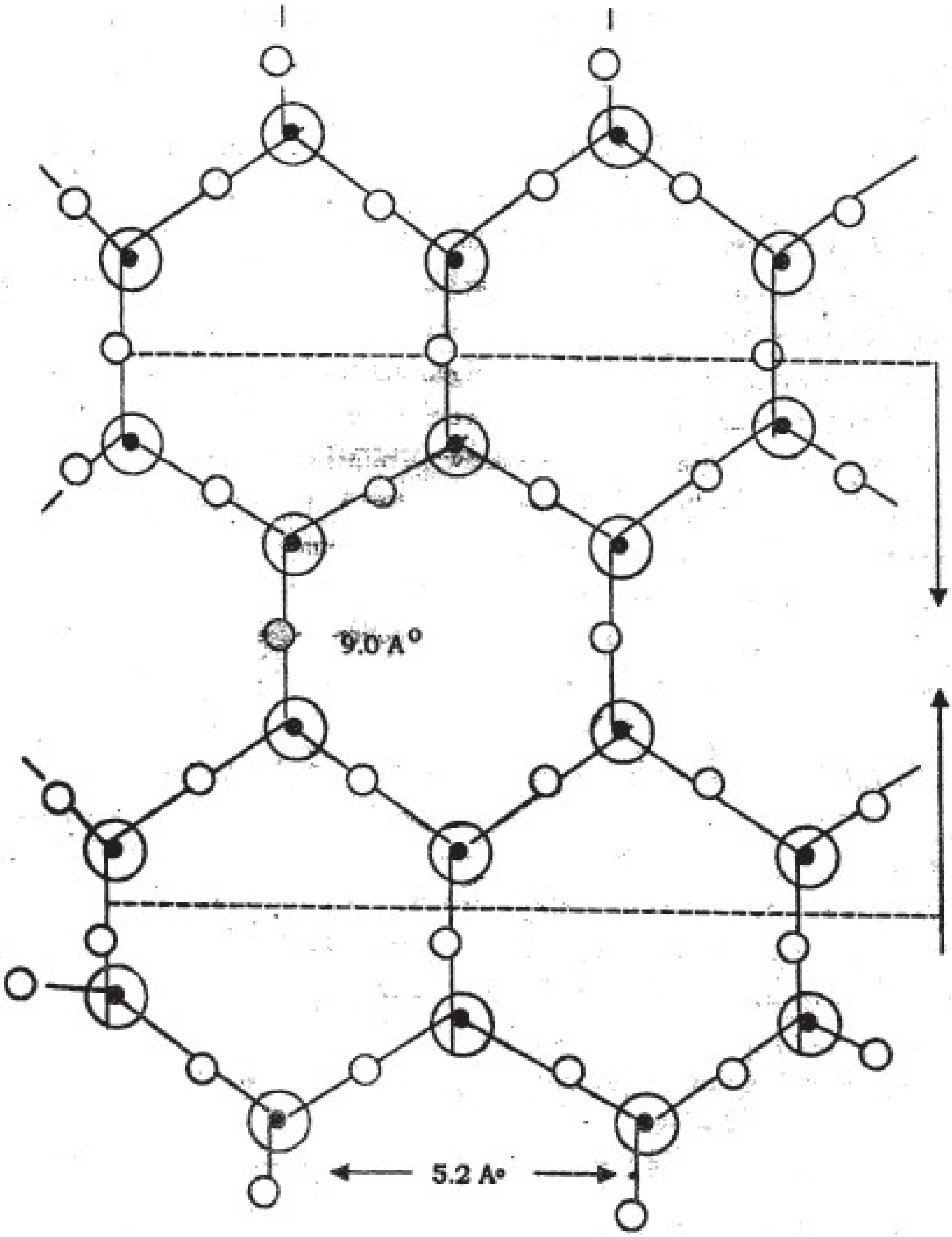


Cross linked $(SiO_4O_{11})^{6-}$ groups

Here the chains are bands and in all cases arranged parallel to the C-axis of the crystal and are bound laterally to one another by coordination of their oxygen atoms around metal ions. The resulting structure is mechanically strongest in the direction in which the anions are oriented, the cleavage of the crystal is highly developed parallel to the C – axis and the minerals frequently exhibit a fibrous structure an example is Asbestos, a form of amphibole.

The process of cross linking of strings of SiO_4 tetrahedra, if carried to completion will produce two dimensional sheets of gross composition $(Si_4O_{10})^{4-}$ such sheets being bound together by strong valency forces are mechanically strong. Parallel sheets are bound more loosely through the weaker electrostatic bonds involving the cations, which must be packed between the sheets the silicon oxygen sheets should consequently coincide with pronounced cleavage planes of the crystal and silicates with this type of structure should exhibit well – developed laminar cleavage.

Sheet structure



Talc, which is notable for its extreme softness, has the composition $Mg_3(OH)_2(Si_4O_{10})$ and it has layers of brucite $Mg(OH)_2$ sandwiched by the sharing of oxygen and hydroxyl between two sheets of $Si_2O^{2-}_5$) giving a composite layer which may be represented as O_6. Si_4. O_4 $(OH)_2$ $Mg_6O_4(OH)Si_4O_6$. The softness and ready cleavage of the mineral follows from the very weak attractive forces between adjacent sheets.

In phlogopite $K_2O.\ 6MgO.Al_2O_3.6SiO_2$ we find that A1 replaces silicon isomorphously with the result that a net anionic charge is present. Alkali ions enter between the sheets to restore neutrality giving

$K_2 \ldots O_6Si_3\ AlO_4\ (OH)_2\ Mg_6O_4\ (OH)_2\ Si_3\ A1\ O_6 \ldots K_2 \ldots)$

Muscovite, the ordinary mica is structurally analogous but with Mg replaced by A1 giving

$K_2 \ldots O_6Si_3\ AlO_4\ (OH)_2\ Al_4\ O_4\ (OH)_2\ Si_3\ A1O_6 \ldots K_2 \ldots)$

When charged layers are bound potassium ions, the hardness is increased and cleavage occurs less readily. Finally in brittle mica, the charged anionic sheets are even more tightly bound by doubly charged Ca^{2+} ion due to which hardness is increased still further and the whole structure becomes brittle.

The Zeolites are aluminosilicate framework minerals of formula Na Al $Si_2O_6.H_2O$ (Sodium zeolite). Here replacing Si with A1 creates and anion. The Zeolite has honeycomb structure with open channels, which have free diameters in the range 4.7A⁰.

The two most striking general property of zeolites are their capacity for base exchange and ability of the hydrated materials to lose water or to dehydrate without any change of crystallographic properties. By 'base exchange' is meant the replacement of one cationic constituent by another on simple treatment with a salt of the corresponding metal. If silver salt is treated, sodium zeolite changes into silver zeolite.

The same phenomenon of base exchange is exhibited also by certain synthetic silicate masses, notably by those materials applied to softening of water. In this case the calcium salts dissolved in the water undergo base exchange with a sodium zeolite with the result that calcium is removed and sodium ions go into solution. At an appropriate stage the base exchange treating with a large excess of NaCl solution can regenerate material.

$$Na_2O.A_2O_3.nSiO_2.mH_2O+CaSO_4 \longrightarrow CaO.Al_2O_3.nSiO_2.mH_2O+Na_2SO_4$$

(water softening)

$$CaO.Al_2O_3.nSiO_2.mH_2O+2NaCl \longrightarrow Na_2OAl_2O_3.nSiO_2.mH_2O+CaCl_2$$

Zeolites are behaving as regeneration molecular sieves also.

Felspars are framework silicates where in the 3- dimensional structure Si^{4+} ions are replaced by Al^{3+}.

To balance the anionic charges +ve ions must be introduced. Felspars make up roughly two – thirds of the igneous rocks. In orthoclase feldspar ($KAlSi_3O_8$) one quarter of the silicon ions are replaced by aluminum and a single univalent ion must be introduced to restore neutrality.

Another class of framework alumina silicates consists of the Ultramarines. An open framework and intense colours characterize them. Ultramarine blue (lapislazuli) probably contains the radical anion S^{-}_{3} and ultramarine green has both S^{-}_{3} and S^{-}_{2}. Although these two anions occur in ultramarine red, the characteristic colour is due to the third species perhaps S^{-}_{4} structurally related but colourless minerals, such as sodalite (containing sulphate anions) are sometimes included in the ultramarines.

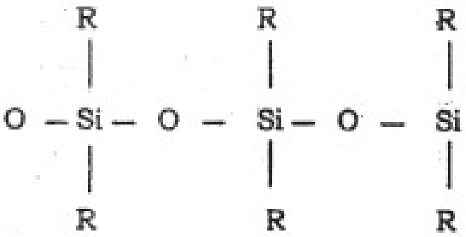
VIII. Silicones

These are synthetic polymeric organo – silicon compounds containing Si-O-Si-O-Si linkages along with C-C-C linkages present in the side chain. Silicones are (1) Linear (straight chain) silicones (2) Cyclic silicones (3) Cross – linked (three- dimensional) silicones.

1. Linear Silicones are obtained by hydrolysis and subsequent condensation of dialkyl or diaryl substituted silicon chloride. Silicon rubbers are composed of units with very high molecular weight bridged together with ethylene or similar groups.

Room temperature vulcanizing (RTV) silicone rubbers are also available. These contain groups like CH_3COO-, which can easily be hydrolysed and cross in the presence of atmospheric moisture.

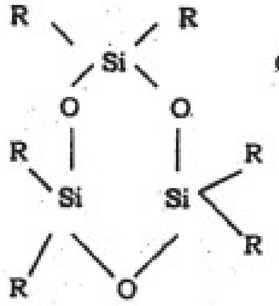
OH^- groups produced as a result of hydrolysis are then made to condense resulting in cross – linking (of vulcanization of organic rubbers). These silicones are completely water repellent in nature and retain their shape over a wide range of temperature.



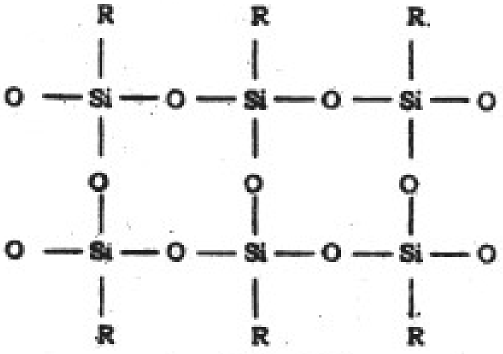
$$O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}$$

Linear silicones

2. Cyclic silicones are obtained by the hydrolysis and subsequent condensation of R_2SiCl_2.


Cyclic silicones.

3. Cross linked silicones : Such silicones are obtained by hydrolysis and subsequent condensation of monoalkyl or aryl substituted silicon chloride. The lower silicones are oily liquids but the highest members containing long chain or ring structure are waxy and rubbery solids. Silicones are remarkably stable towards heat and chemical reagent. These are wetted by water. They are non-toxic and chemically inert. The viscosity of silicone oils remains constant with the change of temperature and as such these silicones do not thicken in cold weather.


Cross-linked silicones

4. Uses

a) Silicone – oils are highly stable and non-volatile even on heating. They are used for high temperature oil baths and high vacuum pumps.

b) They do not become too viscous on cooling. Therefore, used for low temperature lubrication.

c) They are also used in making Vaseline like greases, which are used as lubricants in aeroplanes since they do not freeze at low temperature as 40°C and do not melt at 200°C.

d) They are water repellents and are, therefore used in making water proof clothing and paper by exposing cloth or paper to the silicone vapours.

e) They are also used as insulating materials for electric motors and other electric appliances, since they can withstand high temperature without charring.

f) Silicone – rubber after vulcanization retains its shape and elasticity permanently and has therefore been used in a number of ways.

g) Silicones are mixed with paints and enamels to make them resistant to the effects of high temperature, sunlight, chemicals and damp.

IX. Polyacids

The anions of the weak acids derived from the amphoteric metals of group V A and VI A and particularly V, Mo and W have the interesting property of condensing reversibly as the pH of their solutions is lowered, to give a series of larger anions derived are termed as isopoly acids (anions). If this condensation process takes place in the presence of certain other anions, between which PO^{3-}_4 and SiO^{4-}_4 are the best known, the latter also built into the product, and then it is known as heteropolyacids.

Polymolybdates

$$7(MoO_4)^{2-} + 8H^+ \rightleftarrows (Mo_7O_{24})^{6-} + 4H_2O$$

The $(M_0O_4)^{2-}$ is present at $P^H=10$ but when it is lowered to about 6-8, poly formed.

If it is further acidified to pH 1.5 - 2.9, the octamolybdate $M_{08}O_{26}$ is formed. The ions were established with the help of conductometric and pH titrations etc. Another source of difficulty in all studies on isopoly and heteropoly acids is the relationship between ions in solution and solid phase. The latter can be identified by analysis, but they do not have same ions as in the solution.

Polytungstates

The isopoly tungstates differ in type from the molybdenum compounds as they may be seen;

$(WO_4)^{2-} \xrightarrow{pH6-7} (HW_6O_{21})^{5-} \rightleftharpoons (W_{12}O_{41})^{10-}$

$\searrow pH^3$ Paratungstate A Paratungstate B

$pH<1^{(H_3W_6O_{21})^{3-}} \underset{pH>3}{\overset{pH<3}{\rightleftarrows}} (H_2W_{12}O_{40})^{6-}$ metatungstate

$WO_3 \swarrow$ ψ – metatungstate

When the alkaline solution containing the $(WO_4)^{2-}$ ion is acidified at pH 6-7 there is a fast reaction which can be followed potentiometrically or by conductometric titration.

$$6(WO_4)^{2-} + 7H^+ \rightarrow (HW_6O_{21})^{5-} + 3H_2O$$

The X-ray structure of sodium salt of $Na10(W_{12}O_{41})28H_2O$ has been determined and $(W_{12}O_{46})^{20-}$ is present rather than as $(W_{12}O_{41})^{10-}$. This difficulty was resolved by formulating the sodium salt as $Na_{10}(W_{12}O_{36}(OH)_{10})23H_2O$ which is further helped by NMR studies showing presence of OH group in addition to water molecule.

Heteropoly acids and their salts

The principle underlying the formation of the anions of heteropoly acids is believed to be that the anion of the second acid provides a central group around which octahedral such as M_0O_6 and WO_6 condense by a process of oxygen sharing similar to that encountered in the isopolyacids. It is also important to note that the central group eg. PO^{3-}_4 also shares its oxygen atoms with surrounding octahedra.

Heteropoly acids may have B, Al Si, Ge, Sn, P, As, Sb, Se, Te and I along with Transition metals Ti, Zr, Ce, Th, V, Nb, Ta, Cr, Mo, W, V, Mn, Fe, Co, Ni, Rb, Os, Ir and Pt as central atom. The anions are usually classified in terms of the ratio of the number of central atoms to the number of metal atoms associated with the surrounding octahedral. Most commonly Mo, W or V, the 1:12, 1:9, 1:6 types occurring most frequently. Some heteropoly molybdates having the above relations are;

1:12 P^{5+} AO^{5+} Si^{4+} Ge^{4+} Ti^{4+} Zr^{4+} Ce^{4} Th^{4+}
1:9 Mn^{4+} Co^{4+} Ni^{4+}
1:6 Te^{6+} I^{7+} Ni^{2+} Co^{2+} Mn^{2+} Cu^{2+} Se^{4+} P^{3+} As^{3+} P^{5+}

Ions of heteropoly acids are formed if for e.g. a solution of a molybdate or tungstate is acidified in the presence of ion like PO^{3-}_4. A very familiar example is molybdate test for phosphate in which a solution containing a phosphate is treated with excess of ammonium phosphomolybdate is precipitated. The gravimetric determination of phosphate using this method provided the formula $(NH_4)_3(PM_{012}O_{40})$. Many of the heteropoly acids and their salts are soluble in water and also in solvents such as ethers, alcohols and ketones. The acids are often strong and their anions are stable under more acidic conditions than can be tolerated by the anions of many isopolyacids.

X. Sulphur Nitrides

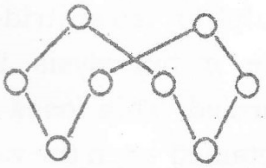
Tetrasulphur tetranitride, S_4N_4, is a yellow crystalline solid of m.p 178^0, which is conveniently prepared by the reaction of ammonia with sulphur chloride (S: Cl = 1: 3-4) in benzene solution. It is also formed slowly from a solution of sulphur in liquid ammonia.

$$10S + 4NH_3 = S_4N_4 + 6H_2S$$

The oxidation number of sulphur in the compound is +3. Hydrolysis in alkaline solution occurs readily and yields ammonia and a mixture of sulphur oxyacids. The compound is endothermic and may explode when heated, or on shock.

The structure shown below (I) is based on both chemical and physical evidence. The S-N bond distance is however, found from an X-ray study to be $1.62A^0$, which is intermediate between the values expected from double and single bonds ($1.54A^0$ and $1.74\ A^0$, respectively), and the fact that the bonds are all of the same length is readily explained on the theory of resonance.


(I)


(II)

The molecule probably has a cradle shape (II). The alternation of sulphur and nitrogen atoms in the ring is indicated by the observation that no hydrazine is formed on reduction. Moreover, reaction with secondary alkylamines converts all the sulphur into the thiodiamine, $AlkN - S - Nalk_2$.

Tetrasulphur tetranitride undergoes a number of interesting reactions. Thus it is reduced by stannous chloride in benzene methanol solution.to the compound $N_4S_4H_4$ and reacts with chlorine to give thiazylchloride, $N_3S_3Cl_3$. The first of these compounds is colourless and crystalline (m.p.152^0), and the oxidation number of sulphur has been shown to be +2. It is readily oxidized to N_4S_4. The ring is puckered and the four hydrogen atoms are attached to nitrogen, since the infrared spectrum shows N-H frequencies, but none attributable to S-H.

The chlorination product is remarkable in possessing a six – member ring, which remains intact in a number of reactions. Thus on treatment with sulphur trioxide an adduct is first formed and this, when heated, loses sulphur dioxide and forms sulphanuric chloride. It reacts quantitatively with $N_4S_4H_4$ reform S_4N_4 according to the equation;

$$4N_3S_3Cl_3 + 3N_4S_4H_4 = 6N_4S_4 + 12HCl$$

Cautious fluorination of N_4S_4 with argentic fluoride gives $N_4S_4F_4$, (i.e. the ring is unattacked), while bromination yields a bronze – coloured solid NSBr, of unknown molecular weight.

Reaction of sulphur monochloride with ammonia yields heptasulphur imide, S_7NH, which contains a ring of seven sulphur atoms with one of nitrogen. The infrared spectrum shows the presence of an N – H bond and the compound can be acetylated or benzoylated. It has also been shown to form the stable mercurous and mercuric derivatives $Hg_2(NS_7)_2$ and $Hg(NS_7)_2$.

When tetrasulphur tetranitride is heated with sulphur in carbon disulphide in an autoclave it forms N_2S_4 (m.p.23°), the structure of which is unknown, though it is likely to be cyclic, with a ring of sulphur and nitrogen atoms. Tetrasulphur tetranitride reacts with disulphur dichloride or acetyl chloride to form the compounds S_3N_4Cl. This is of special interest because it proves to be a salt of the $(S_3N_4)^+$ cation and, indeed, a number of other salts, including the nitrate, bisulphate and thiocyanate, are also known.

The ring in tetrasulphur tetranitride may also be broken by chemical reactions, as for example, in hydrolysis. With ammonia an ammoniate of the formula $S_2N_2.\ NH_3$ is formed. This loses ammonia readily to give disulphur dinitride, which is also obtained when the vapour of S_4N_4 is heated at low pressure to 300^0. It polymerizes readily to a stable brass – coloured compound, of the composition $(SN)_x$, which forms fibre – like crystals and is a semiconductor. The ammoniate $S_2N_2.NH_3$ behaves as an acid amide in liquid ammonia and reacts with potassium amide to form a mixture of K(NS) and K2(N2S). This reaction has been explained by assuming fission of the ammoniate into an imide of sulphoxylic acid and orthosulphurous acid

$$\begin{array}{lcc} H_2N - S = N - S = NH \rightarrow & H - N - S = N - H & + \ S = N - H \\ & \downarrow & \downarrow \\ & K_2N_2S & KNS \end{array}$$

XI. Borazines

The most important ring system of organic chemistry is benzene ring. Inorganic chemistry has two analogues of benzene: borazine $B_3N_3H_6$ and trimetric phosphonitrilic compound $P_3N_3X_6$. Stock synthesized borazine by heating adduct of diborance and ammonia.

$$3B_2H_6 + 6NH_3 \rightarrow 3(B_2H_6)(NH_3)_2 \rightarrow 2B_3N_3H_6 + 12H_2$$

More efficient methods are;

$$3NH_4Cl+3BCl_3 \rightarrow 9HCl+Cl_3B_3N_3H_3 \xrightarrow{NaBh_4} B_3N_3H_6+3/2\ B_2H_6+3NaCl$$

$$3NH_4Cl+3LiBH_4 \rightarrow B_3N_3H_6+3LiCl+9H_2$$

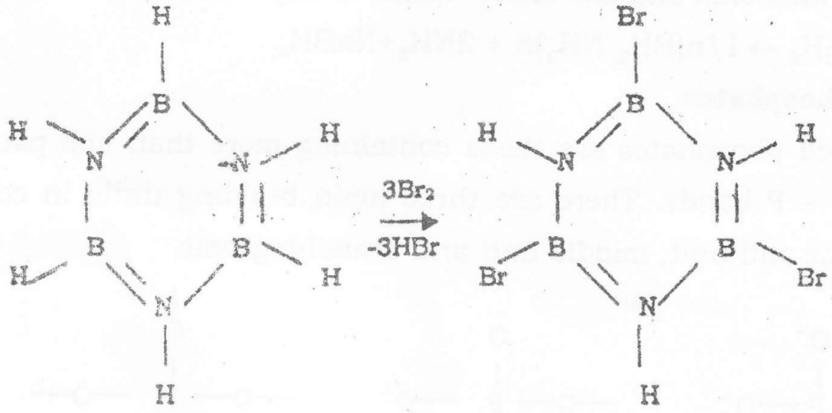
N – or B – substituted borazines may be maae by appropriate substitution on the starting materials prior to the synthesis of the ring.

$$3RNH_3Cl+3BCl_3 \rightarrow 9HCl+Cl_3B_3N3R_3 \xrightarrow{NaBH4} H_3B_3N_3R_3+3/2B_2H_6+3NaCl$$

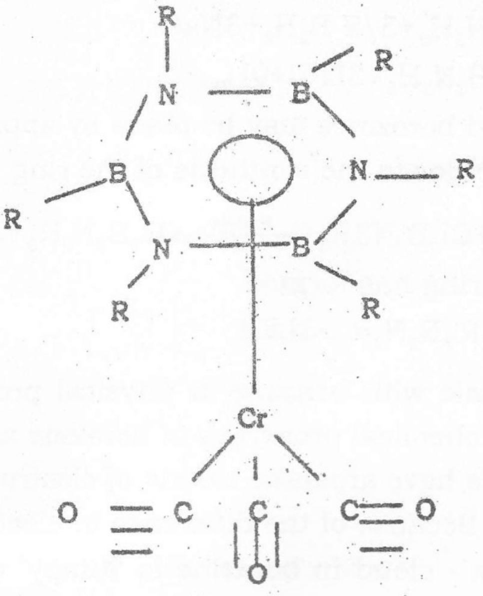
or substitution after the ring has formed

$$Cl_3B_3N_3R_3 + 3LiR' \rightarrow R'_3B_3N_3R_3+3LiCl$$

Borazine is isoelectonic with benzene in physical properties; it is a close analogue of benzene. The chemical properties of borazine and benzene are quite different. Both compounds have aromatic clouds of electron density delocalized overall of the ring atoms. Because of the difference in electronegativity between boron and nitrogen, the π - cloud in borazine is 'lumpy' with more e⁻ density localized as nitrogen. The partial localization weakens the π - bonding in the ring. In addition, nitrogen relation has some of its basicity and the boron some of its acidity. Polar species such as HCl can therefore attack the = bond between N and B. the different electronegativites of boron and nitrogen tend to stabilize bonding to born by electronegative substitutents and to nitrogen by electropositive substitutents. Thus in contrast to benzene borazine readily undergoes addition reaction. The tendency to undergo addition rather than aromatic substitution is well contrasted by the reaction of these two compounds toward bromine.



The electronic difference between benzene and borazine is further supported by the properties of the type $(R_6B_3N_3)\ Cr(CO)_3$. This is analogous to $(C_6H_6)\ Cr(CO)_3$, the bonding is not nearly so strong. The dissociatiosn energy of the ring from the metal appears to be about one – half as strong in the borazine complex as in the arena complex.



Benzene may be hydrogenated to produce the saturated compound cyclohexane. Hydrogenation of borazine results in polymeric materials of indefinite composition. Substituted derivatives of the saturate cycloborazane $B_3N_3H_{12}$ formed readily by addition to borazine.

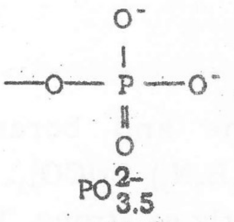
$$2B_3N_3H_6 + 6HCl \rightarrow 2H_3Cl_3\ B_3N_3H_6 \xrightarrow{6NaBH_4} 2H_6B_3N_3H_6 + 3B_2H_6 + 6NaCl$$

A complete series of cycloborazanes may be prepared by the treatment of the adduct of ammonia and diborance with a strong base.

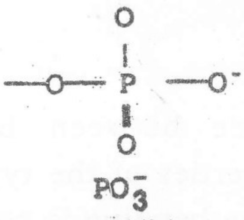
$$2NH_3 + B_2H_6 \rightarrow 1/n(BH_2\ NH_2)n + 2NH_3 + NaBH_4$$

Condensed phosphates

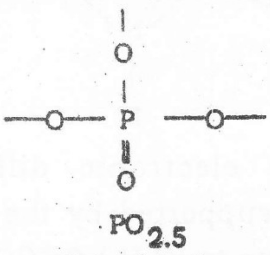
Condensed phosphates are those containing more than one pattern and having P – O – P bonds. There are three main building units in condensed phosphates the end unit, middle unit and branching unit.



$PO_{3.5}^{2-}$
(end)



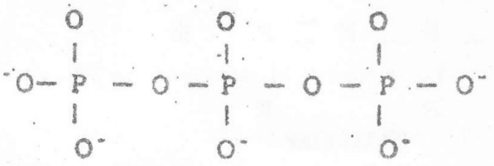
PO_3^-
(middle)



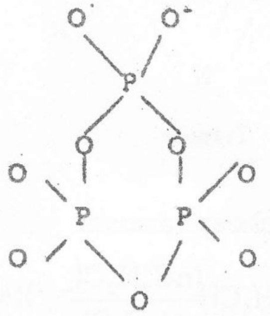
$PO_{2.5}$
(branching)

They are identified by 31p NMR spectra. They are having (a) chain or polyphospates, containing 2 – 10 P atoms (b) cyclic or metaphosphates, containing 3 – 7 or more P atoms (or) (c) infinite chain metaphosphates. Linear polyphosphates are salts of anions of general formula $(PnO_{3n+1})^{(n+2)-}$ Examples are $M_4P_2O_7$(M=alkali metals) which is a pyrophosphate or dipolyphosphate.

$M^{I}_{5}P_{3}O_{10}$ (a tripoly phosphate)



Cyclic



Cyclic Polyphosphones

are having general formula $(PnO_3n)^{n-}$ Examples are $M_3P_3O_9$ a trimeta – phosphate and $M_4P_4O_{12}$ a tetrametaphosphate. The eight member ring of the $P_4O_{12}^{4-}$ ion is puckered with equal P – O bond lengths.

Condensed phosphates are usually prepared by dehydration of orthophosphates under various conditions of temperature (300 – 1200°C) and also by appropriate hydration of dehydrated species.

$(n\text{-}2)\ NaH_2PO_4 + 2Na_2HPO_4 \xrightarrow{Heat} NaP_nO_{3n+1}H + 2$ Polyphosphate $+(n-1)H_2O$

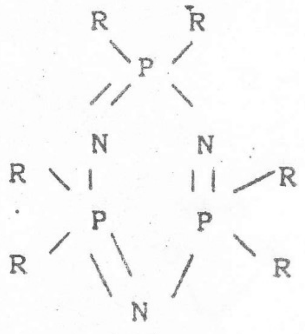
$n\ Na\ H_2PO_4 \xrightarrow{Heat} (NaPO_3)nH_2O$ metaphosphate

They can also be prepared by controlled addition of water or other reagents to P_4O_{10} by treating chlorophosphates with silver phosphates etc. the complex mixtures of anion that can be obtained are separated by chromatographic technique.

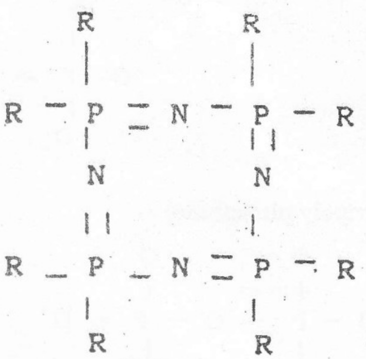
Condensed phosphates form soluble complexes with many metals and chain phosphates are used industrially for this purpose as water softeners.

XII. Phosphonitrilic Compounds

A great many compounds are known with P – N – and P = N bonds $R_2N - P$ bonds are particularly stable and occur widely in combination with bonds to other univalent group such as P – R, P – Ar and P – X. Phosphonitrilic halides are also known as phosphozenes. They are cyclic compounds with alternate P and N atoms with two substituents each on P atom.



Trimer



Tetramer

Hexachlo the synthesis of many other phosphozenes.

$$nPCl_5+nNH_4Cl\xrightarrow[C_6H_5Cl]{InC_2H_2Cl_4}(NPCl_2)n+4nHCl \qquad n=3,4,5,\ldots.$$

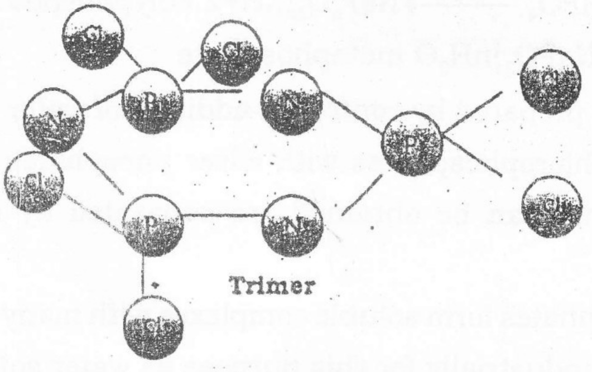
The majority of reported phosphozene ions involve displacement of halogens by OH, OR, NR_2, NHR, NR to give partially or fully subst'tuted compounds.

$(NPCl_2)_3+6NaOR \rightarrow (NP(OR)_2)_3 + 6\ NaCl$

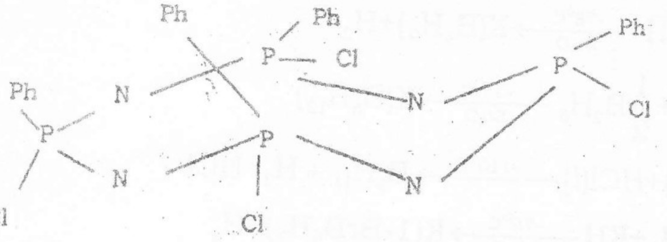
$(NPCl_2)_3+6NaSCN \rightarrow (NP(NCS)_2)_3 + 6\ NaCl$

$(NPF_2)_3+PhLi \rightarrow (NPPh)_2)_3 + 6\ NLiF$

The mechanism appears to be following Si ² attack on P by an anion. In partly substituted molecules more isomers are possible.



Trimer



Tetramer

The rings in (NPF C_2) x wgere x = 3,4 are planar and those with x = 5, or 6 approach planarity. In nonplanar compounds where x is very large NPN angle = 120° and PNP angles are = 132°. From the following figures we are able to throw that P – N distance lie in the range 1.56 – 1.61A° and they are shorter than the expected single bond length of 1.75 – 1.80A°

The problem of π - electron density is complicated owing to the large number of orbitals to the large number of orbitals potentially involved and to the general lack of ring planarity, which means that rigorous assignment of σ and π character to individual orbitals is impossible.

XIII. Boranes

Stock prepared boron hydrides from the hydrolysis of magnesium borides with aqueous acid. As many boranes are susceptible to hydrolysis, he isolated those whose reaction with water was slowest – especially tetraborane (10). This compound then was pyrolyzed to given diborane and other boron hydrides.

$$2MgB_2 + 4Mg + 12HCl \rightarrow B_4H_{10} + H_2 + 6MgCl_2$$

$$B4H10 \xrightarrow{\Delta} B_2H_6 + \text{higher boranes}$$

As stock realized, protonic reagents are not good choices for preparing hydrides since hydrolysis occurs with liberation of H_2. the metal hydrides now available are often employed – for example.

$$2KBH_4(s) + 2H_3PO_4 \rightarrow B_2H_6(g) + 2KH_2PO_4(s) + 2H_2(g)$$

Historically, boranes often were prepared by pyrolsis of B_2H_6. we can write reaction schemes involving successive addition of Bh_3 and H_2 elimination to give most of the known nido and arachno boranes. In recent years, shore has developed systematic procedures for making boron hydrides in good yield, taking advantage of the acidity of μ - H. the anions resulting from H+ abstraction may then react to add BH, presumably at electron rich B – B bonds yielding species subject to cage expansion and to H_2 or MX elimination.

$$B_4H_{10}+KH \xrightarrow[Et_2O]{-78^oC} K(B_4H_9)+H_2$$

$$K(B_4H_2)+\frac{1}{2}B_2H_6 \xrightarrow[Et_2O]{-35^oC} K(B_5H_{12})$$

$$K(B_5H_{12})+HCl(l) \xrightarrow{-110^oC} B_5H_{11}+H_2+HCl$$

$$1\text{-}BrB_5H_8+KH \xrightarrow[Me_2O]{-78^oC} K(1\text{-}BrB_5H_7)+H_2$$

$$K(1\text{-}BrB_5H_7) \xrightarrow[Me_2O]{-78^oC} K(B_6H_{10}Br)$$

$$K(B_6H_{10}Br) \xrightarrow[Me_2O]{-35^oC} B_6H_{10}+KBr$$

In another approach, H^- may be abstracted from anions with BX_3, giving species that transfer BH_3, sometimes with accompanying H_2 elimination.

$$(n\text{-}Bu_4N)(BH_4)+BCl_3 \xrightarrow[CH_2Cl_2]{25^oC} \frac{1}{2}B_2H_6+(n\text{-}Bu_4N)(HBCl_3)$$

$$(n\text{-}Bu_4N)(B_3H_8)+BBr_3 \xrightarrow{0^oC} \frac{1}{2}B_4H_{10}+(n\text{-}Bu_4N)(HBBr_3)+\frac{1}{x}(BH_2)_x$$

$$(Me_4N)(B_9H_{14})+BCl_3 \xrightarrow{25^oC} \frac{1}{2}B_{10}H_{14}+(Me_4N)(HBCl_3)+\frac{1}{2}H_2+\frac{1}{x}(B_8H_{10})_x$$

Commercially available B_5H_9 is a good starting material for preparation of higher boranes. Deprotonation of B_5H_9 in the presence of excess B_5H_9 is a route to $B_9H_{14}^-$

$$B_5H_9+HK \xrightarrow{\text{THF or glyme}} K(B_5H_8)+H_2$$

$$K(B_5H_{14})+B_5H_9 \longrightarrow K(B_9H_{14})+\frac{1}{2}B_2H_6$$

Because the reaction

$$K(B_5H_8)+BH_3 \longrightarrow K(B_9H_{11})$$

is known to occur, the yield of $K(B_5H_{14})$ is maximized with a 1.8 : 1 B_5H_9 : KH stoichiometry rather than the 2 : 1 stoichiometry suggested. $B_9H_{14}^-$ can be protonated to give B_9H_{15} and can be used to make $B_{18}H_{22}$ and B_9H_{13}. MeCN.

Hydride abstraction from $B_9H_{14}^-$ is a route to $B_{10}H_{14}$ in 55 - 60% yield;

$$(Me_4N)(B_9H_{14})+BCl_3 \xrightarrow[\text{glyme}]{25^0C} \frac{1}{2}B_{10}H_{14}+(Me_4N)(HBCl_3)+\frac{1}{2x}(B^8H_{10})x+\frac{1}{2}H_2$$

In a one-pot synthesis starting with B_5H_9, NaH, and (Me_4N) Cl, BC_{13} is generated in situ. Solvent, temperature, and cation choice are critical in these preparations.

Among the closo boranes, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are the most thermally stable and easiest to prepare. The condensation and closure reaction involving a nido boron hydride gives a nearly quantitative yield of $B_{12}H_{12}^{2-}$

$$B_{10}H_{14}+2Et_3N.BH_3 \xrightarrow[\text{hydrocarbon solution}]{190^{\circ}C} (Et_3NH)_2(B_{12}H_{12})+3H_2$$

$B_{10}H_{10}^{2-}$ can be prepared nearly quantitatively by a simple base - promoted closure reaction.

$$B_{10}H_{14}+2Et_3N \rightarrow (Et_3NH)_2(B_{10}H_{10})+H_2$$

Other close hydrides can be synthesized by related processes involving condensations and closures (both base – induced and pyrolytic) or degradation of larger close species to smaller ones. The close hydrides ordinarily are isolated as their salts. By using cationic exchange columns, the crystalling acid hydrate forms of more hydrolytically stable close ions $(H_3O)_2$ (BpHp) (H_2O) m can be prepared. These are strong acids comparable to H_2SO_4 in aqueous solution.

XIV Caboranes

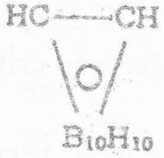
The most important heteroboranes are the carboranes. These are much more stable to air and moisture than the borances. An interesting feature of their structures is the appearance of carbon with coordination number (C,N) up to 6. C's are the most electropositive centers in the frameworks. For species containing two or more C (many are C_2 species), isomers are possible. The most thermodynamically stable ones has maximum separation of the electropositive C's. the most common preparative route is the reaction of boranes with acetylenes.

$$B_5H_9+C_2H_2 \xrightarrow{500\text{-}600^{\circ}c} 2,4-C_2B_5H_7+1,6\text{-}C_2B_4H_6+1,5\text{-}C_2B_3H_5$$

$$B_8H_{12}+MeC \equiv CMe \rightarrow (MeC)2B_6H_9+\frac{1}{2}B_2H_6$$

$$B_{10}H_{12}+C_2H_2 \longrightarrow 1,2-C_2B_{10}H_{12}+2H_2$$

The isomers of close icosahedral $C_2B_{10}H_{12}$exhibit extremely high kinetic and thermodynamic stability. The 1,2 – 1,7- and 1,12- isomers have the common names O¯, m¯ and p¯ carbonate, respectively. O – Carborane has been given the following symbol in the literature;

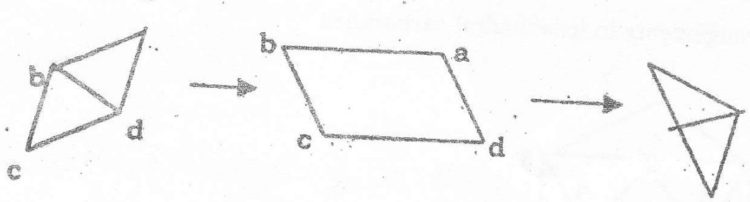


Reactions and B centers in carborances parallel to those of the boranes; bridge proton abstraction and electrophilic substitution, including halogenation. The terminal H atoms attached to electropositive C are relatively acidic. Hence these C centers can be metallated.

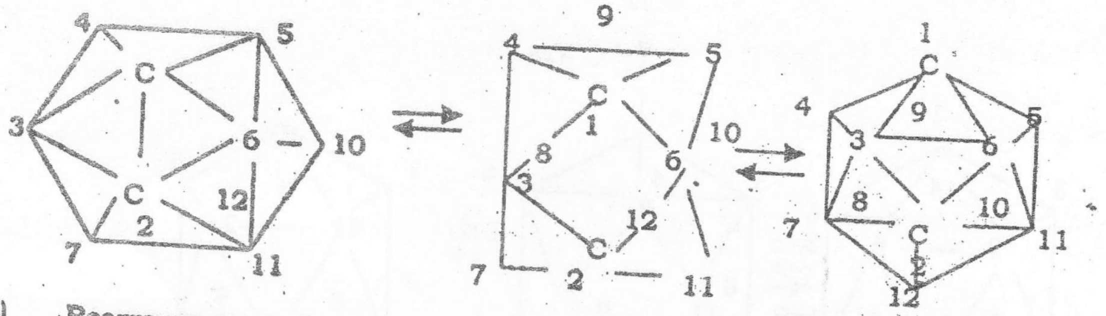
$$1,7\text{-}C_2B_4H_6 + 2\ n\text{-}BuLi \longrightarrow Li_2(1,7\text{-}C_2B_4H_4) + 2C_4H_{10}$$

The metallated products retain structural integrity and can react as nucleophiles to produce a large number of C – substituted derivatives. O – Carboane has a very extensive organic chemistry. O- Carborane ismerizes to m – carborane at 450°C. Lipscomb proposed that this reaction occurs via the diamond – square – diamond (DSD) mechanism in which a pair of triangular faces open into a square by breaking a bond. Bond formation in an orthogonal direction leads to a rearranged icosahedron; the motion involved in forming a square stretches and breaks five other bonds, leading to the intermediate. This model can account for the rearrangement of O – to M- carborane.

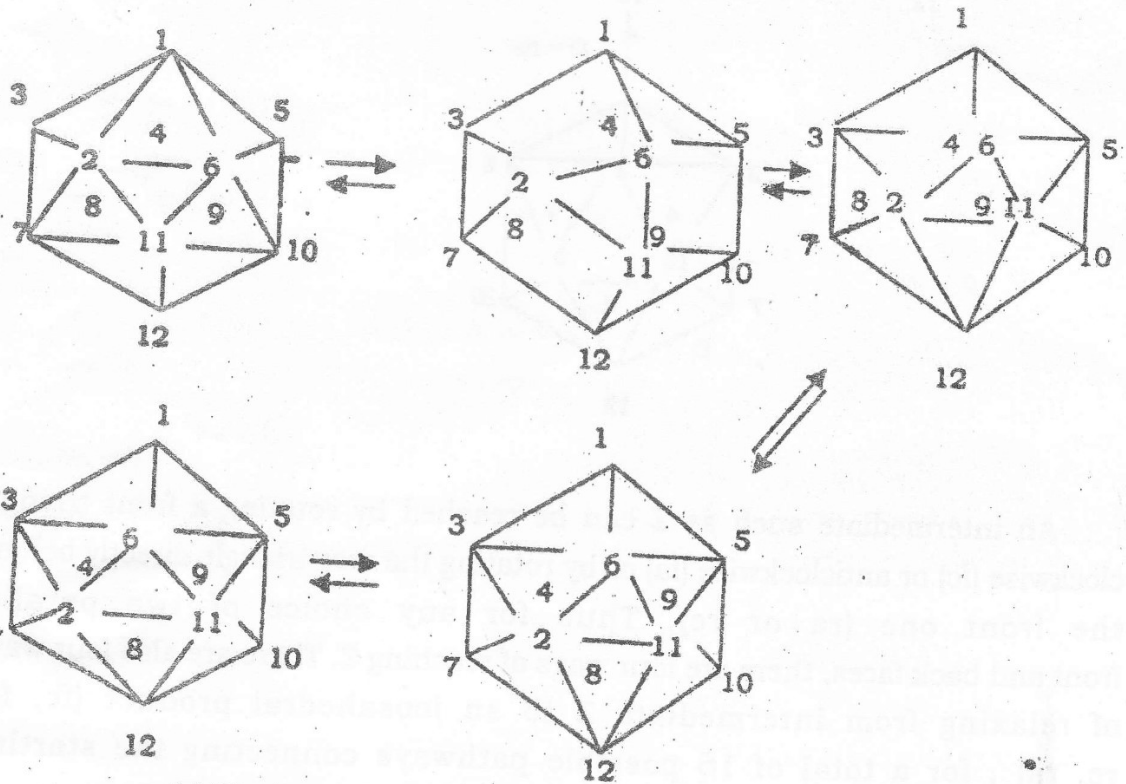
At still higher temperatures M-carborane rearranges to the thermodynamically stable product P – carborane. The DSD mechanism cannot however, produce P – from either O – or m- carborane. A more general mechanism is the extended triangle rotation (ETR) mechanism depicted. one triangular face rotates anticlockwise through a 30° angle, giving a transition state having three – square faces resulting from cage bonds broken by the motion. A further 30° rotation gives an intermediate Z containing all triangular faces, but with the rotated triangle on the front now congruent with the triangle on the back Z possesses a plane of symmetry passing though framework atoms 1,5 10, 12, 7, and 3. If the back triangle is now retated anticlockwise through 30° then another 30°, another icosahedron with interchanged vertices is reached. The result is equivalent to the DSD mechanism; however, the ETR mechanism has the advantage of preserving maximum number of triangular faces and their attendant three – center bonding.



(a) The DSD mechanism

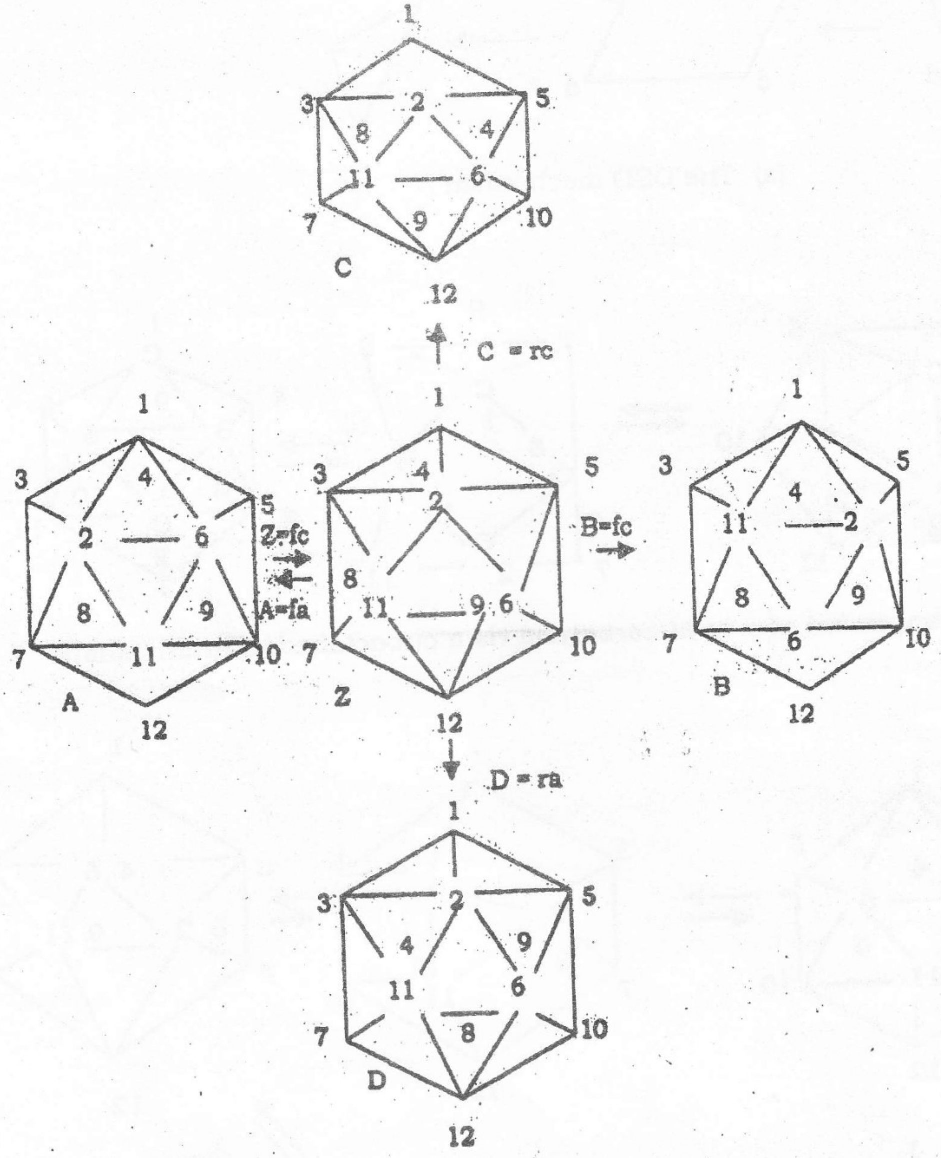


(b) Rearrangement of o- to m-carborane via a cuboctahedral intermediate



(c) The ETR equivalent of DSD

(d) Rearrangements in icosahedral carboranes



An intermediate such as Z can be reached by rotating a front triangle clockwise (fc) or anticlockwise (fa) or by rotating the rear triangle directly behind the front one (ra or rc). Thus for any choice of two parallel front and back faces, there are four ways of reaching Z. There are also four ways of relaxing from intermediate Z to an icosahedral product (fc, fa, rc, ra) , for a total of 16 possible pathways connecting the starting and ending icosahedra. Because there is a choice of ten pairs of faces to rotate, a total of 160 rearrangement pathways are available, not all of which lead to different products (for example, fc, fa leads back to the starting configuration).

The ETR mechanism in conjunction with the assumption that some triangular faces undergo preferential rotation is helpful in product distribution in thermal rearrangements of substituted icosahedral carboranes. O – Carborane is attacked by base that excise a BH group, generating a nido anion that retains structural integrity. The 1.7 isomer can be obtained by thermal regarrangement of the anion or by starting with m – carborane.

$$1,2\text{-}C_2B_{10}H_{12} + OEt^- + 2EtOH \xrightarrow{85^0C} 1,2-C_2B_9H + H_2 + B(OEt)_3$$

Questions

1. Discuss the occurrence and isolation, purification, properties and uses of Zirconium.
2. Show how plutonium is extracted from radioactive neptunium.
3. What are the important ores of uranium? Where are they obtained? Give a method to extract uranium from carnotite.
4. Give the flow chart for extraction of uranium from pitchblende. What are the isotopes of uranium/
5. Discuss the nature of Oxides of uranium
6. Discuss how thorium is extracted from thoria
7. Discuss the various structures of silicates
8. Write short notes on Zeolites and felspars.
9. How silicones are synthesized? Mention their type and their applications.
10. What do you mean by isopolycides? How heteropoly acids are different from polycids?
11. Discuss the structure of sulphur tetranitrides
12. Show how borazines are different from benzene in their chemical properties.
13. Discuss the structure of trimeric phosphonitrilic compounds
14. Discuss how the carboranes can be interconverted.

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M.Sc. DEGREE EXAMINATION APRIL 2004

First Year – Non – Semester

Chemistry

PAPER II – INORGANIC CHEMISTRY – I

(For those who joined in july 2003 and afterwards)

Time: Three hours Maximum: 100 marks

PART – A (10x2=20 marks)

Answer All the Questions.

1. Write the electronic configuration of Ti^3. what is the n and l value for the valence electron?
2. The bond length in HF is 0.95A° and the dipole moment is 1.92A° Calculate the percentage ionic character of H – F bond.
3. When KCl is heated with potassium vapour, it becomes lilac coloured. Why?
4. If first order reflection from a crystal lattice occurs at 9° 25; at What angle, the third order reflection will occur?
5. Explain the term fissile and fertile isotopes with an example.
6. Explain spallation reaction with an example.
7. What is normal and inverse spinel? Whether $Fe_3\ O_4$ will be a normal or inverse spinel?
8. Tetracarbonylnickel is tetrahedral but diamagnetic whereas $NiCL_4^{2-}$ is tetrahedral but paramagnetic. Explain.
9. Talc is soft whereas mica is hard. Explain
10. How ultrapure zirconium can be prepared?

PART – B = (5x6=30 Marks)

Answer all the questions by choosing either (a) or (b)

11. a) For the hyphothetical molecule BN, draw the M.O. diagram and deduce the bond order and magnetic properties. What will be the bond order and magnetic property for BN- and BN+ molecules? (or)

    b) Based on VSEPR theory, predict the shape of the following : $SnCl_2$, SF_4, ClF_3, ICl^-_4, XeF_2, XeF_6.

12. a) Sketch and explain the unit cells of Zinc blende, Flourite and Pervoskite. (or)

    b) Write an account of Hall effect and its applications.

13. a) Discuss the construction and working of Geiger – Muller Counter.(or)

    b) Write a short notes on Stellar energy.

14. a) Explain the effect of spin – orbit coupling on the magnetic moments of transition metal complexes. For the complex $CoCl^{2-}_4$, the magnetic moment is 5.64 BM and $10D_q$=3100cm^{-1}. Find the value of spin-orbit coupling constant λ (or)

b) Sketch the splitting of d orbitals in octahedral, tetrahedral and square planar configuration. For d^3 metal ion calculate CFSE in octahedral and tetrahedral field.

15. a) Discuss the structure of Zeolites. How the physical properties of Zeolites can be explained interms of its structure. (or)

b) What are the important ores of Thorium? How the metal is extracted? What are its uses?

PART C – (5x10=50 marks)

Answer All the questions choosing either (a) or (b)

16. a) i) Define electro negativity. How pauling evaluated electro negativity of elements? The H-H, C-C and C-H bond energies are 104.2, 83.1, and 98.0 k.cal mol^{-1} respectively. What is the electro negativity of carbon? (5)

ii) Write a short notes on Bent's rule and its uses (5)

(or)

b) i. Derive Born – Lande equation. Using the above equation calculate that lattice energy of Nacl. A = 1.7475, r_0 = 2.79A°.

ii) Describe Born – Haber cycle for the formation of Nacl. Using the following data, evaluate the lattice energy of NaCl.

Heat of sublimation of sodium = 25.9 kcal mol^{-1}
Dissociation energy of chlorine= 58..0 kcal mol^{-1}
Ionisation energy of sodium = 118.0 mol^{-1}
Electron affinity of chlorine = -83.0 kcal mol^{-1}
Enthalpy of formation of Nacl = -91.0 kcal mol^{-1}

17. a) Explain the powder method of analysis of crystals using X – Rays. Powder photograph of a crystal belonging to cubic system shows diffraction at angles 13.75°, 16,00°, 22.75°, 27.0°, and 33.75°, Index these lines and find the lattice type and unit cell dimension. The wavelength of X – Ray used is 1.54 $\overset{0}{A}$

(or)

b) Discuss the band theory of solids. With the above theory explain the electrical conductivities of conductors, insulators, semiconductors, n – type semiconductors and p-type semiconductors.

18. a) i) Explain the principle of isotopic dilution analysis. To a sample, aureomycin labelled with ^{14}C was added. The amount of radioactive sample added is 10.1 mg with activity 128 cpm mg^{-1}. After through mixing, the activity of aureomycin in the mixture was 68.3cpm mg-1. Calcualte the amount of aureomycin present in the sample (5)

(ii) Explain the radiometric titrations. (5)

(or)

b) i) Compute Q value for the reaction ^{14}N (αp) ^{17}O mass of ^{14}N, α, p, 17O are 14.007518, 4.003837, 1.008144, 17.004529 amu respectively. (2)

ii) In the fission of $^{239}_{94}Pu$, the fragments have the mass number 100 and 138 whose stable isobars are $^{100}_{42}Mo$ and $^{138}_{56}Ba$. What are the primary fragments? (3)

iii) Complete the following :

$^{40}_{20}Ca(n,\alpha)......$

$^{227}_{89}Ac \rightarrow ..... 5\alpha + 3\beta$

$^{249}_{99}Es + n \rightarrow {}^{87}_{35}Br + 2n + ...$ (5)

19. a) (i) How the study of magnetic properties are useful in understanding the stereochemistry of four coordinated Ni (II) complexes? A compound with empirical formula Ni $(en)_2$ $(CN)_2$ can be formulated either as (Ni $(en)_2$) (CN) or (Ni$(en)_2$) $(CN)_2$). How the study of magnetic property can distinguish between the two forms?

(ii) Calculate the magnetic moment of Ce^{3+}. (6)

(or)

b) i) CoF_6^{3-} is paramagnetic whereas $Co(NH_3)_6^{3+}$ is diamagnetic. Explain this observation using VBT and CFT.

ii) Write a brief account of Jahn – Teller effect. (5)

20. a) Write a brief account of boranes and carboranes.

(or)

b) i) How Pu is recovered from spent fules? (5)

ii) What are the important ores of uranium? How the metal is extracted? Mention its uses

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