Editorial

Science is a wonderful thing; it solves 10 times more problems than it causes. But technology confers its full benefits only if we are willing to follow its path wherever it leads. One of the toughest scientific challenges has been to effectively and inexpensively separate a desired isotope of a chemical element from the remaining isotopes for uses ranging from medicine to energy to weapons applications.

The Indian population has already crossed the magical figure of a billion and is growing at a steady rate. The energy sources on the other hand have been reducing at a much greater pace. The decline is alarming. The reserves with mother India would not sustain her teeming billions.

The future of the world, dependent as it is upon atomic energy, requires more understanding and knowledge about the atom. I hope that in some small way our efforts have helped people to learn about the atom and the way in which it works and may have helped them to see that isotopes are real and that they may hold much promise for the future - that in them lies a principal hope for the betterment of human life on earth and for the preservation and improvement of our standard of living. In all fields from industry and medicine to pure scientific research, there are numerous applications of isotopes as yet unmade which in themselves may well increase by large factors the large total of benefits mankind now receives from them. We hope that this honor Professor Hevesy has done us will bring the time of further realization of these benefits closer and will help all mankind to live better and be happier through the atom and isotopes.

IANCAS is indebted to Dr. S.K. Sarkar, the Guest Editor and all the authors for providing lucid articles for this bulletin.

         G.A. Rama Rao

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Prof. M.N. Sastri

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is happy to confer

IANCAS Dr. M.V. Ramaniah Memorial Award

on

Prof. M.N. Sastri

Mumbai, India

For his outstanding and lifetime achievements in teaching and research in the field of radiochemistry. The discipline of nuclear and radiochemistry flourished in Andhra University during his long and memorable academic career. He has made significant contributions in the area of chemical kinetics, chromatography and other analytical techniques using radiotracers. He was responsible for setting up of Centre for Nuclear Techniques at Vishakhapatnam that promoted and encouraged research in this discipline. Prof Sastri has been an exemplary teacher and guided a large number of students for doctoral work. He has numerous publications in reputed journals and has authored eight books. A receipient of several awards, his academic services have been recognized by the Government of Andhra Pradesh in the form of distinguished teacher award. He is member of many scientific committees and founder vice-president of IANCAS.

March 16, 2005

(V. Venugopal)
President, IANCAS

IANCAS Dr. Tarun Datta Memorial Award to

Shri Suresh Chandra Parida
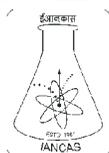
INDIAN ASSOCIATION OF NUCLEAR CHEMISTS AND ALLIED SCIENTISTS (IANCAS)

is happy to bestow

IANCAS Dr. Tarun Datta Memorial Award

on

Shri Suresh Chandra Parida

Fuel Chemistry Division
Bhabha Atomic Research Centre
Mumbai, India

For his important contributions in the field of thermodynamics of nuclear materials relating to experimental methods and theoretical modeling of thermodynamics of alloys, intermetallics and complex oxides. Shri Parida has generated thermodynamic parameters for some of the alloys and intermetallics of lanthanides and actinides with platinum group metals and carried out a systematic study on the thermodynamics of complex oxides using a variety of experimental methods such as solid-state electrochemical, vapor pressure and calorimetric techniques. His theoretical contributions are on the improvement of Meidema's semi-empirical model for the estimation of enthalpies of formation of lanthanide and actinide binary alloys with platinum group metals & development of different types of phase diagrams. They are isothermal oxygen potential diagram, two- and three-dimensional chemical potential diagrams for ternary systems, modeling the heat capacity of perovskites, garnets and, the "computer coupling of phase diagrams and thermochemistry" which is the basis of the so-called CALPHAD approach.

March 16, 2005

(V. Venugopal)
President, IANCAS

IANCAS Prof. H.J. Arnikar Best Thesis Award to

Dr. Alok Diwakar Bokare
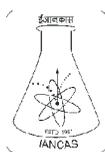
INDIAN ASSOCIATION OF NUCLEAR CHEMISTS AND ALLIED SCIENTISTS (IANCAS)

is happy to bestow

IANCAS Prof. H.J. Arnikar Best Thesis Award

on

Dr. Alok Diwakar Bokare

Department of Chemistry
Indian Institute of Technology, Madras
Chennai, India

For his work on the use of positrons as novel microprobes in the study of structureproperty correlations in different chemical systems. Dr. Bokare has contributed significantly to the understanding of positron behavior in both macroscopic and microscopic molecular environments. His work amply demonstrates that positron annihilation spectroscopy takes precedence over most of the conventional spectroscopic techniques for imaging structural reorganizations and phase transitions. In addition, his work demonstrates the extreme sensitivity of the positron to probe pre-transition effects and conformational changes occurring in a localized microenvironment.

March 16, 2005

(V. Venugopal)
President, IANCAS

Isotope Enrichment Techniques

Guest Editor

Sisir K. Sarkar

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Bhabha Atomic Research Centre
Mumbai 400 085
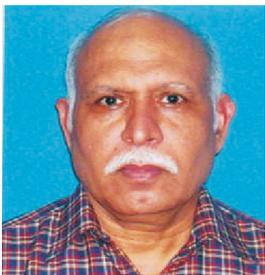
FOCUS

Shri D.S. Shukla

Uranium is the most commonly used fuel in Nuclear Power Reactors, other being Plutonium. Uranium is the only element occurring in nature which has fissile isotope and can be used as fuel in Nuclear Power Reactor. Naturally occurring Uranium has three isotopes, namely U-235 which is only about 0.7%, U-238 which is 99.28% and the other isotope is U-234 (0.005%). Only U-235 takes part in fission reaction in nuclear reactors.

Uranium can either be used after converting into suitable chemical and physical form, in reactor as such in natural form or after enrichment. Increasing the percentage of U-235 in Uranium above than that occurs in nature is called Uranium enrichment. Using enriched uranium in power reactors has certain advantages over natural uranium. If natural uranium is used as fuel in Nuclear Reactor, the moderator has to be heavy water. India has decided in her first phase of power programme to go for natural uranium fuelled heavy water moderated power reactor also called Pressurised Heavy Water Reactor (PHWR).

For reactors using ordinary water, the fuel is to be enriched to about 3 to 4% of U-235. Research reactors which are very compact in size use highly enriched Uranium. Uranium required for strategic purposes need to be enriched beyond 90% U-235. Most of the reactors operating in the world use enriched Uranium and more than 80% of the electricity production in the world today is by such reactors. The enrichment requirement of all such reactors in the world in 2000 was estimated at 38.7 million Separative Work Units (SWU) and projected to increase to 41.5 million SWU by year 2015 (source: International Nuclear Model-2001,Energy Information Administration, Department of Energy, USA)

The uranium enrichment processes (also called isotope separation processes) for large scale application were developed during World War-II under Manhattan Project of USA. A number of processes were evaluated, prominent among them being gas diffusion, gas centrifuge, thermal diffusion and electro magnetic etc. Based on the status of development at that time and other factors, gaseous diffusion process was selected for establishing a large scale production facility. These facilities were established initially for production of enriched uranium for strategic application.

All the processes available for uranium enrichment are energy intensive and require huge investment. For this reason, initially only a few countries had enrichment facilities.

After World War-II, US Gaseous Diffusion plants were supplying most of the civilian enrichment requirement of the world. Other countries which are having Gaseous Diffusion plants are France, China & USSR (now Russian Federation). Since the requirement of enrichment was estimated to increase with the increase in demand for nuclear energy it became apparent that enrichment industry is going to be a big business and hence many other countries also started working on various enrichment processes, prominent among them being UK, Germany, Holland, Japan etc.

First three of these countries formed a joint company called Urenco to carry out development work on Gas Centrifuge Process and to establish commercial scale plants based on this process. The plants based on

gas centrifuge proved to be a commercial success and became a preferred process over Gas Diffusion because of certain advantages. Urenco is reported to have gas centrifuge plants of capacity more than 5 million SWU. United States is also reported to go for new plants based on gas centrifuge technology. Since the development work was carried out in a large number of countries, a variety of gas centrifuge models have been developed with a large variation in design and capacity. Because of commercial interest, most of the details of the modern gas centrifuges are closely guarded secret, though their principle and general mechanical features are well known and published.

Other processes which were investigated by different countries are Aerodynamic or gas nozzle process and photochemical process. These processes had matured to a semi commercial level. Brazil and South Africa had small plants operating on gas nozzle process or its variant which have since been closed. Some countries are continuing to work on photochemical process using lasers but commercial scale plants are still not reported to be operational.

India has two reactors of 160 MW each located at Tarapur (TAPS) which use enriched Uranium. It is also constructing two 1000 MW(e) each capacity VVER type reactor at Kudamkulam in collaboration with Russian Federation which will use enriched uranium.

The special issue of IANCAS Bulletin on 'Isotope Enrichment Techniques' is thus appropriately timed and contains details which the interested readers will find quite informative.

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Guest Editorial

Dr. Sisir K. Sarkar

The discovery of stable ''isotopes" began with J. J. Thomson's identification of neon-22 in 1912. More than 90 naturally occurring elements have been identified on the earth; they exist as nearly 270 stable isotopes - forms of the elements that do not decay or emit radiation and hundreds of radioactive isotopes. The various isotopes of a given element differ from one another only in the number of neutrons in their atomic nucleus (the number of protons in the nucleus differentiates the elements from one another), and even highly purified samples of an element are generally a mixture of several isotopes. Pure silver, for example, is composed of nearly equal amounts of silver-107 and silver-109. Iron is mostly iron-56 (92 percent), but it contains small amounts of three other isotopes as well, and tin is a mixture of 10 stable isotopes, the most abundant of which makes up only 33 percent of the total.

One of the toughest scientific challenges has been to effectively - and inexpensively - separate a desired isotope of an element from the remaining isotopes for uses ranging from medicine to energy to weapons applications. The main thrust is aimed at developing workable isotope separation method for nuclear industry: (i) uranium-235, the fissile isotope of uranium needed to fuel light water reactors and (ii) deuterium for heavy water moderated reactors. Enriched refers to material that consists largely or exclusively of a single isotope and is usually obtained by one of the enrichment techniques described in this issue.

No doubt the common man today knows a lot more of the atom; all the same perhaps not enough to appreciate the role of atomic age affecting their daily activities. For many, bombs and power plants are their only associations with the term. The uses and benefits of isotopes, stable and/or radioactive, in medicine, agriculture, industry, and science are now widespread. In the last three decades the use of enriched isotopes has offered substantial advantages to scientists and clinicians involved in the rapid growth of research on human body composition, energy balance, protein turnover, and fuel utilization. Today, increased awareness of the role played by the elements in human health and as etiologic factors in diseases (osteoporosis, heart disease, cancer, diabetes, kidney disease) as well as diagnostic and therapeutic adjuncts (obesity, inborn errors of metabolism, heart disease) has created an explosion in the need for isotopes. Although stable isotopes occur naturally, their utility can be greatly enhanced when they are isolated and enriched through processes such as electromagnetic separation, gaseous diffusion, centrifuge, chemical exchange, cryogenic distillation, thermal diffusion, or other advanced processes like laser isotope separation. Since in principle these processes can also be employed to enrich uranium to very high U-235 concentrations, required for the manufacture of nuclear weapons, the technical details of almost all enrichment processes are subject to strict security regulations and can only be discussed to a very limited degree of detail in this issue.

Judging from the development since the days of Manhattan project, it is quite clear that uranium enrichment is a dynamic field and even today new and interesting technology is being pursued throughout the world. Therefore, assessment of evolving technology must also be a continuing activity, not only to recognize the impact of the scientific achievements themselves, but also to keep the entire uranium enrichment endeavour

in step with a changing world-wide economic and political environment. The nuclear industry was born in a military programme and will never be allowed to forget it. Whether the rights and wrongs of possessing nuclear weapons, and there are cogent arguments on both sides, the technology and materials must by common consent be kept out of irresponsible hands.

I take this opportunity to thank Dr. V. Venugopal and Dr. G.A.Rama Rao who initially conceived the idea of bringing out this thematic issue. I am grateful to Dr. D.S. Shukla, Director Chem Engg & Technology group, for kindly agreeing to provide the 'focus' to this issue. Finally, I want to acknowledge the individual and collective contributions of the authors of this issue. They represent an admirable example of busy but unselfish professionals volunteering their limited time tending to the scientific "commons" on which we all depend. It was a special opportunity to have worked with such an outstanding group.

Separation of Stable Isotopes Using Electromagnetic Fields

Dr. K.L.Ramakumar *is currently the Head, Radioanalytical Chemistry Section, Radiochemistry & Isotope Group in Bhabha Atomic Research centre, Mumbai. He is a specialist in the fields of trace elemental analysis by Mass Spectrometry and ion chromatography, thermal analysis by differential scanning calorimetry as well as in analytical chemistry. Dr. Ramakumar has been a Peer Reviewer. for International Science Foundation (USA) Program for providing research grants to Russian Scientists. He was also on an Expert assignment to IAEA's Safeguards Analytical Laboratory (SAL) at Seibersdorf, Austria to check and establish calibration procedures for precise and accurate mass spectrometric analysis. He is a recognized Research Guide of Mumbai University. He has more than 180 publications to his credit.*

Introduction

Electromagnetic separation of isotopes of elements makes use of principle underlined in mass spectrometry. In short, whenever an ion of charge ne (n is number of charges) and mass m (amu) is accelerated in an electric potential of V (volts), it gains kinetic energy, which is given by

$$K.E. = \frac{mv^2}{2} = neV \tag{1}$$

where v is the velocity of ions. If these accelerated ions pass through a magnetic field of strength H (Tesla), in a direction normal to the application of magnetic field, then a force equivalent to Hev is experienced by the ions. The direction of this force is mutually perpendicular to the direction of the ions as well as magnetic field. This force is balanced by the centripetal force given by $\frac{mv^2}{r}$.

$$Hev = \frac{mv^2}{r} \tag{2}$$

Where r is the radius of the path described by ions under the influence of the magnetic field. Eliminating velocity (v) term from equations 1 and 2, we get the well known mass spectrometric equation

$$\frac{m}{ne} = \frac{H^2 r^2}{2V} \tag{3}$$

Thus, ions of different masses but with same kinetic energy and charge describe different radii in the applied magnetic field and can be resolved according to their mass to charge ratio. For a given constant magnetic field and kinetic energy,

$$\frac{m}{ne} \; \alpha \; r^2 \tag{4}$$

Electromagnetic separation of isotopes is therefore possible.

Historical Perspective

Electromagnetic separation of uranium isotopes was one of the three major processes considered by USA under the "Manhattan Project" during World War II period. The other two were gaseous diffusion and centrifugal separation. Of the many electromagnetic schemes suggested, three soon were recognized as being the most promising: the "calutron" (a name representing a contraction of "California University cyclotron") mass separator, the magnetron-type separator later developed into the "ionic centrifuge," and the "isotron" method of "bunching" a beam of ions. The first two of these approaches were followed at California and the third at Princeton. Calutrons are basically 180^0 deflection magnetic analysers. The isotron is an

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electromagnetic mass separator using extended source of ions, in contrast to the slit sources used in ordinary mass spectrographs. The ions from the extended source are first accelerated by a constant, high-intensity, electric field and are then further accelerated by a low-intensity electric field varying at radio frequency and in "saw tooth" manner. The effect of the constant electric field is to project a strong beam of ions down a tube with uniform kinetic energy and therefore with velocities inversely proportional to the square root of the masses of ions. The varying electric field, on the other hand, introduces small, periodic variations in ion velocity, and has the effect of causing the ions to "bunch" at a certain distance down the tube. (This same principle is used in the klystron high frequency oscillator, where the electrons are "bunched" or "velocity-modulated."). The bunches of ions of different mass travel with different velocities and therefore become separated. Separation of isotopes using Magnetron or ionic centrifuge was based on the fact that the strong centripetal acceleration in a rotating plasma typically of the order 5×10^{10} m/sec^2, can be used for separating difference species of elements and isotopes.

Isotope Separators

Electromagnetic separators are large-radius (e.g., 24 in.), 180^0 deflection mass spectrometers. Ions are normally obtained in low voltage (100-150 V) arc discharge sources. The arc current is about 3-5 A, while the ion current obtained is of the order of a few hundred mA. Ionization efficiency is usually of the order of 5%. Gaseous materials, often in the form of chlorides $SnCl_4$, $SiCl_4$) are continuously fed into the arc chamber through a controlled leak. The pressure inside the arc chamber must be kept constant to obtain a steady ion beam. Compounds which can be volatilized in the 100-600°C temperature range (chlorides, bromides of many elements) are introduced through a heated stainless steel "charge bottles". Temperatures as high as 1200°C can be obtained with graphite "charge bottles".

The pumping systems of large separators are impressive indeed. The main requirement is pumping capacity rather than ultimate vacuum. In a large instrument, total pumping capacity as high as 20,000 liters/sec is employed to maintain a vacuum of 10^{-5} torr.

The collection of the separated isotopes presents many problems. First of all, considerable cooling is necessary. When an ion beam of 100 mA, accelerated to 35 kV, impinges on a metallic receiver, the heat generated is of the order of 3.5 kW. Other problems which must be considered in the design of a collector system are erosion, sputtering, efficiency, and technique of isotope removal. Graphite and copper are the most frequently used collector materials. The collected material is often removed from graphite by simple scraping or by the burning of the entire pocket in oxygen. Dissolution in nitric acid is a frequent removal method with copper pockets. Mercury isotopes may be collected in silver pockets from which removal is easily accomplished by heating in vacuum.

Enrichment factor and production rate are two important performance parameters in electromagnetic separators. The enrichment factor is the ratio of the ratios of the isotopic concentrations in the product and the starting material, i.e., A/B in the product over A/B in the feed gas, where A is the "wanted" isotope. Enrichment factors are normally in the 30-50 range; in special applications enrichment may be as high as 1000. The production rate of the separators greatly depends on the throughput. A current of 1 mA corresponds to 6.3×10^{15} unit charges per second. A current of 100 mA will produce about 10 g of a nuclide of mass 100 in a full day's operation; about one-half of this amount may be recovered from the collector. Since the efficiency of ionization, as mentioned, is below 10%, at least 100 g of charge material is required. When the "wanted" isotope is a rare nuclide, production rate may be very poor; for example, 4OK can only be produced at a rate of 0.5 mg/day. In cases like this, other separation methods such as chemical exchange, thermal diffusion, and distillation should be used if at all possible.

Principal Considerations of Electromagnetic Separators

They are threefold: First, it is difficult to produce large quantities of gaseous ions. Second, a sharply limited ion beam is usually employed so that only a fraction of the ions produced are used. Third,

too great densities of ions in a beam can cause space-charge effects which interfere with the separating action. Electromagnetic methods developed before 1941 had very high separation factors but very low yields and efficiencies. Since that time it has been shown that the limitations are not insuperable. In fact, the first appreciable-size samples of pure U-235 were produced by an electromagnetic separator. In addition to the foregoing factors, one has to consider the ensuing factors:

(a) The Number of Stages. As in all methods, a compromise must be made between yield and separation factor. In the electromagnetic system, the separation factor is much higher than in other systems so that the number of stages required is small. There was a possibility that a single stage might be sufficient. Early studies indicated that attempts to push the separation factor so high as to make single-stage operation feasible cut the yield to an impracticably small figure.

(b) the size of a unit as determined by the radius of curvature of the ion path the length of the source slit, and the arrangement of source and receivers;

(c) the maximum intensity of magnetic field required;

(d) whether or not to use large divergence of ion beams:

(e) the number of ion sources and receivers per unit;

(f) whether the source should be at high potential or at ground potential;

(g) the number of accelerating electrodes and the maximum potentials to be applied to them;

(h) the power requirements tar arcs, accelerating voltages, pumps, etc.;

(i) pumping requirement,

(j) number of units per pole gap

Calutron Separation of Isotopes

It should be mentioned that much of the work on electromagnetic separation of isotopes was
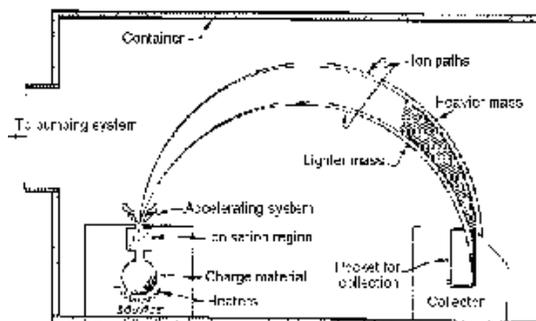
Fig. 1 Schematic of a typical Calutron for separation of isotopes of an element

carried out during Manhattan Project in USA and only in the fall of 1945 it became possible to examine the electromagnetic isotope separation equipment to see if it could be adapted to the separation of isotopes of elements other than uranium and which find wide spread applications in fundamental or applied scientific research. This program is operated now almost entirely for the isotopes produced and the scientific findings which they make possible.

Fundamentally, there is little difference between a laboratory mass spectrometer and its production counterpart, the calutron. The primary difference is that the calutron is designed to collect useable quantities of desired isotopes, while the laboratory spectrometer is used almost entirely as an instrument for detection or analysis. Of course, if one desired, very small quantities of virtually any isotope could be collected in the laboratory instrument, but the collection rates would be exceedingly small. Figure 1 shows a schematic diagram of the calutron.

The electromagnetic separation of isotopes by the calutron involves the following phases:

(a) preparation of suitable charge material for the calutron ion source,

(b) operation of the calutron in separating the isotopes,

(c) quantifative recovery from the collectors and chemical purification.of the separated isotopes,

(d) spectrochemical analysis of refined isotopes, and

(e) preparation of suitable sample and mass spectrometer analysis of enriched isotopes.

The flexibility which makes possible the electromagnetic separation of isotopes is derived primarily from the magnetic field which can be set at a predetermined value to focus ions of mass ranging from lithium to uranium at the collector. Also, ion accelerating and focusing voltages are variable.

Calutron Ion Sources

Usually these are arc discharges. Calutron ion source units should possess a certain degree of flexibility as to temperature range, accelerating electrode arrangement, arc number and size, and cooling system. In processing a variety of elements and compounds having widely varying vapour pressures, it is desirable to have source units operable over temperature ranges required for realizing sufficient vapour pressures. Earlier investigations carried with uranium indicated that the temperature range of uranium-type ion source units could be extended sufficiently to cover approximately half of the elements having more than one nuclide if the charge compound of the element under consideration is carefully chosen.

Charge Materials

For charge materials occurring as liquids or gases at room temperature, sample introduction systems external to the ion source can be employed. The flow of feed material to the arc region should be controllable with the help of a sensitive needle valve. In the case of Solid materials, usually they are introduced in a contained inside the ion source and are heated. Usually it is desirable to have a small flow of gas such as nitrogen into the arc is beneficial, and with some elements necessary, for stabilizing the arc and promoting production. The problem of producing ions of all isotopes for calutron operation is not completely solved; however, methods and equipment now in use are adequate to produce ions, with varying degrees of efficiency, from virtually any element in the periodic chart.

Magnetic Analysers

A special class of shaped magnetic lenses, used successfully in beta-ray spectroscopy have found
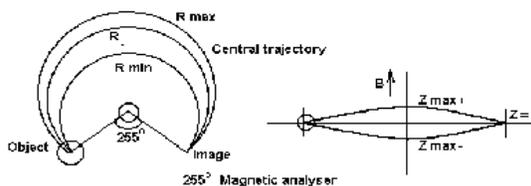
Fig. 2   Schematic of a 255^0 magnetic analyser with radial and azimuthal focusing

wide spread applications in isotope separations. The fundamental concept of this focusing system relates to the use of magnetic field that decreases in intensity with increasing

radius. The approximate magnetic field intensity distribution across the mid plane in these "inhomogeneous systems" is given by the relationship

$$\beta_r = \beta_0 \left[\frac{r_0}{r} \right]^n \qquad (5)$$

where β_r is the mid plane magnetic field as a function of radius, r_0 is the radius of the centra orbit, β_0 is the mid plane magnetic field strength at r_0 and n is the inhomogeneous filed index. Siegbahn and Svartholm have shown that under these conditions, both radial (φ_r) and azimuthal (φ_z) focusing occurs when $\varphi_r = \varphi_z = \sqrt{2}\,\pi = 255^0$ and at this focusing angle and for n = 0.5, spherical aberration is minimized. The focusing properties of the 255^0 system is shown in Fig. 2.

Both the radial and azimuthal or axial trajectories converge to the same image point. As a result, the transmission of a 255^0 analyser can approach 100% for reasonable ion source limits relating to angular divergence and ion energy spread. In addition, increase in mass or energy dispersive power is realized. The increased dispersion is extremely valuable for it permits the use of a magnet smaller than a homogeneous type. For a magnet having a basic radius of curvature r_0, with the object and image symmetrically located, the dispersion D is given by

$$D = \frac{r_0 \Delta m}{m_0 (1-n)} \qquad (6)$$

where n is the index of inhomogeneity of the magnetic field. For a 0.5 index the dispersion is doubled. Such an isotope analyser has been constructed. It had a transmission approaching 100% for several types of ion sources. The mean radius of curvature of this 75 ton electromagnet is 6 cm, the pole-piece gap width at this radius is 10 cm, and the mass dispersion at mass 100 is about 1.5 cm.

Isotope Collectors

For each element processed, an isotope collector must be designed, providing properly spaced receptacles for whatever isotopes may be present. Isotope collector structural materials, structural design, and cooling, all require considerable attention and have to be chosen depending on the system being studied. Since one mass unit separation at the collector decreases as the mass of the ions increase, each element requires especially designed collectors. In addition to this consideration, which is essentially a problem in pocket placement, suitable pocket materials and cooling techniques must be chosen in order to retain the deposited material. The temperature of receiving surfaces, which must necessarily be bombarded With ions, must be kept sufficiently low that deposited material Will be retained and not lost to cooler surfaces such as walls of the vacuum chamber through the vacuum system. The problem of building a collector for any element then consists of calculating proper pocket spacing for the desired isotopes, and from vapor pressure considerations, determining suitable pocket material and cooling techniques.

Usually the design of a collector is dictated by the desire for having maximum flexibility so that collectors could be constructed for any element from a minimum number of parts. The all-purpose type collector, in which pockets up to 10 can be assembled at predetermined spacings has been fabricated for this purpose. This basic structure permits the placing of collectors to receive the isotopes of any element in the periodic chart; pockets may be replaced easily if desired, and cooling may be employed as required.

Collector Materials

These vary with the element being processed, and the receiver parts may or may not be water-cooled, depending on the energy to be dissipated and the vapor pressure of the collected material. Furthermore, with some elements, special retention techniques are required. For example:

Sulfur is allowed to combine chemically with copper shavings packed in the collector pocket.

Mercury is retained by allowing it to amalgamate with silver collector pockets, and by cooling the pockets with a circulating refrigerant. In the processing of mercury, the problem of high vapor pressure in the calutron and the contamination of collected isotopes by the condensation of neutral mercury vapor in the collector pockets, needs to be eliminated by refrigerating the, vacuum chamber.

Charge Materials for Production of Ions

The availability or synthesis of suitable calutron charge materials is essential. Several requirements must be met, such as suitable vapor pressure, at calutron operating temperatures, simplicity of molecular structure, stability of the compound and absence of water of crystallization. If the element itself has a suitable vapor pressure, it is generally used as charge material since its use greatly reduces" extraneous ions or sidebands. For the same reason, simple compounds generally are preferred over the more complex compounds; thus, halides are used widely. Anhydrous compounds are necessary because the water of crystallization gives rise to increased vacuum chamber base pressure and prolonged start-up time.

The ultimate choice of the compound best suited for use in the electromagnetic separation of the isotopes of an element in the calutron is often made only after the systematic testing of a number of compounds. The criterion of suitability of such compounds is whether or not they give rise to a satisfactory rate of production of the separated isotopes of the given element. While a number of properties of the compounds are considered, chief consideration is usually the vapor pressure-temperature relationship, since such compounds must be sublimed into the arc chamber where positive ions are formed. Usually laboratory

studies involving mass spectrometer are a more satisfactory method for the evaluation of compounds. The compound under consideration is introduced into a mass spectrometer, and the ion current due to each of the fragments or species formed is plotted as a function of the mass of the fragment. This gives the relative abundance of the ions formed due to dissociation and ionization by the slow electrons used. The appearance potential is also determined for the singly charged metal ion involved, It then follows that if the number of singly charged metal ions formed is a fair proportion of all of the positive ions thus produced from a compound, and if the appearance potential of the metal ions is not greatly in excess of the ionization potential of the metal, then the rate of positive ion production, and therefore the rate of production of the isotopes of the element in question, will be high.

A wealth of basic inorganic chemistry has resulted from these charge material developments. Suitable charge materials of some 43 elements have been supplied for calutron separations of isotopes, including the synthesis of many unusual compounds and, the development of methods of purification to meet special requirements.

Calutron Operational Procedures

After suitable ion sources, collectors, and charge materials are identified and assembled, the components are placed in an evacuated volume between the poles of an electromagnet. Metered ion currents at the collector are necessary to properly monitor the isotope beams and afford a means for estimating total isotope collection. Thus, for a singly charged ion, 1 amp.-hr, at the collector represents approximately 0.04 gm.-atom of the monitored isotope. The length of time allowed for a collection is determined from the metered production rates on the desired isotopes, with some allowance for collector rejection and chemical losses.

Chemical Purification of Separated Isotopes

From the collector pockets, the isotope contents are removed by one of several methods depending on the element and pocket material. Extreme care is exercised during this phase to prevent isotope contamination and to assure quantitative removal of the product isotope.

Chemical purification procedures vary widely, depending upon the element being processed. Reactions must be complete, filtrations or eentrifugations must be carefully performed, and care must be exercised to minimize losses caused by discarding reaction side products.

It may be mentioned that by the beginning of 195I, adequate purification techniques had been worked out in USA for every element which had been processed in the calutron. These included radioactive materials such as beryllium-10 and potassium-40, rare earths such as cerium, neodymium, and samarium, and toxic materials such as selenium and mercury. Procedures for separation of elements with similar chemical properties have also been worked out. For example, a method for the production of pure zirconium and hafnium fluorides was developed. It was found that indium may be separated from gallium by the use of mandelic acid. It was also found that mandelic acid precipitates some of the rare earths and is useful in their separation. The physical and chemical properties of the mandelates of zirconium and hafnium were thoroughly investigated. Also, it was found that the homogeneous precipitation of the rare earths by hydrolysis of methyl oxalate is a selective process.

Chemical and Mass Analysis of Separated Isotopes

Upon completion of chemical purification, product isotopes are subjected to chemical and mass analyses. Methods for handling small samples of precious isotope materials are being continuously improved. In mass spectrometry, experience and development have made it possible to mass analyze isotope collections from all elements thus far processed in the calutron. More than 700 samples of isotopes of elements were prepared as compounds suitable for mass analysis.

The interest in using certain stable isotopes as tracers has stimulated the development of microwave methods for isotopic analyses. The resolution of the microwave spectrometer is so great that theoretically there is room for more than 50 million rotational lines in the present experimental region. Although considerable progress, has been made, isotopic analysis by microwave techniques do not yet meet the high precision of a mass spectrometer.

Isotopes Enriched Electromagnetically

By December 31, 1950, a total of 43 elements from lithium to lead comprising 177 isotopes had been separated in the calutron in milligram to multigram quantities. Now a days enriched isotopes of almost all elements are available from USA and Russia.

Diffusion Separation Processes for Uranium Enrichment
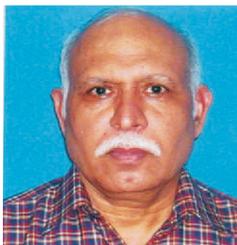
Shri D.S. Shukla completed his B.E. in Chemical Engineering in 1969 from University of Roorkee (now IIT, Roorkee). He had a brilliant academic career and is recipient of university Gold Medal. He joined Bhabha Atomic Research Centre (BARC) in 1970 after one year postgraduate training in BARC Training School. His field of interest includes separation processes for light and heavy isotopes and solvent extraction for metal purification. He has more than thirty five years of experience in this field. Production facilities have been installed based on the processes developed by him and his group. He has worked in various capacities after joining Bhabha Atomic Research Centre including Project Manager, RMP, Mysore. He is presently the Director, Chemical Engineering & Technology Group of BARC, Member, Heavy Water Board and Member of number of other Committees.

Intoduction

Diffusion generally means the mixing caused by random motion of molecules. This is more pronounced in gases and liquids than in solids. These phenomena cause the mass transfer and hence can be used in separation processes. The term diffusion processes normally refer to the separation processes in which mass is transferred from one phase to other phase in which diffusion is considered to be rate controlling mechanism. Distillation, gas absorption, solvent extraction etc. are conventional separation processes, which are termed as diffusion separation processes.

Since the advent of nuclear energy a number of special processes have been developed for difficult separations such as separation of isotopes. These include diffusion separation processes, where separation takes place because of different rates of diffusion, as well as many other processes viz. photochemical, electrolysis, electromagnetic etc. Some of the diffusion separation processes are gas diffusion, thermal diffusion, gas centrifugation, and aerodynamic processes. The most important industrial application of the diffusion separation processes has been for increasing the Uranium-235 isotope concentration in uranium above that occurring in nature also known as uranium enrichment. This article describes the basic principle and application of the three most important processes namely gas diffusion, gas centrifuge and nozzle separation as applied to uranium enrichment. Since uranium enrichment is basically the separation of uranium isotopes, a small note on the isotopes and general methods of their separation is also included.

Isotopes and their Application

Isotopes were discovered in early 1900's. Elements with same atomic number but with different atomic weights are called isotopes. As the name implies ('Iso' meaning 'Same' and 'topos' meaning 'place' in Greek), all isotopes of an element have the same position in the periodic table. Since the isotopes of a given element have the same number of protons (& electrons), their physical & chemical properties are very similar, whereas their nuclear properties are different because number of neutrons in their nuclei is different. An element can have as many as ten naturally occurring isotopes (e.g. Sn-50 has isotopes from mass no.112 to 124) to as low as zero (e.g. fluorine has no stable isotope). The elements that do not have any stable isotopes are called anisotopic elements. Isotopes can also be made artificially in nuclear reactors or accelerators (e.g plutonium). All the artificially or man made isotopes are radioactive.

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Some Useful Isotopes

The large number of isotopes both stable and radioactive are used in nuclear and other industries. Some of them are:

Element	Isotopes (Natural Abundance)	Uses of Isotopes in Nuclear industry
Uranium*	U-235 (0.72%)	Fissile fuel for nuclear reactors (enrichment may be required depending on the type of reactor)
	U-238 (99.28%)	For production of plutonium
Plutonium	Pu-239	Fuel for nuclear reactors
Hydrogen	H-1 (99.9844%)	As a moderator and coolant in light water moderated nuclear reactors.
	H-2 (0.0156%)	As a moderator and coolant in Heavy Water Reactors#
	H-3 (tritium)**	Fusion reactor
Boron	B-10 (18.98%)	For reactor control
Lithium	Li-6 (7.52%)	As a shielding material and for tritium production [Li-6 + n → He-4 + T-3]
	Li-7 (92.48%)	As a moderator or coolant in nuclear reactors

**Uranium isotopes are unstable, but their half-lives are large with respect to our time scales and small with respect to geological time scale. For all practical purposes uranium isotopes can be treated as stable.
*this isotope is a man-made isotope;
requires up-gradation to reactor grade

There are 92 naturally occurring elements. Of these, 82 elements (up to lead-82) have stable isotopes. Among them, these 82 elements have about 275 isotopes. Elements beyond atomic number 82 do not have stable isotopes. No stable isotope has mass number greater than 208.

Some of the isotopes those are used outside nuclear industry are:

- He-3 (1.3E-04%) → for production of ultra-low temperatures

- C-13 (1.11%), O-17, O-18 → used as tracer

- C-14 → used in carbon dating

- Ne-20 (90.92%), Ne-22 (8.82%) → for He-Ne laser

Variety of radioactive isotopes is used in radiopharmaceuticals both for diagnostic as well as therapeutic purposes. Radioactive isotopes are also used for irradiation of food for preservation.

Methods of Isotope Separation

Almost all the methods used for separation in conventional industries can be used for separation of isotopes also with varying degree of success. The methods can be broadly classified into physical & chemical methods.

(a) Physical methods are those in which difference in physical properties e.g. inertia, density,– electrical properties etc. is harnessed. Some of the methods in this category are:

- Gaseous Diffusion
- Centrifugation
- Aerodynamic separation
- Thermal Diffusion
- Electrolysis
- Electromagnetic separation
- Laser isotope separation

(b) Chemical methods are those in which difference in chemical properties e.g. chemical

potential is harnessed. Some of the methods in this category are:

- Distillation
- Chemical exchange·
- Exchange distillation·
- Ion exchange·
- Liquid-liquid extraction

Chemical methods are more suitable for light isotopes and are extensively used for separation of hydrogen isotopes e.g. production of heavy water. Physical methods are in general more suitable for separation of heavy isotopes e.g. uranium enrichment. The remaining part of this article will be dealing only with first three of physical process as applied to uranium enrichment.

Gaseous Diffusion

The Principles of Separation by Gas Diffusion

The principle of this method is based on the phenomenon of molecular diffusion. In a closed cell in thermal equilibrium with its surroundings, all molecules of a gas mixture have the same mean kinetic energy. Hence lighter isotopic molecules travel faster and strike the cell walls more frequently than do heavier ones. A hole in the wall or barrier, if it is small enough i.e. of the order of mean free path of the gas, will prevent the outflow of the gas as a whole (viscous flow). This will however allow the passage of a larger proportion of light molecules, which strike the wall more frequently, in relation to their concentration, than of the heavy ones. Thus if a gas consisting of two isotopes starts to diffuse through a barrier into an evacuated vessels, the lighter isotope (of molecular weight M1) diffuses more rapidly than the heavier (of molecular weight

M2). The result, for a short period of time, at least, is that the relative concentration of the lighter isotope is greater on the low pressure side of the barrier than on the other side. But if the process is allowed to continue indefinitely, equilibrium will become established and the concentrations will become identical on both sides of the barrier. Even if the diffused gas (the gas which has passed through the barrier) is drawn away by a pump, the relative amount of the heavy isotope passing through the barrier will increase since the light isotope on the near side of the barrier has been depleted by the earlier part of the diffusion. For this reason it is important that the gas on both sides of the barrier is replaced at fast enough rate without allowing it to achieve equilibrium. For a single diffusion operation, the increase in the relative concentration of the light isotope in the diffused gas compared to the feed gas can be expressed in terms of the separation factor, 'α', or the enrichment factor, α-1. This separation factor represents the relative ease of escape of light molecule over heavy molecules through barrier.

The most outstanding application of GD process is the large capacity plants built for separation of uranium isotopes by United States of America Manhattan Project. Subsequently diffusion plants were also built at Copenhurst, England and Pierrelatte, France and also in other countries. These plants exclusively met the uranium enrichment requirements, for both civilian as well as strategic, for a long time.

Process Description

The basic unit of the system is gaseous diffusion stage. The main components are converter for holding the barrier (Fig. 1), compressor or pump
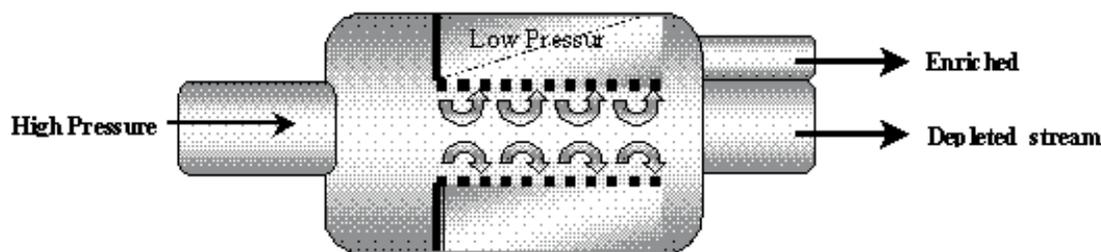
Fig. 1   Converter

which move the gas from stage to stage and a heat exchanger which removes the heat of compression. The other components are connecting piping, instruments and controls to maintain desired pressure and temperature.

For Uranium isotope separation, feed gas is Uranium Hexafluoride (UF_6), also called 'Hex'. In the diffusion chamber the gas flows along the barrier. About half of the feed gas is permitted to diffuse through the barrier in the low-pressure zone which is enriched in the light molecular weight component i.e. $U^{235}F_6$. The enriched gas is fed to the stage above after recompression and cooling. The portion of the gas which does not diffuse through the barrier is depleted in the light component. This fraction, after leaving the chamber is fed to the stage below after recompression and cooling along with the enriched stream from the stage below.

The fact that the two streams to be compressed to the same pressure are at different pressure levels, provide ample scope for innovative design for optimum performance. The two streams can either be compressed by same compressor or two different compressors can be used. Some other mode of operation can also be made possible. A number of such options have been tried to arrive at optimum configuration. A large number of such stages connected together are called 'cascade'. The Fig. 2 illustrates the way the 'stages' can be connected to form a cascade.

If the stages are connected such that no mixing of the two streams of different isotopic concentration take place the cascade is called ideal cascade. The cascade is designed for a given duty i.e. product and waste concentration and quantity of the product desired.

The Process Gas

Uranium hexafluoride, also known as "hex", has been mentioned as a gas that might be suitable for use in the plant as "process gas"; not the least of its advantages is that fluorine has only one isotope so that the UF_6 molecules of any given uranium isotope will have the same mass. This gas is highly reactive and is actually a solid at room temperature and atmospheric pressure. For this reason the cascade has to operate at relatively higher temperature and
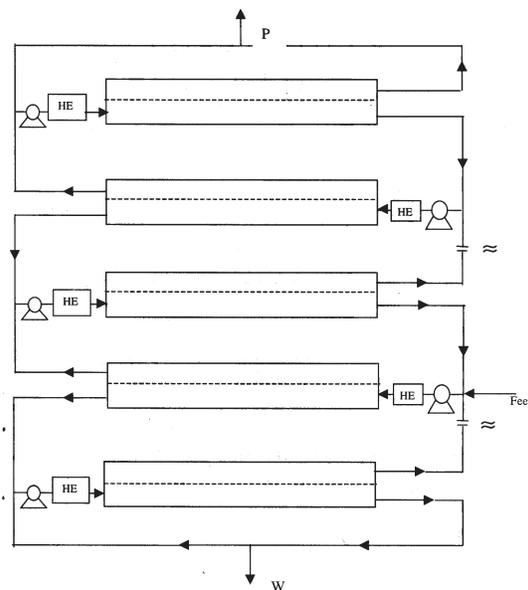
Fig.2

HE – Heat Exchanger

  - Compressor

Fig. 2

low pressure to keep the UF_6 in gaseous state. This necessitates large volume of the gas to be handled for a given production rate which increases the cost of equipments, piping etc. Numbers of other uranium compounds were therefore studied to find an alternative of UF_6. Out of all the compounds studied UF_6 is still the best compound for use in uranium enrichment.

Stage Separation Factor

The separation in a stage is due to differential rate of diffusion through the barrier. An ideal separation barrier is the one which permits flow by diffusion only. This will happen only when the diameter of pores in the barrier is sufficiently small compared to mean free path of the gas molecules. The rate of flow of the gas through the barrier is governed by Knudsen's law:

$$F = \frac{4}{3}\sqrt{\frac{1}{2\pi MRT}}\,\frac{\Phi d}{l}\,(pf - pb)$$

where F is molar flow of gas per unit area, M, molecular weight, R gas constant, Φ fraction of barrier area open to flow, d effective diameter of the pores, l length of the pore or thickness of the membrane and pf & pb are the high and low side of pressure.

Not all the flow through the barrier is molecular and some non separative viscous flow also occurs. This is through those pores whose diameters are of the order of mean free path or higher. The two flows are additive and can be given as

$$F = \frac{a}{\sqrt{M}}(pf - pb) + \frac{b}{\mu}(pf^2 - pb^2)$$

where a & b are functions of temperature for a particular barrier to be evaluated experimentally and μ is the viscosity of gas.

An Ideal point separation factor is defined for a separation when a binary mixture flows through an ideal barrier into a region of zero back pressure. For this case the form of equation for flow given above can be written for each component. The flow of light component is proportional to $pfy/\sqrt{M_1}$ and flow of the heavy component is proportional to $pf(1-y)/\sqrt{M_2}$ where y is the mole fraction of the light component on the high pressure side of the barrier and M_1 & M_2 are molecular weight of light and heavy components respectively.

The concentration of diffusing gas, y', is therefore,

$$y' = \frac{y/\sqrt{M_1}}{y/\sqrt{M_1} + (1-y)/\sqrt{M_2}}$$

and from definition of separation factor, the ideal separation factor 'α*', is

$$\alpha* = \frac{y'/(1-y')}{y/(1-y)} = \sqrt{\frac{M_2}{M_1}}$$

which for uranium isotope separation with UF_6 is 1.00429. It can also be shown to be equal to the ratio of the velocity of light molecules to heavy molecules.

Actual separation factor of a stage, 'α', is appreciably different from ideal separation factor, 'α*' because of the following efficiency factors.

1. Barrier efficiency factor (Eb) : In practice the barriers do not behave ideally i.e. not all flow is Knudsen's flow. In addition at finite pressure the Knudsen's flow is not separative to the extent $\sqrt{M_2/M_1}$. Instead it is less by an amount that depends upon pressure of operation and characteristics of the barrier.

2. Back pressure efficiency (Ep) : Since the diffusion stage operates with low side pressure, pb, which is not negligible compared to high side pressure, pf, some of the light components preferentially diffuse back through the barrier. This factor is approximately equal to 1-(pb/pf).

3. Mixing Efficiency (Em) : The gas flowing on the high pressure side of the barrier gets depleted in the region adjacent to the barrier, as the light component diffuse through it. As a result a concentration gradient is set up perpendicular to the place of barrier as high pressure side. This reduces the concentration of the light component close to the barrier compared to the average concentration. A value can be calculated from a consideration of diffusion through an effective film representing the resistance to diffusion.

4. Cut correction factor (Ec) : The stage separation factor is defined in terms of concentration leaving the stage. Since the concentration on either side is changing continuously, the relationship between the concentrations of streams differs from the point relationship. The exit concentration of stage upflow is average concentration of the diffused gas whereas the exit concentration of the stage downflow is equal to the terminal concentration of the undiffused gas which is at maximum and not average depletion. Consequently stage separation factor relating to exit concentration is higher than point separation factor and hence cut efficiency factor exceeds unity.

The stage separation factor can therefore be related to ideal point separation factor by (α-1) = Eb.Ep.E_M.Ec(α*-1). The net effect of these
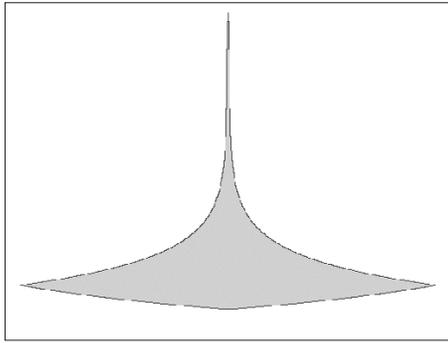
Fig. 3   Flow rates as a function of stage number

efficiencies is to reduce the actual stage separation factor below that of ideal point separation factor by an amount which is to be determined experimentally.

The Cascade

The separation cascade can be designed using the standard principle of cascade design for a given duty i.e. concentration of and quantity of product and feed and quantity of product desired, once the performance characteristics of the individual stages are known. The important parameter is the stage separation factor and flow rate through the barrier both of which largely depend upon the characteristics of the barrier. If the stages are assumed to be connected in an ideal cascade and it is assumed that separation factor is small, which is actually the case for uranium isotopes, the number of stages required, $N_{ideal,}$ can be calculated by

$$N_{ideal} = \frac{2}{\ln \alpha} \ln \left(\frac{\dfrac{y_p}{1-y_p}}{\dfrac{y_w}{1-y_w}} \right) - 1$$

The stage upflow, L_{ideal}, which is twice the minimum upflow, at any point in the enriching section of the cascade is given by

$$L_{ideal} = \frac{2P(y_p - y)}{(\alpha - 1)y(1-y)} = 2L_{min}$$

Where, α = Stage separation factor, y_p = Concentration of light isotopes in the product, y_w = Concentration of light isotopes in the waste, P =

Product rate and y = Concentration of light isotopes at a stage n.

The flow rates as the function of stage number is schematically shown in Fig. 3.

In an ideal cascade, the pumping requirements change from stage to stage. In practice it is not economical to provide a different size of pumps, valves etc for every stage. Therefore the actual cascades are not ideal cascade but are what is called squared-off cascade. In squared-off cascade the flow rate is not varied at all the stages but after a large number. The group of number of stages where flow rate is same is called a square cascade. In squared-off cascade total cascade flow and hence energy consumption etc. -is more than the ideal cascade but the capital cost is low because of smaller number of sizes of equipments required and also lower inventories of spares. The departure from ideal cascade is determined based on overall economic considerations to get minimum cost of production.

In actual practice the number of stages and flow rates required are considerably different than that given by the above equations. If it is desired to produce 99 per cent pure $U^{235}F_6$, and if one uses a cascade in which each stage has a separation factor reasonably close to maximum possible then it can be shown that the cascade will have roughly 4,000 stages, a very large number by all standard. There is also to be a "stripping" cascade of several hundred stages, the exact number depending on how much unseparated U-235 could economically be allowed to go to waste. Calculations also show that for an actual uranium-separation plant the flow through the barriers of the first stage will roughly be as much as 100,000 times the volume of gas that comes out the top of the cascade (i.e. as desired product $U^{235}F_6$). The corresponding figures for higher stages fall rapidly because of reduction in amount of unwanted material ($U^{238}F_6$) that is carried along. Typically, to enrich natural uranium into product having 3% (which is generally required in Pressurised Light Water Reactors (PWR) & waste having 0.2% of U-235 concentration, it would require about 1300 stages of Gaseous Diffusion. Very large (compared to product) flow rates and large number of stages required make gaseous diffusion process a complex and costly process.

When first started, the plant must be allowed to run undisturbed for some time, also called equilibrium time, until enough separation has been affected so that each stage contains gas of appropriate enrichment. Only after such stabilization is attained it is desirable to draw off from the top stage any of the desired products. Both the amount of material involved (the hold-up) and the equilibrium time required are great enough to constitute major problems in their own right.

Barrier Design

We have seen that the total volume of gas that must diffuse through the barriers is very large compared to the volume of the final product. The rate at which the gas diffuses through unit area of barrier depends on the pressure difference on the two sides of the barrier and on the porosity of the barrier. Even assuming full atmospheric pressure on one side and zero pressure on the other side, and using an optimistic figure for the porosity, calculations showed that many hectares of barrier would be needed in a large-scale plant.

The principle of this method is based on the phenomenon of molecular diffusion. In gaseous diffusion cell, the diffusion barrier that separates the isotopes is a critical element. The pore size of the barrier through which the molecules effuse is extremely important. The diffusion barriers have to be compatible with UF_6 which is a quite corrosive medium. While the barrier should be thin enough to provide less resistance to flow, it should be mechanically strong enough to withstand a pressure differential of about one atmosphere. For separation of isotopes to take place, the pore size should be such that a molecular flow regime is attained. In molecular flow no collisions take place between molecules, and the molecules move independent of each other. Under such condition, molecular effusion depends on molecular weight of the gas, which is responsible for the separation of isotopes, while viscous flow is not. The flow in a conduit (pores) depends on the mean free path of molecules, λ, which is an inverse function of pressure. Typically for UF6 molecules, the variation of mean free path with pressure is as shown in Table 1.

TABLE 1.

Pressure (mbar)	Mean Free Path
1 mbar	20 µm
100 mbar	0.20 µm or 2000 Å
1000 mbar	200 Å

If mean free path is lower than the pore size then the flow is viscous flow, which is governed by viscosity of the gas. While if mean free path is longer than the pore size then the flow is Molecular flow, which is governed by molecular weight. Thus, at a feed pressure of about 1 bar, a barrier of 200 Å pore size would give molecular flow through the pores.

To ensure "diffusive" flow of the gas, the diameter of the myriad holes in the barrier must be less than the mean free path. Therefore the barrier material must have almost no holes which are appreciably larger than 0.01 micron but must have billions of holes of this size or smaller. These holes must not enlarge or plug up as a result of direct corrosion or dust coming from corrosion elsewhere in the system. The barrier must be able to withstand a differential pressure of close to one atmosphere. It must be amenable to manufacture in large quantities and with proper quality control. A number of different barriers are made on a small scale and tested for separation factor and porosity before one is used in actual plant. The barriers made of sintered nickel powder have been found to be most suitable. All countries those have developed it have kept diffusion barrier technology a secret.

Compressors and other Circulating Systems

In any given stage approximately half of the material entering the stage passes through the barrier and on to the next higher stage, while the other half passes back to the next lower stage. The diffused half is at low pressure and must be pumped to high pressure before feeding into the next stage. Even the undiffused portion emerges at somewhat lower pressure than it entered at and cannot be fed back to the lower stage without pumping. Thus the total quantity of gas per stage (comprising twice the amount which flows through the barrier) has to be circulated by means of compressors or pumps.

Since the flow of gas through a stage varies greatly with the position of the stage in the cascade, the pumps also vary greatly in size or number from stage to stage. The type and capacity of the pump required for a given stage depends not only on the weight of gas to be moved but on the pressure rise required. The discharge pressure of the pumps is close to one atmosphere and a back pressure (i.e., on the low pressure side of the barrier) of one tenth of an atmosphere. It can be estimated that thousands of pumps would be needed and that thousands of kilowatts would be required for their operation. Since an unavoidable fallout of pumping gas is heating a large cooling system need to be provided. A good deal of work had been done on developments of suitable pumps. It must be remembered that these pumps are to be operated under reduced pressure, must not leak, must not corrode, and must have as small a volume as possible. Centrifugal pumps appear attractive in spite of the problem of sealing their shafts. Many other types of systems have also been tried.

The whole circulating system comprising pumps, barriers, piping, and valves would have to be vacuum tight. If any lubricant or sealing medium is needed in the pumps, it should not react with the process gas. In fact none of the materials in the system should react with the process gas since such corrosion would lead not only to plugging of the barriers and various mechanical failures but also to absorption (i.e., virtual disappearance) of uranium which had already been partially enriched.

Summary

Since the amount of separation that could be affected by a single stage is very small, several thousand successive stages were required. It was found that the best method of connecting the many stages, required extensive recycling so that thousands of times as much material would pass through the barriers of the lower stages as would ultimately appear as product from the highest stage.

The principal problems were the development of satisfactory barriers and pumps. Acres of barrier and thousands of pumps were required. The diffusion barrier that separates the isotopes is a critical element. The pore size of the barrier through which the molecules effuse is extremely important

and quite difficult to obtain. Development of suitable diffusion barriers that can resist UF_6 corrosion is a very difficult task. The barriers made of sintered nickel powder have been found to be most suitable. It is reported that improvements in barrier technology has allowed performance enhancement by a factor of more than 20. All countries that have developed barrier technology have kept it classified. The obvious process gas was uranium hexa-fluoride for which the production and handling difficulties were so great that a search for an alternative was undertaken. However UF_6 as process gas, is still the best option available for uranium enrichment. Since much of the separation was to be carried out at low pressure, problems of vacuum technique arose, and on a previously unheard-of scale. Many problems of instrumentation and control are also to be solved.

Although basic plant construction is within the capabilities of standard chemical engineering technology today, developing barriers is a problem that must be overcome. Diffusion plants consume much less energy than electromagnetic plants, but the consumption is still quite large. Capital costs still dominate the cost of operation. A commercial gaseous diffusion plant typically takes 1-2 months to reach equilibrium after start-up (a plant producing highly enriched uranium would take longer, due to the greater number of successive stages).

In 1979 more than 98% of the global uranium enrichment requirement was met through this process. Recently this figure has dropped to about 50% as the highly energy intensive gas diffusion technology is slowly giving way to the more energy efficient advanced gas centrifuge technology.

Gas Centrifuge

Introduction

The history of centrifuges started more than hundred years back and these have been- in use for separation of insoluble or immiscible component from a liquid medium for a long time. The principle of separation in centrifugal field is same as the separation under gravitational field. The centrifugal field however can be varied over a vast range, from a few times to hundreds of thousand times of gravity depending upon the requirement and hence can be more efficient. The centrifuges consist of a spinning

rotor, a drive mechanism and arrangement for feed and withdrawal of separated phases. Gas centrifuges are similar to these centrifuges except that the rotors are much larger and speed of rotation is much higher producing very high centrifugal ffield capable of separating at molecular level.

Early development work on gas centrifuges were carried out prior to and during Second World War for separation of isotopes of uranium and other elements. The first attempt to use the gas centrifuge for achieving significant separation of isotopes was made in the United States during the Second World War with the purpose of producing highly enriched uranium for the atomic weapons program. Although the centrifuge was built & operated successfully, the centrifuge technology was not, at that time, up to the mark and the centrifuge method was abandoned in 1943 in favour of the gaseous diffusion process. Professor J. W. Beams and his team in United States of America, Professor W. E. Groth et al in Germany and Prof. G. Zippe in USSR did pioneering work in the early years in the development of machine and also the theory of separation. Later the major development work was carried out by Urenco, a company jointly owned by Holland, Germany and U.K. Urenco developments began, after its formation, in the early 1970s. Starting point of Urenco developments was based on the work already carried out in the three participating countries. They pursued the concept of a lightweight rotor operating on pin bearings at the bottom and magnetic bearings at the top. The development potential was based upon the possibility of combining improvements in speed, arising from the use of materials with higher specific strength; length, from improved understanding of supercritical rotors and separation efficiency. These countries subsequently established commercial uranium enrichment plants based on gas centrifuges and are providing enrichment services at competitive rates. Urenco have had a continuous development program for more than 30 years and now have a lead cascade of the latest generation of machines in operation (their sixth generation). Many other countries are also developing gas centrifuge technology for Uranium Enrichment.

After many years of research into the alternative possible methods for enriching uranium,

it now appears that each of the major players has reached a common conclusion, that high speed gas centrifuges hold the key to the future (advantages of gas centrifuges and comparison with other processes are given in Appendix B). Alongside the recent announcements that the atomic laser enrichment programs are being brought to a halt, there have been new proposals to revive the development of the gas centrifuge technology. The details of the latter developments are closely guarded secret for national and commercial reasons and no details of these centrifuges have been released. However, the principle of gas centrifuges and their main design features are well known and are discussed in this article.

The centrifuges have been designed to operate either in co-current or countercurrent mode. All discussions in this report are for counter current centrifuges which are at present accepted mode of operation universally.

Principle of Separation

One of the main merits of centrifuge process is that it is a process in which the separation factor depends on the difference of the molecular weights (ΔM) of the two isotopes rather than on the fraction $\Delta M/M$ or $\Delta M/M^2$ like in some other methods .This makes this process especially attractive for heavy molecules because $\Delta M/M$ will go on reducing with increase in M for a fixed ΔM. The principle is based on the difference in centrifugal force acting on two isotopic masses that rotate at considerably high angular speeds. The recent technological advancement, particularly in material development, has led to the development of centrifuges of very high separative power that consumes nominal energy per unit separative work. Centrifugal force (F) acting on a particle is proportional to its mass and is given as

$$F = m\omega^2 r.$$

where, m= mass of particle, r = radial location of the particle and ω = angular velocity of rotation.

The pressure gradient established by this force is given by

$$\frac{dp}{dr} = \rho\omega^2 r$$

which for an ideal gas can be written as

$$\frac{dp}{dr} = \frac{Mp}{RT}\omega^2 r$$

Where p is the pressure at any point r, ρ is the density, R is universal gas constant, T is absolute temperature and M is molecular weight of gas.

When a gas (say UF6) containing isotopic molecules of U-235 & U-238, is made to rotate in a rotor at a very high angular speed, then the isotopic molecules will experience different centrifugal forces depending on their masses or molecular weights. For such cases the above pressure gradient equations can be written in integrated form for each gas molecules with molecular weight M_1 and M_2 as

$$p_1(r) = p_1(0)e^{\left(M_1\omega^2 r^2/2RT\right)}$$

and

$$p_2(r) = p_2(0)e^{\left(M_2\omega^2 r^2/2RT\right)}$$

The ratio of these two pressures gives the radial separation at any point, r, in the gas centrifuge under equilibrium condition (i.e. when no gas is fed or withdrawn). The radial equilibrium separation factor ($\alpha_{(radial)}$) between gas at the periphery and the gas at the axis of a centrifuge can therefore be given by

$$\alpha_{(radial)} = \exp\left[\frac{(M_1 - M_2)\times\omega^2 r^2}{2RT}\right]$$

Since $V = \omega r$, this equation can also be written as :

$$\alpha_{(radial)} = \exp\left[\frac{(M_1 - M_2)\times V^2}{2RT}\right]$$

Where, M_1 & M_2 are the molecular weights of the two isotopes, ($M_1 = 352$ for 238-UF6 & $M_2 = 349$ for 235-UF6), V is the peripheral speed of the rotor, R is Universal gas constant, T is the absolute Temperature of the gas inside the rotor.

The radial equilibrium separation factor or elementary separation effect obtained above may be multiplied manifold by inducing counter-current inside the centrifuge. An axial counter-current imposed on the radial separation enhances the axial separation, leaving the enriched gas at one end & the depleted gas at the other end of the rotor. The maximum axial separation factor, which is achieved under total reflux, α_z, that includes the effect of counter-current is much higher than the elementary radial separation factor and can be given by

$$\alpha_z = \exp\left[\sqrt{\frac{E}{2}}\times\frac{\Delta MV^2}{2RT}\times\frac{Z}{r}\right]$$

Where, E is flow pattern efficiency (explained later) and Z and r are the length and radius respectively of the centrifuge rotor. α_z, determines the number of centrifuges that have to be connected in series to achieve a particular separation.

The performance of a centrifuge can best be described in terms of separative power can deliver. The theoretical maximum separative power a centrifuge can deliver is given by

$$\delta U_{max} = \frac{\pi(\rho D)}{2}\left[\frac{\Delta MV^2}{2RT}\right]\times Z$$

Where ρ & D are the density & diffusivity of the gas (UF6) at the given temperature and Z is the effective length of the rotor. Separative power of a centrifuge determines the number of centrifuges that have to be connected in a cascade for a given duty. It can be observed that in centrifuge the separative power is directly proportional to fourth power of the peripheral speed & the linear function of length of the rotor and inversely proportional to the average temperature. Because of very high dependence of the capacity of centrifuge on the velocity of operation, efforts have been made to operate the centrifuges at as high a speed as possible being limited by the strength of material. As a matter of fact commercial success of centrifuge technology has been possible only after it has been possible to operate long centrifuges at very high speeds.

In practice centrifuges do not produce maximum separative work, $\delta U_{max,}$ due to the following four efficiency factors:

A. Flow pattern efficiency factor (E_F): The gas in the centrifuge is made to flow in a counter-current pattern to enhance the radial separation effect as discussed earlier. The shape of the velocity profile determines the flow pattern efficiency and can be evaluated if the actual hydrodynamic behavior of the circulating gas is known. This information is usually not known and therefore this parameter is calculated for assumed velocity profiles. For the optimum for velocity profile in which the mass velocity is constant over radius of the centrifuge except at the wall , the flow pattern efficiency $E_F = 1$

B. Circulation efficiency (E_C): Axial concentration gradient is established in the counter-current centrifuge because of the axial flow. Due to this axial gradient back diffusion takes place which reduces the separative capacity. As the circulation rate increases the effect of back diffusion reduces increasing the circulation efficiency approaching unity. For obvious reasons circulation rate can not be increased very high and hence this efficiency will always be less than unity.

C. Ideality efficiency (E_I): In a given centrifuge flow is same through out the length of the centrifuge which can be treated as a square cascade which is different than ideal cascade described in previous paragraphs. In square cascade flow pattern is such that mixing of gases of two different isotopic concentrations takes place. This efficiency is therefore associated with the departure of actual flow from the ideal flow. It can be shown that in a counter current gas centrifuge when the flows are optimized the ideality efficiency has a maximum value of 0.81.

D. Experimental efficiency (E_E): This factor takes into account all those parameters which have not been considered in the previous terms. This takes into account the effect of flow turbulences and end effect etc and has to be determined experimentally.

The actual separative capacity, δU, can therefore be related to maximum separative capacity , δU_{max}, by $\delta U = E_F.E_C.E_I.E_E.\delta U_{max}$. The net effect of these efficiencies is to reduce the actual separative
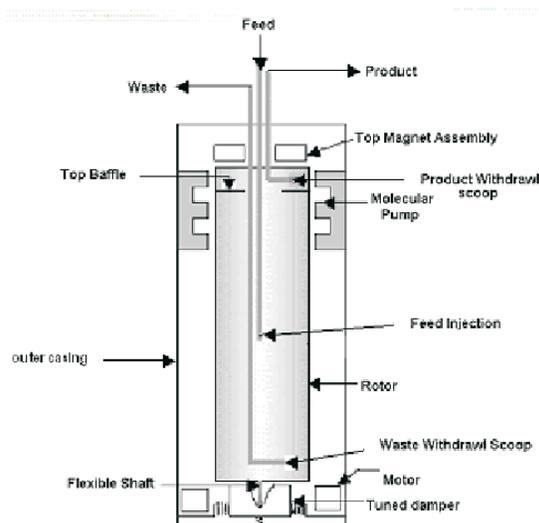
Fig. 4   Schematic diagram of a Gas Centrifuge

capacity of the centrifuges below that of maximum separative capacity by an amount which is to be determined experimentally.

Process Description

In this process, gaseous UF6 consisting of isotopic mixture of U235 & U238, is fed into a cylindrical rotor that spins at very high speed inside an evacuated casing. The heavier isotope which experiences higher centrifugal force tends to move closer to the rotor wall than the lighter one, resulting in partial radial separation of the two. The schematic diagram of one such centrifuge is shown in the Fig. 4.

As shown in the figure, the major components of centrifuge are rotor, magnetic / hydrodynamic bearings at top & bottom, drive, gas feed & withdrawal system and molecular pump among others, which are all housed in a casing. The feed gas is introduced in the centre of the rotor, at a point where the isotopic composition of the gas inside the rotor is close to isotopic concentration of feed. The product is withdrawn from the top of the rotor whereas depleted or waste stream is withdrawn from the bottom end. The product and waste streams are withdrawn through the pipes called scoops, which open to the opposite of the direction of rotation. The driving force for the flow of gas is provided by converting the part of kinetic energy of the rotating

gas in pressure energy. The feed and withdrawal rates depend on the design and speed of operation. The effect of these parameters as well as the counter current circulation rates have earlier been discussed under the efficiency factors.

As discussed earlier the separation effect in a centrifuge can be enhanced several fold if an axial countercurrent is induced. This is achieved either by thermal means or by mechanical or both. In former, one end of the rotor is kept at higher temperature compared to other. In mechanical arrangement, a scoop is provided at both ends, shielded by baffle at one of the ends. The drag created by the scoop disturbs the pressure gradient established by the centrifugal force and establishes an axial flow. Large types of scoop designs have been tried to establish optimum shape and size. In many designs these scoops are used for both providing an axial flow as well as to withdraw product and waste streams. Scoop design decides one of the most important process parameter i.e. internal circulation rate of the gas.

The rotors are contained in an outer casing which is maintained under high vacuum in order to minimize friction drag. It can be shown that a pressure of 10^{-3} millibar of UF_6 can cause a drag of 100 watts/meter in a tube of 200mm diameter rotating at a peripheral speed of 500 m/s. Apart from waste of power, this would also upset the counter current flow by setting up convective current in the rotor. Another reason for keeping the rotor in the casing is to contain the debris and absorb the energy produced in case of crash of the rotor. It has also to be ensured that energy produced during the crash does not disturb the neighbouring machines. High vacuum is also important for the stability of rotor during operation. The vacuum can be provided either by connecting the casing to an external vacuum pump or by molecular pump as shown in the diagram above.

Since in general the separative capacity (Appendix A) and separation factor of a gas centrifuge is much smaller compared to that required for a commercial scale plant, a large number of these have to be connected in series as well as in parallel, called cascade, to achieve desired capacity. A commercial size enrichment plant based centrifuges may contain a few thousands of them. As against
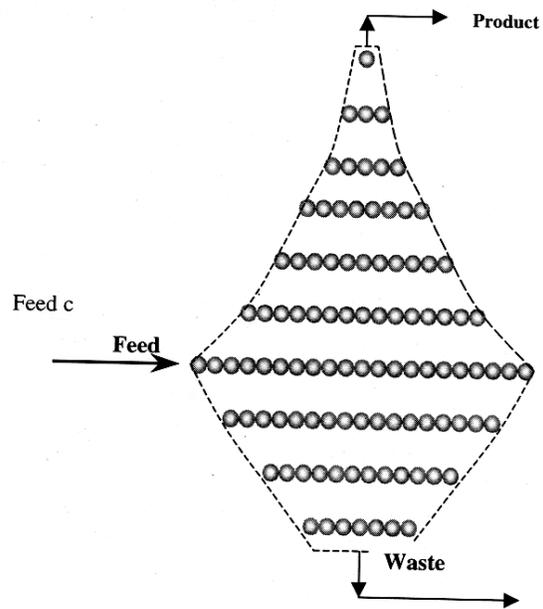
Fig. 5   Schematic shape of a Gas Centrifuge cascade

Fig. 6   A view of part of a URENCO Gas Centrifuge cascade (from site http://www.uic.au/graphics/centrfge.jpg)

gaseous diffusion plant where each stage capacity can be as large as desired, in gas centrifuge based plants capacity of each unit is fixed and hence desired capacity can be obtained only by adding more machines in parallel. For this reason flow at each stage of gas centrifuge cascade can be kept very close to ideal cascade flow and hence gas centrifuge

The following table gives the list of various rotor materials along with their maximum attainable speeds.

Material	σ, Tensile Strength (kg/cm^2)	ρ, Density (g/cm^3)	σ/ρ (x 10^3)	V_{max} (m/s)
Al-alloy	5,200	2.8	1.857	425
Ti-alloy	9,100	4.6	1.978	440
HS steel	17,000	8.0	2.125	455
Maraging steel	25,000	8.1	2.777	550
Carbon fiber resin	8,500	1.5	5.666	950
Kevlar	15,000	1.3	11.538	1100

cascade are likely to be more efficient compared to gas diffusion cascade. Also, since separation factor for gas centrifuges are much higher the number of stages required for a given enrichment are much smaller. Fig. 5 shows a schematic shape of centrifuge cascade (compare this with Fig. 3, schematic shape gas diffusion cascade). Fig. 6 shows a view of part of a URENCO gas centrifuge cascade.

Mechanical Features

As mentioned in previous paragraphs the separative capacity of a gas centrifuge is directly proportional to the fourth power of velocity, it is very important that the centrifuges are operated at the highest possible speed. The spinning rotors can achieve certain speed depending on the tensile strength (σ) & density (ρ) of the rotor material. The maximum linear speed a rotor can attain is given by the formula.

$$V_{max} = \sqrt{\frac{\sigma \times g_c}{\rho}} \text{ m/s}$$

where g_c is gravitational constant.

The table gives the maximum speed with respect to rotor materials. Actual speed at which the rotor can be operated will depend on many other parameters.

At higher speeds rotor dynamics is extremely important. And even more important is the design & manufacturing of hydrodynamic bearings. The rotors could be sub-critical rotors (running below their natural frequency) or could be super-critical (running above their natural frequency) depending on their length & speed. Flexible members (bellows)

are incorporated in super-critical rotors in order to bring down their natural frequencies to a certain manageable value. If the rotors are operated at frequencies close to their natural frequencies the vibration amplitude will increase uncontrollably leading to the failure of the machine. The rotor operating speed should be as far away from its natural frequency as possible.

At higher speed the main problem is that of rotor balance. Irrespective of how carefully rotors are balanced, balancing is never perfect and this can lead to considerable vibration. This vibration can sometimes be violent enough to destroy rotor and its bearing. The most important modes of vibration are the transverse or flexural modes. Concept of flexible rotors and tuned dampers are used to limit the vibration. Figs. 7&8 show mathematical model of such a concept.

The longer the rotor i.e. higher the length to diameter ratio, higher the number of criticals i.e flexural resonance must be overcome during acceleration to operating speed. Although peripheral speed of rotor is limited by its material properties, final speed is prescribed by the designer based upon subcritical or supercritical operation and capability of dampers to withstand the number of criticals. In order to get over the critical speeds super critical rotor must pass through various modes. The vibration absorber allows operation above flexural vibrations of the shaft itself for the supercritical rotors. Apart from the mechanical problems, there happens to be fluid dynamics problems inside the rotor due to gases in strong rotation. Gases under strong rotation (at supersonic speeds) pose a special
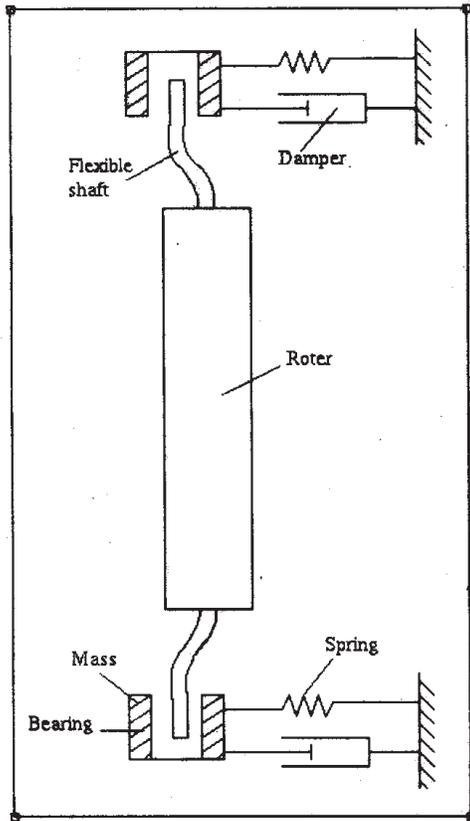
Fig. 7   *Subcritical rotor with tuned dampers, flexible mountings. Dampers control critical vibration caused by flexible support, provided for self-balancing*
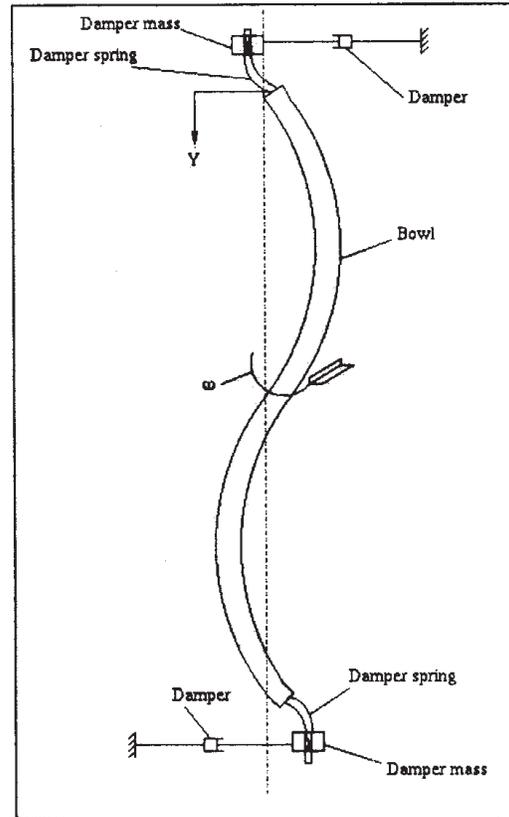
Fig. 8   *Supercritical rotor with tuned dampers. Supercritical rotor exhibits "S" mode shape for second flexural resonance*

fluid dynamic problem and are quite difficult to manipulate.

Aerodynamic (Nozzle) Separation Process

This process was developed by Prof E W Becker and coworkers at Karlsruhe Nuclear Research Center in Federal Republic of Germany. In this process a partial separation of isotopes is obtained in flowing gas stream that is subjected to a very high centrifugal acceleration. The isotopic molecules depending on their mass number will experience different centrifugal forces that effect separation.

In the process as shown in the Fig. 9, feed gas consisting of a mixture of about 5% UF6 & 95% H_2 is made to flow in a convergent-divergent nozzle. The
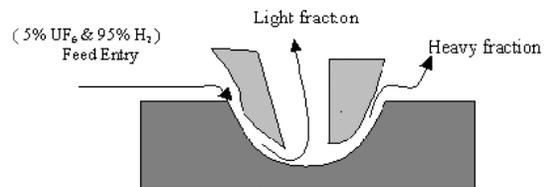
Fig. 9   *Separation due to difference in centrifugal forces*

nozzle accelerates the gas mixture to a super-sonic speed. The accelerated gas mixture then moves in a curved path of which the radius of curvature is of the order of a fraction of a millimeter. The centrifugal force being proportional to v^2/r, where v is the linear speed of the gas & r is radius of curvature of the flow path, a high degree of centrifugal force is imparted on the gas molecules. The lighter isotopic molecules

experiencing lower centrifugal force tend to remain in the center, while heavier molecules tend to remain at the periphery.

In a typical separation nozzle, the diameter of the deflecting groove is about 0.2 mm and the width of nozzle at throat is about 0.03 mm. The feed gas consisting of a mixture of about 5% UF_6 & 95% H_2, at a pressure of about 0.25 bar & a temperature of 40°C, is expanded to obtain an optimum expansion ratio of about 4.

The dilution of UF_6 with H_2 has a beneficial effect as the mixture has a very high sonic speed than pure UF_6. The sonic speed for UF_6 is about 90 m/sec, whereas that for the mixture is about 400 m/sec (sonic speed is the square root of $(\gamma RT/M)$). Thus it is possible to attain a very high speed and thereby a higher separation factor. Separation factor of up to 1.05 is reported to have been obtained in this process.

The process is characterized by a low separation factor, compared to gas centrifuge process but higher than gas diffusion process (hence large number of stages are required for a given enrichment), difficult to manufacture nozzle assemblies and very large (higher than even gas diffusion process) power requirement The enrichment cascades based on this process were reportedly operated in Brazil & South Africa which were shut down subsequently. No other country is working on this process.

Acknowledgement

Appendix A : SEPARATIVE POWER

In conventional industrial separations, where the level of separation is almost 100% (or some standard level), throughput parameter is sufficient to indicate the capacity of the separating plant e.g. a heavy water production plant, where the grade is fixed for reactor use. However it may be observed that unlike in heavy water production, varied degree of separation of isotopes is required in case of uranium. These varying levels of enrichment required for different applications ranging from 3% for LWRs to 90% & above for weapon grade is typical of uranium isotope separation. So when the enrichment levels are different in different plants then a question arises as to how to compare the capacities of two different plants. Because only throughput may not be sufficient to gauge the size of an enrichment plant, particularly when enrichment levels at which the plants are operating are different. Thus, there arises a need to define an additional parameter, which would be a combined function of quality & quantity of separation performed by a separating element or a plant. That is why a unique concept of separative power or separative capacity is introduced, particularly for uranium enrichment. The separative power should be so defined that it

combines both the quality & quantity of separation performed by a given separating element, and at the same time it is independent of the level of concentration of feed material.

The separative power is defined as a change in the Value effected by a separating element, i.e. the increase in the value of output over the value of input. A quantity called value function is defined as a function of the concentration, x, of the desired isotope by the relation:

$$V(x) = (2x - 1) \ln[x/(1 - x)]$$

and the value of the material is defined as the product of its quantity and value function. Thus the separative power (or separative work per unit time) of an enrichment facility, δU, is

$$\delta U = [\text{Value of } (P\&W] – [\text{Value of F}]$$

or,

$$\delta U = PV(xp) + PV(xw) – PV(xf)$$

It is expressed in kgU/yr or more commonly expressed as SWU/yr (i.e. Separative Work Units per year).

In the above given equations, F, P & W are the mass flow rates of feed, product & waste respectively, x_f, x_p, x_w, are mole fraction of desired isotope in feed, product & waste and $V_{(xf)}$, $V_{(xp)}$ & $V_{(xw)}$ are the value functions of feed, product & waste respectively.

APPENDIX B: ADVANTAGES OF GAS CETNTRIFUGE OVER GAS DIFFUSION

The gas centrifuge process is considered superior over gas diffusion process for the following reasons

- Higher separation factor hence requires less number of stages.

- Absence of inter-stage gas compressors in centrifuge plant allows it to be squared off more towards ideality. Whereas in case of gas diffusion plant use of compressors makes it necessary to go for bigger squaring off (more off from ideality) in order to avoid use of large number of compressors of different capacities. This makes the centrifuge cascades more efficient.

- Gas centrifuge being modular in construction, capacity addition can be done more easily. The plant can initially be constructed for lower capacity and can subsequently be expanded without much penalty.

- Gas diffusion plants must be of large capacity to be economical due to requirement of large number of supporting systems like captive power plants etc. Whereas the gas centrifuge plants can be economical in smaller capacities.

- Higher material inventory in gas diffusion plant makes it more difficult to switch over from one level of enrichment to another in an operating plant without a sufficient lead-time. This reduces flexibility of the plant in catering to different users requiring different enrichment levels in short delivery periods. In G.C. plants this problem does not arise due to much lower material inventories.

- It has low equilibrium time which reduces time between start up of the plant and start of withdrawal of product.

Gas centrifuge process is considered superior above nozzle process also because of low separation factor (compared to gas centrifuge) and very high energy consumption of nozzle process.

Finally a process must be technically feasible in commercially viable terms otherwise it is not adoptable, e.g. Nozzle process (look at the following table) is good everywhere, but is not technically feasible as there are practical difficulties in building up commercially acceptable plant.

The table below compares the relative performance parameters of the three processes:

Process	Separation Factor	High Throughput	Low Inventory	Energy Efficiency
Gaseous Diffusion	Poor	Excellent	Poor	Poor
Gas Centrifuge	Very good	Poor	Very good	Good
Nozzle Separation	Good	Good	Good	Poor

APPENDIX C: WORLD URANIUM ENRICHMENT CAPACITY

(Http://www.uxc.com/fuelcycle/enrichment/capacity-enrichment)

Company (Country)	Nameplate Capacity Million SWU (as of Dec. 31, 2001)	Technology
CNNC (China)	1.0	Gaseous Diffusion & Centrifuge
Eurodif (France)	10.8	Gaseous Diffusion
JNC (Japan)	0.9	Centrifuge
Minatom (Russia)	20.0	Centrifuge
Urenco (Germany) Urenco (Netherland) Urenco (UK)	5.25	Centrifuge
USEC (USA)	11.3	Gaseous Diffusion
Total	49.25	

Updated : 2/2/02

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Laser Isotope Separation

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1.   Introduction

One of the toughest scientific challenges has been to effectively - and inexpensively - separate a desired isotope of a chemical element from the remaining isotopes for uses ranging from medicine to energy to weapons applications. The advent of tunable lasers opens the prospect of frequency-selective excitation of matter. Since the selective excitation could change the properties of atoms and molecules drastically, tunable lasers can be used for isotope separation. The main thrust is aimed at developing workable isotope separation method for uranium-235, the fissile isotope of uranium which is needed to fuel light water moderated reactors. In addition, there is also a promising market for isotopes of lighter elements such as D, T, 6-Li, 10-B, 13-C, 15-N, 17,18-O, 33,34-S etc., some in connection with energy production (D, T, Li, B) and others as non-radioactive tracers in analytical, medical and environmental studies. In comparison with existing methods of various isotope separation laser process promises to yield higher enrichment per stage, consume less power and savings in capital investment. Laser isotope separation has blossomed into a full-scale discipline and interest is growing at an amazing rate. So much so, that presently we must restrict our attention to the most important ideas, methods, and experimental results. Thus the present article is conceptual and exemplary in nature and not meant as a wide coverage review, which would require a very large space.

2.   Concept, Requirements and Classification of Methods

The general concept of laser isotope separation is illustrated in Fig. 1. When two types of atoms and molecules of different isotopic composition (A and B) have at least one non-overlapping spectral line, it is possible to excite selectively with laser light an atom or molecule ("particle" A) of a desired isotopic composition. The excitation of the A particles changes their chemical and physical properties and, hence, may be used to separate substances by several approaches based on differences in the characteristics of excited and unexcited particles.

In photochemical approach, one can organize a chemical reaction of A* with a suitable partner to give products designated AR, before the excited particle starts to relax to its ground state or near-resonant energy transfer to B, yielding B* upon inevitable collisions (see Fig. 1). On the other hand,

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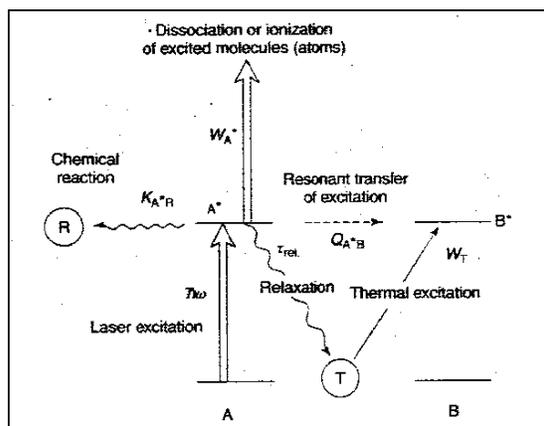
Fig. 1 General concept of the selective laser excitation of A particles and classification of processes causing the loss or conservation of selectivity.

the photophysical approach is based on subsequent laser-induced dissociation or ionization of the particles pre-excited in an isotope-selective manner. In both approaches, new products enriched with the desired isotope are formed, and can be extracted from the mixture by the standard methods. Summarizing the above facts, all laser enrichment strategies have three requirements in common:

(1) The isotopic species must posses absorption features with a well-resoled spectroscopic isotope shift (section 2.1). In the visible or ultraviolet portion of the spectrum of gaseous atoms or molecules, the dense array of electronic transitions display small isotope shifts (due to different nuclear mass, size, shape and spin) which range from $1:10^5$ to $1:10^8$ of transition energy. In the infrared spectral region the vibrational transitions of molecules are directly related to the reduced mass of constituent atoms, and the relative isotope shift is typically of the order of 1:100 to 1:1000.

(2) The laser employed must be monochromatic (to the limit of the spectral line width of the absorber) and preferably, tunable so as to allow selective excitation of the desired isotope without having to rely on fortuitous coincidences between laser emission lines and isotopic absorption features.

(3) There must be an efficient extraction step of the desired isotope, which may be magnetic, electrical, optical, thermal or chemical that acts preferentially on the excited species before relaxation, collisional energy transfer or charge transfer can occur. This turns out to be the most stringent condition for practical implementation of laser enrichment of isotopes. Several schemes have been explored on a laboratory scale, viz., (a) single photon (b) two photon and (c) multiphoton processes.

The photochemical approach has not found much application due to the difficulty of finding a suitable chemical reaction whose rate substantially exceeds both the relaxation rate of the pre-excited particles and the near-resonant energy transfer rate to particles containing the other isotope. However, with the availability of highly intense UV, visible and IR-pulsed laser radiation, it is possible to develop different types of methods of affecting atoms and molecules in an isotope-selective manner. These include the method of resonance stepwise photoionization of atoms (this method was given the acronym AVLIS, from Atomic Vapor Laser Isotope Separation), the method of resonance stepwise IR-UV photodissociation of molecules, and the method of resonance multiple photon dissociation (IRMPD) of polyatomic molecules by IR laser (the latter two methods were given the acronym MLIS, from Molecular Laser Isotope Separation). In effecting the photoionization of the atom, or the photodissociation of the molecule of interest by an additional laser pulse (Fig. 1), it is necessary that the rate of these processes be higher than the excitation transfer rate and the relaxation rate. AVLIS and MLIS formed the basis for the laser isotope separation techniques currently being implemented.

Changes in the reactivity of atoms and molecules due to photon absorption are well known and have long been used in photochemistry, including isotopically selective photochemistry. The first successful experiment was conducted by Kuhn & Martin in 1933, who exposed phosgene ($CO^{35}Cl_2$) molecules to a strong spectral line of an aluminum spark at λ = 281.62 nm. With the advent of laser sources of intense monochromatic radiation, it became possible to selectively excite many atoms and molecules without depending upon accidental coincidences between strong lines of spontaneous

radiation source and absorption lines of atoms and molecules. First few attempts of laser isotope separation were made by two groups, Tiffany, Moos & Schawlow in 1966 and Mayer et al in 1970. These experiments relied on the photochemically induced, increased chemical reactivity of excited molecules. Both failed because the overall chemistry did not preserve the initial excitation selectivity (Requirement 3).

Selective photophysical methods based on dissociation and ionization have met with greater initial success. The first proposal for laser isotope separation appears in a 1965 patent by Robieux & Auclair for two-step photoionization of UF_6 molecules. While this method remains impractical, selective two-step atomic ionization and selective two-step molecular dissociation were suggested by Letokhov and demonstrated experimentally. Isotopically selective molecular dissociation of sulphur hexafluoride, SF_6 by high-power IR laser radiation was discovered at Institute of Spectroscopy, Russia in late 1974 and Los Alamos National Lab, USA in early 1975. All of these methods have yielded good isotope separations and further developed for commercial application.

2.1 Spectroscopic Isotope Effect

The spectra of isotopes show small shifts in their characteristic frequencies. The isotope shift in the spectra of the lightest atoms is a result of the mass-differences of the nuclei of the isotopes. Consider, for example, hydrogenic atoms; the lines of the hydrogen-like atoms are described by the Rydberg formula : $\nu_H = R_H (1/n^2 - 1/n'^2)$

$$R_H = [2\pi^2 me^4] / [ch^3 (1+ m/M)]$$

where m and M are the masses of the electron and the hydrogen-like atom. Comparing hydrogen and deuterium, we find that the deuterium lines are shifted towards the blue by the amount

$$\Delta\nu_{HD} = \nu_H m [M_D - M_H] / [mM_H + M_H M_D]$$

For the Balmer Hα line at $\lambda = 656.28$ nm ($\nu = 15253$ cm^{-1}), the isotope shift is $\Delta\nu_{H\alpha} = 4.12$ cm^{-1} or 1.77 A^o. Since the mass shift is proportional to 1/M, it becomes very small for atoms of atomic number ~40 and almost non-measurable for heavier atoms. However, fairly large isotope shifts are
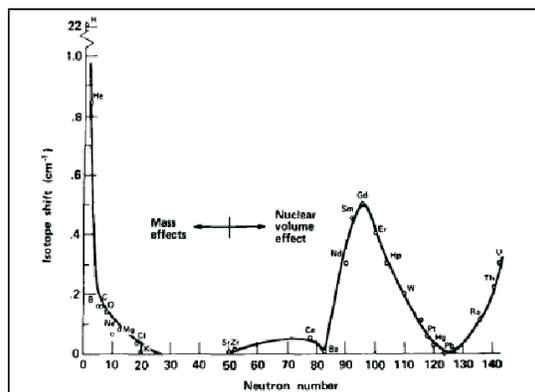
Fig. 2   Atomic isotope shifts vs neutron number

experimentally observed again in the spectra of the very heavy atoms. These shifts are explainable by the "field" or "volume effect" of the isotopic nuclei. Because of differences in shape and charge distributions of the isotopic nuclei, the orbits of s-electrons are distorted, an effect that becomes large for the heavy nuclei. The isotopic shifts are dominated by the change in the interaction of the electron angular momentum with the nuclear spin (the hyperfine interaction) and the change in the nuclear volume. They are of the order of a few tenths of a cm^{-1} or smaller. Figure 2 shows how the atomic isotope shifts varies with the neutron number of the elements. Isotope shifts in the atomic spectra have been investigated for a long time, and a considerable body of experimental information exists. Two of the most thoroughly investigated spectra are those of 238-U and 235-U of which the isotope shift of ~5000 lines has been tabulated.

Isotope shifts in the vibrational spectra of molecules are strictly the result of the isotopic mass effect. The shifts can easily be predicted theoretically. Consider the simplest case of a diatomic harmonic oscillator; its fundamental vibrational frequency ν is given by the relationship:

$$\nu = (1/2\pi) (k/\mu)^{1/2}$$

where k is the characteristic force and $\mu = Mm / (m + M)$ is the reduced mass of the molecule. Isotopic substitution changes only the reduced mass μ. The frequency of the isotopic variant of the molecule, therefore, becomes: $\nu_i = \nu (\mu / \mu_i)^{1/2}$

For larger molecules, the fundamental frequencies of two isotopic molecular variants are related by the Teller-Redlich rule. The molecular isotope shifts are large; the fundamental band of HF for example, is at 4000 cm^{-1}, the same band in DF is at 2900 cm^{-1}, an isotopic shift of 1100 cm^{-1}. Of course, the shifts for larger and heavier molecules are smaller.

In molecular spectra, the isotope shifts of vibrational and rotational levels are superimposed on the electronic energy shifts. The vibrational level spacing is inversely proportional to the square root of the vibrational reduced mass and the rotational level spacing is inversely proportional to the moment of inertia. Except for some small molecules, however, the complexity of the very closely spaced rovibronic levels often forbids the description of isotope shifts of individual lines. Instead, one considers the isotope shifts of the rotation-vibrational bands. In many cases, even for heavier molecules, the isotope shift of a narrow band can be comparable to or larger than the half-width of the band, which is of the order of a few cm^{-1} at room temperature. The half-width of rotational structure is given by the approximate expression: $\Delta\nu_{rot} \approx 4.6 \ (B_o \ T_{rot})^{1/2}$, where B_0 is the rotational constant, T_{rot}, is the rotational temperature (in cm^{-1}), Only in light molecules ($^{i}BCl_3$, $^{i}SF_6$) does the isotope shift for the i-atom exceed the rotational bandwidth (I.S. between 10 & 11-BCl$_3$ is 9 cm^{-1} and between 32 & 34-SF$_6$ is 17 cm^{-1}). The situation is somewhat better for the molecules with a well-pronounced Q-branch in their vibrational band. The bandwidth of Q-branch is usually much smaller than the rotational bandwidth, $\Delta\nu_{rot}$ and, therefore, even for some heavy molecules (for instance, $^{i}OsO_4$) it is possible to ensure isotopically selective excitation. However, for many polyatomic molecules even the Q-branch width is much larger than the isotopic shift. In this case the rotational broadening of the Q-branch maybe reduced by cooling the gas. To prevent the liquefaction of the gas, it is advisable to make use of dynamic cooling during adiabatic expansion of molecular gas (section 5). The low translational temperature narrows the Doppler width and the low rotational temperature brings all of the molecules into the lowest molecular rotational states. These effects produce a great simplification of the spectrum. It has been demonstrated that this method is extremely useful in selective excitation of the ν_3 band of 235-UF$_6$ (I.S. between 235 & 238 UF$_6$ is 0.6 cm^{-1}).

2.2 Separation Selectivity

For quantitative comparison of the separation methods, the coefficient of separation selectivity of A and B atoms or molecules is defined by the relation

$$K(A/B) = [N_{AR}]_f / [N_{BR}]_f : [N_A]_o / [N_B]_o$$
$$= R_f \ (A/B) : R_o \ (A/B)$$

where $[N_A]_o$ and $[N_B]_o$ are the initial concentrations of A and B particles in the mixture, $[N_{AR}]_f$ and $[N_{BR}]_f$ are the final concentrations of new resultant molecules in the mixture that contains the A and B atoms or molecules being separated. The parameter $K(A/B)$ is defined as the final isotopic ratio $R_f \ (A/B)$ divided by the initial isotopic ratio $R_o \ (A/B)$. With no separation effect present, we have the selectivity coefficient $K(A/B) = 1$. The values $K(A/B) > 1$ correspond to a high selectivity of separation. For example, in natural uranium, which contains one part 235-U in 140 of natural uranium, the isotope ratio $R_o(235/238) = N_o(235)/N_o(238)$, is equal to 0.0072. The mole fraction is $\chi_o = N_o(235) / [N_o(235) + N_o(238)] = 0.0071$. For reactor fuel the mole fraction needs to be about 3% or $N_f(235) / [N_f(235) + N_f(238)] = 0.031$. So, for uranium, a $K(235/238) = 4.25$ yields a reactor-grade product. Now this factor can be achieved through a series of cascaded stages as in the gaseous diffusion processes. For the laser separation process this value of the separation selectivity may be achieved through a single-stage process.

3.   Advantages of Laser Isotope Separation

The potential advantages of the laser methods for separating isotopes over the traditional techniques are as follows:

1.   The high selectivity of the elementary separation act : In the majority of the traditional techniques, the separation factor α in a single stage is very small, close to unity, and so to attain a high degree of separation, K, one has to use a large number ($n \gg 1$) of separation stages: $K = \alpha^n \gg 1$. While, the laser methods of isotope-selective ionization of atoms and dissociation of molecules can, in principle, provide for $\alpha \gg 1$. This makes it possible to greatly minimize

the number of separation stages, reducing it in many cases to one separation stage.

2. The possibility of separating the desired isotope without affecting the other isotopes of the same element. When the element of interest has several isotopes of intermediate mass (for example. 17-O, 33-S or 40-K), one can selectively excite the atoms or molecules of the desired isotopic species and separate them without affecting in any substantial manner the particles of other isotopic species by using tunable laser radiation of appropriate frequency.

3. Low expenditures of energy: For the traditional methods, the expenditure of energy per atom of the targeted isotope is usually 10 to 10^4 times higher than for the laser methods.

4. Non-contact separation capability : In the laser methods the absence of the traditional separating elements (plates, membranes, etc.) minimizes the contact between the enriched product and the surface of the separating plant and hence the contamination of the latter. This is especially important, for example, in separating radioactive isotopes.

5. Versatility: With rare exception, the laser methods can be used with a sufficiently high efficiency to separate isotopes of any elements, be they light, medium weight, or heavy, as distinct from the traditional methods whose efficiency depends on the mass of the isotope being enriched. Apart from separating isotopes, it can be used to separate atoms with different isomeric nuclei. This technique is also being successfully used for separating isobars, i.e., atoms of different elements having the same mass.

6. Short start-up time: With the laser methods, steady state operation is attained practically at once, whereas in the traditional methods, the start up period may last a few months.

4. Photophysical Methods

Among the basic photophysical methods of practical interest under active development in many countries is selective multistep photoionization of atoms. Figure 3 illustrates various schemes of selective atomic ionization of special interest for laser isotope separation. Each of these has been demonstrated in laboratory experiment, and has its own advantages and disadvantages.

4.1 Selective Multistep Photoionization & AVLIS

Selective photoionization of atoms is the most universal photophysical method for selective separation of substances, particularly isotopes, at the atomic level. A common feature of all schemes for selective ionization is the sequence of the two processes: (a) isotopically selective excitation and (b) ionization of the excited atoms. The two-step photoionization scheme is the simplest. The three-step scheme can be used for atoms with a high ionization potential. Normally the small photoionization cross section which is about 10^{-4} - 10^{-6} times the resonant excitation cross section, can be enhanced by tuning the frequency of last-step radiation to that of the transition to an autoionization [spontaneous or electric-field-induced] state (Figure 3c). Finally, high-lying Rydberg states can be ionized by IR radiation or a pulsed electric field (Figure 3d,e).

Besides uranium isotope separation, laboratory experiments are being carried out on selective ionization of other isotopes, potentially useful in much smaller quantities, such as K, Ca, Rb, rare-earth, and of course, transuranium elements. An effective ionization of excited atoms at an average, moderate intensity of the ionizing radiation presents a serious problem in these cases. The ionization schemes given in Figure 3 a-c cannot be practically applied here, so greater attention is paid to the ionization scheme of highly excited atoms shown in Figure 3 d-e. The above three methods enable one to ionize selectively excited isotopic atoms of any element in the periodic table. High separation factors like 10^2 - 10^5 can be achieved quite comfortably.

4.2 AVLIS of Uranium

Results on LIS of uranium have been published from early research programs at Avco Everett Research Laboratory and the Lawrence Livermore Laboratory. In 1974, the results of the first Livermore experiments were presented in which, CW dye lasers were used for excitation of 235-U and the UV radiation of mercury lamps were used for ionization. The selectivity separation factor was
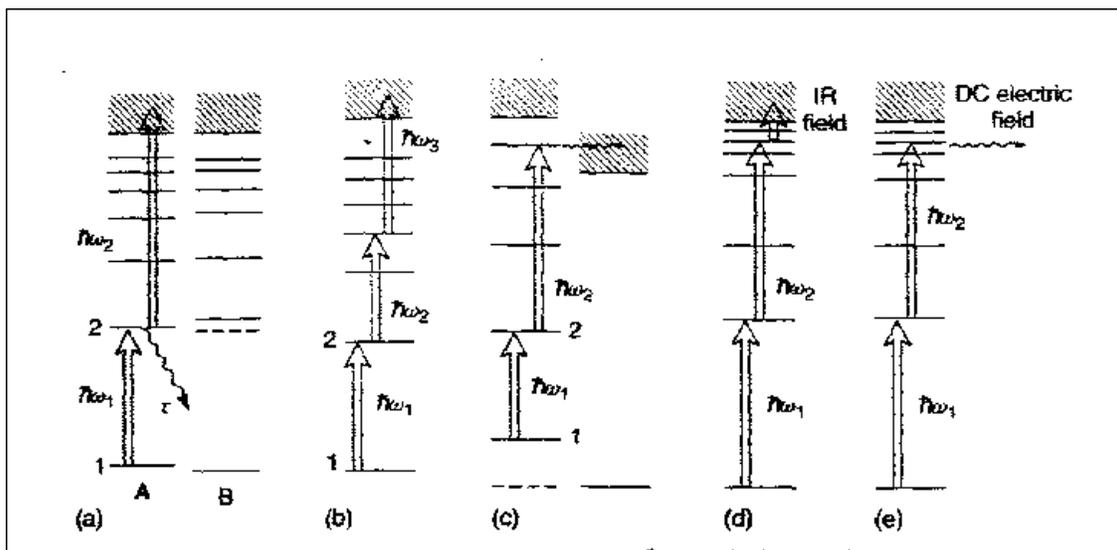
Fig. 3   Schemes of selective step-wise photoionization of atoms by laser radiation: (a) two-step photoionization; (b) three-step photoionization; (e) two-step photoionization through an autoionization state; (d) two-step selective excitation of a Rydberg state and its photoionization by IR laser radiation; (e) two-step selective excitation of a Rydberg state and its ionization by dc electric field.

about 100. In 1975 the results of two-step ionization of uranium atoms by xenon and krypton ion lasers were published. The ion yield rate of 235-U$^+$ in their experiments was 2 mg/ hr, which is 10^7 times higher than the rate obtained in the early experiments. After this, a joint R & D program was started by Avco Everett Research Laboratory and Exxon Nuclear Co. In 1975, they obtained separation factor K(235/238) of about 140 in an experiment in which the exciting, pulsed dye laser was scanned over the 235-U transitions, and the pulsed N$_2$ laser was used to photoionize the excited species.

Soon the information available in open literature became scanty as most of the countries made these investigations classified. Development of AVLIS technology were mainly performed in USA, France, Japan and few more countries. In the first half of the 1980s, an experimental separation plant with a potential output of around 10^3 kg of low-enrichment uranium per year was built at Lawrence Livermore National Laboratory (LLNL) in the United States. The production of a few kilograms of such uranium was reported. Metallic uranium is first vaporized in a separator unit contained in a vacuum chamber. Even this process makes demands on high technology, since the vapour pressure of uranium is very low even at high temperatures (10^{-4} Torr at 2000 K). At the same time, molten and as-vaporized uranium are extremely powerful reactants. Therefore, the metal kept in a water-cooled crucible is evaporated with an electron beam from where it expands with a velocity of ~5 x 10^4 cm/s. Another important parameter need to be considered is the share of uranium atoms in the ground state level, which is only 47% at 2800 K. A metastable state at 620 cm^{-1} is populated to the extent of 28% and the rest are distributed among higher levels due to thermal excitation. This means that to access most of the desired uranium isotopes, two laser frequencies must be provided, one from the ground and the other from 620 cm^{-1} level, just to reach the first excited state.

The vapor stream is then illuminated with laser light tuned precisely to a color at which 235-U absorbs energy. Three wavelengths of red-orange light of dye lasers were used as a radiation source. These were pumped by copper-vapor lasers that provided the necessary 20 - 30 ns pulse duration at a
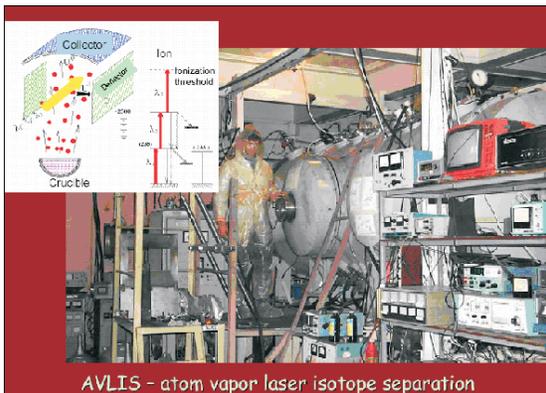
Fig. 4   The Selective scheme flow chart (inset) and the AVLIS set up at IMP, Russia

repetition frequency of around 10^4 Hz. Each color selectively adds enough energy to ionize or remove an electron from 235-U atoms (IP = 6.2 eV), leaving other isotopes unaffected. Because the ionized 235-U atoms are now "tagged" with a positive charge, they are easily collected on negatively charged surfaces inside the separator unit. The product material is condensed as liquid on these surfaces and then flows to a caster where it solidifies as metal nuggets. The unwanted isotopes, which are unaffected by the laser beam, pass through the product collector, condense on the tailings collector, and are removed. Figure 4 shows a similar lab scale AVLIS set up for uranium enrichment at the Institute of Molecular Physics, Russia.

Over the years, funding of about $2 billion was invested to develop the technology at Lawrence Livermore and to successfully demonstrate it with an integrated, full-scale pilot plant. This step was achieved in the early 1990s for special nuclear materials separation and in the late 1990s for commercial uranium enrichment applications. This has produced enriched uranium between 3-5% 235-U. The system is remarkably compact and the vacuum chamber holding one separator unit produces output equivalent to that of several thousand of best commercial centrifuges. But after this, United States Enrichment Corporation (USEC) suspended funding for the project in mid-1999. LIS technology, however, is currently finding other important applications in energy, medicine, astronomy, and industry. Livermore scientists are also proposing its use for tapping the energy value remaining in the tailings left from decades of government uranium enrichment activities.

5.   *Photochemical Methods*

The classical photochemical process (Fig. 5a) is based on a one-step ultraviolet/visible excitation of an electronic state of a molecule. Single step excitation of an electronic state of molecule has serious disadvantage, particularly for polyatomics of having broad structureless electronic absorption bands at room temperature. The scheme cannot be used for isotopically selective excitation. Only for a few simple molecules the absorption line is narrow enough for isotope selection. However, excitation of electronic state does give a high quantum yield for the photochemical reaction.

On the other hand, single step excitation of molecular vibrational state features rather high excitation selectivity for both simple and complex molecules. The main disadvantage of this method is that the fast relaxation of vibrational excitation to heat leads to a low quantum yield of the subsequent photochemical processes. But two step excitation (Fig. 5b) of a molecular electronic state through an intermediate vibrational state by joint action of IR and UV radiation removes the above disadvantages. Thus this kind of two frequency (IR + UV) excitation combines sufficiently high selectivity with high quantum yield for photochemistry. The infrared multiple photon process (Fig. 5c) differs fundamentally from all other methods in that infrared photons alone are responsible for both exciting selectively and subsequently dissociating the molecule. The manifold of vibrational energy states of one or more modes of the molecule in the ground electronic state acts as a selective infrared pathway through which the absorption of photons excites the molecule to a level at which dissociation occurs.

5.1   *Infrared Multiphoton Chemistry & MLIS*

Probably none of the phenomena in laser photochemistry discovered in the recent past is as exciting as infrared multiphoton excitation and dissociation (IRMPE and IRMPD). Recognition of this method as a means by which selective photochemistry may be realised, has whetted the
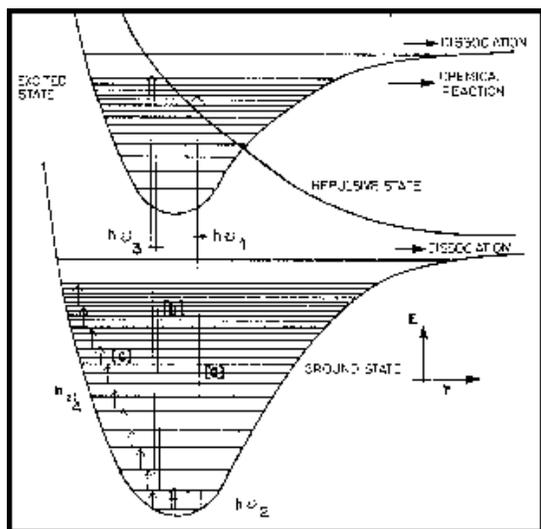
Fig. 5 Various types of selective excitation : (a) single step electronic excitation (ν_1); (b) two step electronic excitation through intermediate vibrational state ($\nu_2 + \nu_3$) and (c) multiple photon excitation in the ground electronic state (ν_4)

appetite of photochemists who are excited by its possible applications in dissociation, isomerisation, control of chemical equilibria, synthesis of complex molecules and finally in bond selective chemistry.

The nature and characteristics of the photophysical and photochemical processes induced by multiphoton excitation (MPE) of collisionless, isolated molecules triggered hectic experimental and theoretical activities. The following qualitative picture has emerged out of the numerous experimental and theoretical studies in this subject. The molecular energy levels are separated into three regions (Fig. 6). In the lowest energy range (region I), the density of molecular states is very low and laser field interacts with isolated discrete molecular states. Several possible mechanisms to overcome the anharmonic detuning at several successive transitions of the excited vibrational mode have been considered viz. (a) power broadening (b) rotational anharmonicity compensation (c) multiphoton transitions. Once the molecule has absorbed a few quanta, the density of molecular states become very large and time evolution can no longer be described in terms of a few isolated molecular states. This
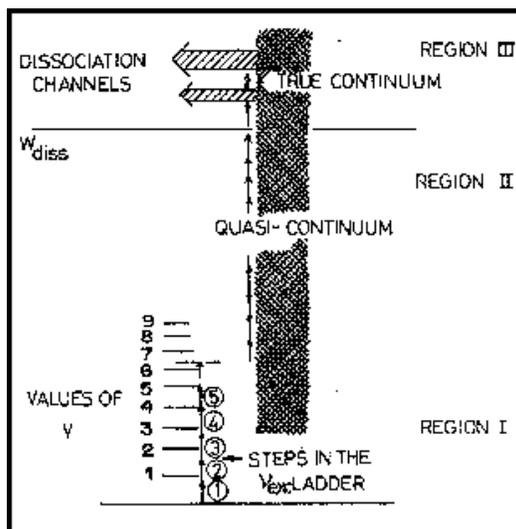
Fig. 6 Schematic model for infrared multiple photon excitation (IRMPE) and dissociation (IRMPD)

region is denoted as quasi-continuum (region II) and its exact theoretical treatment is still a subject of intense investigation. Finally, when the molecule acquires enough amount of internal energy, it enters a true continuum (region III) where in addition to all the complications of region II, dissociation or predissociation or isomerisation channels open up.

Many experiments on isotopically selective MPD have thus been performed which covered many isotopes, from light ones (H, D, T) to heavy ones (Os, U) contained in very different molecules. Many of these became the basis of laser isotope separation methods developing in numerous laboratories of several countries. Table 1 presents some of the LIS successes from our laboratory. Later we will present detailed information on recently developed MLIS process of carbon isotopes (section 6.2).

5.2 MLIS of Uranium

The molecular Uranium compound suitable for using the MLIS approach is the UF_6 molecule. The vibration, ν_3, in this molecule that is active in IR absorption lies in the region of 16μm. The isotope shift in this vibration between 235-UF_6 and 238-UF_6 is comparatively small, that is, ~0.6 cm^{-1}. Therefore, to resolve the isotopic structure of IR transitions, use

TABLE 1. Isotope selective laser photochemistry at BARC

Isotopes	Pressure (Torr)	Typical results		
		Laser line	Fluence (J/cm^2)	Selectivity
Sulphur 34 / 32	SF_6 1.0	10 P(20) CO_2 laser	2.0	10
Uranium235 / 238	$UO_2[(CF_3CO)_2CH]_2$.THF Molecular beam	10 P (4) CO_2 laser	0.08	1.2
Carbon 13 / 12	CF_2HCl 100.0	9 P(20) CO_2 laser	4.0	60
Stage 1	$CF_3Br/Cl_2(1:4)$ 50.0	9 P(32) CO_2 laser	4.5	65
Stage 2	CF_3Cl/Br_2 (1:6) 20.0	9 P(8) CO_2 laser	1.7	200
Deuterium D / H	CHF_3/Ar (1:2) 75.0	10 R(10) CO_2 laser	30.0	> 40
Tritium T / H	CHF_3/Ar (1:2.5) 28.0 (0.2 ppm CTF_3)	9 R(8)-9 R(14) CO_2 laser	65.0	38
T / D	$CDCl_3/Ar$ (1:5) 12.0	828 cm^{-1} NH_3 laser	21.0	5000.0

is made of gas-dynamic cooling of UF_6 to temperatures ~100 K. To effect isotope-selective IR excitation of UF_6, special lasers like CF_4 and para-hydrogen Raman laser tunable in the region of 16 μm were developed.

Work on the development of the MLIS technology was done in the United States, Japan, France, and few more countries. Two approaches as discussed earlier - two-step IR + UV photodissociation and IR MPD were investigated. In the summer of 1976, experiments were carried out at Los Alamos national Laboratory for uranium enrichment. The scheme involves irradiating expansion-cooled UF_6 gas with infrared and ultraviolet lasers. The expansion supercooling produces a substantial density of UF_6 monomers at low temperature. After expansion through the nozzle, the cooled gas is irradiated by a sequence of infrared and ultraviolet laser pulses (Fig 7). Either one or two infrared lasers tuned in the 16-micrometer range provide selective vibrational excitation of 235-UF_6. The two-frequency infrared excitation provides higher selectivity than single-frequency excitation. The first low-intensity laser is tuned near the resonant frequency of the 235-UF_6 Q-branch, and the second high-intensity laser is tuned far to the red of this peak to achieve maximum excitation of the 235-UF_6 molecules. The probability for ultraviolet dissociation is substantially higher for the highly infrared-excited 235-UF_6 molecules than for the 238-UF_6 molecules. Thus, an ultraviolet laser tuned near the low frequency edge of the dissociation spectrum of unexcited molecules will provide large dissociation yields for 235-species and small dissociation yields for 238-species. In addition, ultraviolet dissociation of UF_6 to UF_5 is very efficient, occurring with a near unity quantum yield in the 200-300 nm region. The UF_5 product forms particulate that are easily separated from the gas flow by a sonic impactor / collector assembly. A few milligrams of slightly enriched uranium sample collected on the impact plate is also shown in the figure.

Although ultraviolet dissociation has been chosen for the Los Alamos uranium enrichment process, the intensity of the second infrared laser can
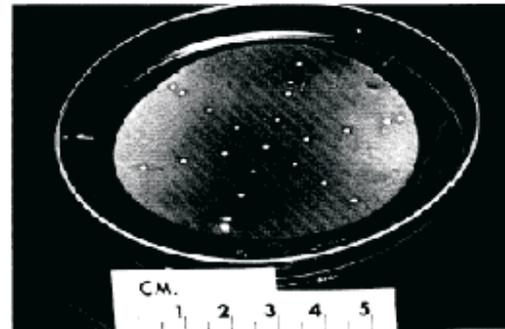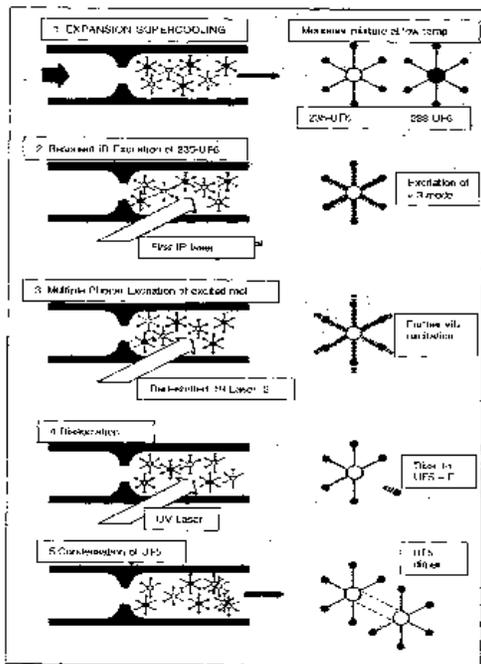
Fig. 7   *The sequence of events in Los Alamos MLIS scheme and collected enriched sample*

be increased to provide dissociation (IRMPD) without an ultraviolet laser. However, for a number of reasons this project gave way to the AVLIS project and was closed early in the 1980 s. The approach based on the purely infrared excitation and dissociation of UF_6 seems to be more promising, both econoniically and technologically. Use can be made of both two and three-frequency MPD. By appropriately selecting the laser radiation parameters, one can attain the necessary selectivity $\geq$ 4, which is, in principle, sufficient for the production of nuclear fuel. The development of an industrial prototype of a uranium isotope separation plant in Japan & South Africa based on this MLIS version was reported

6.   Development of Industrial LIS Technology

The above-considered AVLIS and MLIS methods are capable of very high elementary separation act parameters, namely, the separation factor and yield of the desired isotope. However, going from laboratory experiments to industrial technology normally require a great deal of work on the scaling of the process. To develop an efficient industrial LIS technology, it is necessary that the following two conditions be satisfied.

1.   Availability of a laser source with an average power from 1 kW to 1 MW, depending on the required output capacity.

2.   Realization of sufficiently high separation factor and yield for the given working substance with the desired isotope.

Besides, when scaling an LIS process, it is necessary to retain the high separation factor and yield values unchanged. It should also address satisfactorily various problems like efficient photon utilization factor while irradiating the working substance with high repetition-rate pulses of high average power, and optimal process scheme, including the extraction and subsequent processing of the enriched products. All these problems have been solved, to certain extent, when developing the AVLIS and MLIS technologies.

6.1   The Scaling of the AVLIS Technology

As discussed earlier, the AVLIS process consists of three stages:

1. Vaporization of the starting material and obtaining a flow of atomic vapor of the necessary density and volume.

2. Selective photoionization of desired isotope by laser radiation.

3. Extraction and collection of the ions on special collectors.

The selectivity of multiple-step photoionization of atoms may be very high : $\alpha \geq 10^2$ to 10^5. But this is only true of single, non-interacting atoms. To attain high output capacity for industrial implementation of the AVLIS requires increased atomic vapor densities. This substantially reduces the separation factor attained in practice. A number of factors limit the density of the atomic vapour and the size of the irradiation region to the following typical values ; vapour density $\leq 10^{14}$ cm^{-3}; cross-sectional dimension of the irradiation region - a few cms (mainly because of resonance charge exchange); length of the irradiation region - a few tens of meters. A number of constraints exist on the laser parameters as well. The characteristic lifetime of excited atomic states, as regards their spontaneous decay ranges from 10^{-8} to 10^{-7} s. Therefore the laser pulse duration should not be longer than a few tens of nanoseconds. The characteristic velocity of particles in atomic vapours is around 10^5 cm^{-1}. For this reason, to maximize the "interception" of the atoms crossing the laser beam, the laser pulse repetition frequency should be a few tens of kHz.

Though the work on the AVLIS technology at LLNL was announced suspended in 1999, further progress will apparently be possible when the new generation of laser radiation sources based on wholly solid-state systems gets perfected. As for the separation of the isotopes of other elements, LLNL reported experiments on the industrial-scale extraction of the 157-Gd isotope, There is also a report on the development of an industrial plant in Russia for the commercial production (gm per month) of the 168-Y for medical applications.

6.2 The Scaling of the MLIS Technology

In the MLIS approach, the isotope of interest is incorporated in a polyatomic molecule. As compared with the AVLIS technology, this opens up additional possibilities for selecting a starting working compound suitable for the existing IR lasers. The most serious work on the scaling of the MLIS technology was done in separating isotopes of uranium and carbon. In the following we describe in detail our prototype facility developed for carbon isotopes.

MLIS programme for Carbon-13

Natural carbon consists of two stable isotopes, viz. C-13 (1.11%) and C-12 (98.99%). Carbon-13 is an important isotope as a tracer in chemistry, life science, medicine, and biochemical synthesis. An optimistic projection of hundred-fold increase in the market demand is anticipated in view of rapid development of routine medical applications such as breath tests and whole body NMR. There are immediate uses of such isotopes in DAE activities like high resolution spectroscopy, catalyst development, isotopically labelled gas lasers, tracer in biology and making 'super' diamonds. In view of the growing demand we in BARC are actively engaged in developing MLIS processes.

The present methodology is based on CO_2 laser induced Infrared Multiple Photon Dissociation (IRMPD) of CF_2HCl molecule. Excitation and dissociation selectivities are extremely high for this system so that CF_2HCl MPD is possible even at fairly moderate pressure (133 mbar) at room temperature yielding C_2F_4 with 50 % 13-C:

$$^{13}CF_2HCl \rightarrow {}^{13}CF_2 + Hcl$$

$$^{13}CF_2 + {}^{13}CF_2 \rightarrow {}^{13}CF_2 \, {}^{13}CF_2$$
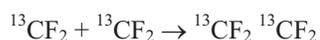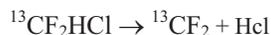
The prototype facility with the major components is shown in process flow sheet (Fig. 8):

(1) Laser and accessories include various optical elements like windows, gratings, mirrors, lenses etc, detectors of energy and temporal profile, oscilloscopes and control electronics

(2) Photochemical reactor (PCR) includes Herriott multipass refocusing (MPRF) optics in flow configuration with circulatory pump / blower, mass flow meter, metering valves, pressure transducer etc.

(3) Product separator / collector include (i) cryogenic distillation unit and (ii) preparative gas chromatograph
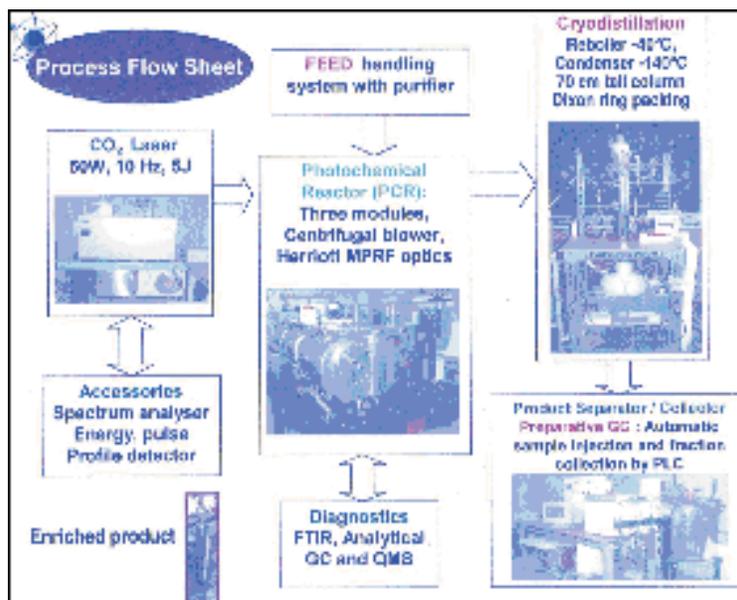
Fig. 8   Process Flow sheet for MLIS of carbon isotopes in L&PTD, BARC

(4) Diagnostics includes FTIR spectrometer, gas chromatograph and quadrupole mass spectrometer

(5) Feed includes gas handling system with purifier etc

Summarizing, we have developed a prototype facility for laser separation of carbon isotopes. Presently, in a production run of 8 hr, the unit provides about 100 mg of Carbon (40% C-13) with 10 Hz CO_2 laser (ca. 20 gm / yr). Overall, this facility has generated database, operating experience and trained manpower in the general area of laser processing of high value and strategic materials.

7.   Conclusion

From this brief but extensive account of laser isotope separation, it is quite clear that there is a massive effort by scientists and engineers around the world during past 30 years for developing AVLIS and MLIS processes. Among them some of the methods have been selected, which can be used for the industrial production of isotopes on various scales, in quantities of both up to a kilogram for scientific and medical applications and up to a few tons for nuclear power plants.

The large-scale production of isotopes requires highly reliable, efficient, and cost effective lasers with an average energy from a few kilowatts to a few hundreds of kilowatts. Among such lasers are CO_2 gas lasers that are being successfully used in the MLIS of 13-C/ 12-C.The development of semiconductor laser arrays for pumping solid-state lasers is progressing so swiftly that it seems quite realistic that the AVLIS technology based on this new, much more consummate laser equipment may be implemented on an industrial scale in the near future, as the demand for enriched uranium grows higher. Opportunities in this field are enormous and lots of exciting questions are at hand and if they can be answered and if their answers are encouraging it might revolutionize the world of science.

8.   Acknowledgement

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Chemical Exchange: Heavy Water Technology

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Shri M.R. Ashraf is a post graduate in chemical engineering from MUICT and joined the process development group of HWB in 2005 after undergoing training at BARC Training School. He was associated with development and setting up of the TBP plant at HWP Talcher. He is presently associated with the Research, Process & Technology Development Group and is involved in the Heavy Water Clean up facility activities. He is also associated with the various activities of process modeling and simulation works at HWB.

1. Introduction

The process of heavy water production from the naturally occurring deuterium sources like water and natural gas depends principally on the difference in the separative potential between Hydrogen and Deuterium bearing species. Deuterium was first separated by the fractional evaporation in 1932 by Urey, Brickwedde and Murphy. In the subsequent years, a number of processes including electrolysis, water distillation, and hydrogen distillation were investigated as potential separation methods. Due to the strategic importance of heavy water, large efforts were put in to evaluate and develop methods for large-scale production of heavy water. Despite major efforts, only a handful of these efforts could be converted into feasible technologies. Major research and development to investigate heavy water processes was carried out in those countries that built prototype Pressurised Heavy Water Reactors (PHWRs). Amongst these countries, Indian nuclear programme pursued PHWR technology rigorously and have a successful program for production of large quantities of heavy water.

Heavy Water Plants are inherently complex due to very low abundance level of deuterium and are capital and energy intensive. Among the successful commercial processes for heavy water production, chemical exchange process is widely used. As the complexity of the technology increases, associated environmental and safety aspects also becomes complex due to many unknown factors. It becomes imperative that the technology developer

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takes into consideration all the factors related to safety and environment at the design stage itself and carries out an innovative design, which addresses the environmental concerns in a most comprehensive manner. The technology of development of Heavy Water Plants in India is a case in consideration where the technology was developed from concept to commissioning and, there are very few parallels in the Indian scenario.

The technology of heavy water production in India is largely developed on indigenous efforts and today India is one of the world leaders in this field. There are seven heavy water plants in the country and these are based on two different technologies. The Hydrogen sulphide-Water bi thermal chemical exchange process technology using water as a raw material is being used in the plants located at Kota in the state of Rajasthan and Manuguru in Andhra Pradesh and, the Ammonia-Hydrogen monothermal exchange process technology using the hydrogen of the ammonia synthesis gas of a fertiliser plant as feed gas is being used in the plants located at Baroda & Hazira (Gujarat), Thal (Maharashtra) and Tuticorin (Tamil Nadu). The first Heavy Water Plant at Nangal in Punjab based on Hydrogen distillation process is currently de-commissioned.

The complexity of Heavy Water Plants arises from the fact that the natural occurrence of deuterium is very low i.e in ppm and the final purity requirements are 99.8%+. Besides, Heavy Water for the nuclear power generation is required in tonnage quantities as first charge and about 2-3% as yearly makeup. Thus, heavy water forms a significant part in the cost of power generation from a PHWR (Pressurised Heavy Water Reactor). These factors call for a very innovative process design and heat integration systems in order to make the process economically viable. Thus instead of simple distillation process of water for production of heavy water a complex H_2S-H_2O bi thermal exchange process or Ammonia-Hydrogen monothermal process is used so that the energy consumption and there-by cost of production is brought down by a factor of magnitude. While a simple water distillation consumes about 500 GJ/kg of heavy water produced, a chemical exchange process consumes about 30-40 Gj/kg of heavy water. On a conventional scale, this itself is huge and even the so

called difficult process for production of some of the complex petrochemicals (like ethylbenzene from xylene) consumes energy which is only a fraction of the above.

The complex deuterium exchange reactions for isotopic separations are a special category in the field of reactive distillation process. In this case, the separation between the two isotopes is achieved through a chemical reaction of two components (each component being predominant in one of the phases). There are number of species containing hydrogen (and consequently deuterium) as one of its constituents and, therefore can form potential candidate for such a separation process. The important criterion which finally decides the selection of the two species are (i) ease of chemically converting one of the species into the other species and provide the reflux essential for the deuterium transfer or (ii) the dependence of the chemical exchange reaction constant to the temperature which would allow provision through shift in the temperature. While the deuterium exchange reactions involving NH_3-H_2 fall under category (i) described as monothermal processes, the deuterium exchange reactions involving H_2S-H_2O fall under category (ii) described as bi-thermal process. In the following section, the chemical exchange process is illustrated with the mono-thermal ammonia–hydrogen exchange process.

2. Basic Scheme of Exchange Process

The ammonia–hydrogen exchange process is based on deuterium transfer reaction between liquid ammonia and gaseous hydrogen.

$$NH_3 \text{ (l)} + HD \text{ (g)} \underset{\text{Hot}}{\overset{\text{Cold}}{\longleftrightarrow}} NH_2D \text{ (l)} + H_2 \text{ (g)} \qquad (1)$$
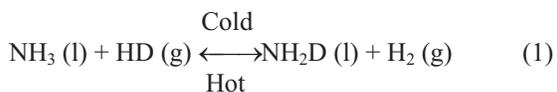
However, the process based on the above reaction did not get importance, as the rate of reaction was extremely small for consideration as a commercial process. In 1950, Clays, Wilmarth and Dayton showed that the rate of the above transfer reaction could be enhanced using potassium amide dissolved in ammonia as a catalyst. Though the homogeneous potassium amide did improve the rate of reaction, the rate was still far less compared to that
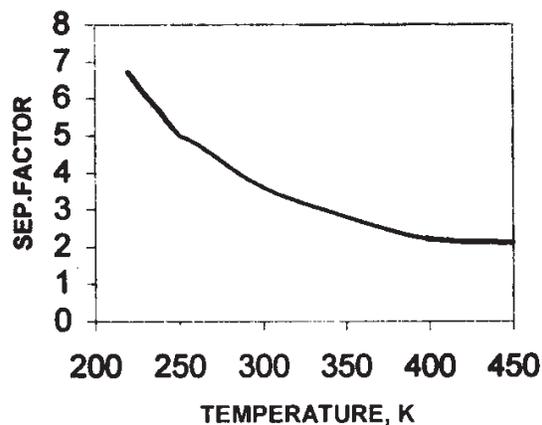
Fig. 1 *Dependence of separation factor on temperature for NH_3-H_2 system*

Fig. 2 *Monothermal NH_3-H_2 exchange process*

of hydrogen sulphide –water process and needed improved gas-liquid contactors for mass transfer.

When ammonia (l) and hydrogen (g) having different isotopic concentrations are brought into contact, deuterium accumulates in the liquid phase based on the equilibrium conditions. The separation obtained is governed by the separation factor, which is defined as ratio of the deuterium content in the liquid phase to that in the gaseous phase.

Separation factor, $S = (D/D+H)_{liquid} / (D/D+H)_{gas}$
(2)

The separation factor for the ammonia –hydrogen exchange process is 2/3 rd of the equilibrium constant. The separation factor is a strong function of the temperature and the dependence is indicated in Fig. 1.

A large number of separation contacts between liquid ammonia and gaseous hydrogen are essential for obtaining the desired level of separation and this is done in a countercurrent fashion. The chemical exchange process based on the continuous countercurrent contact of the liquid and gas needs provision of a reflux stream to the column. In the monothermal mode of the chemical exchange process the reflux is provided by a phase converter, which changes the component completely into the other by chemical reaction. Ammonia –hydrogen exchange process is fairly easy to adapt to monothermal operation as the heat of formation of
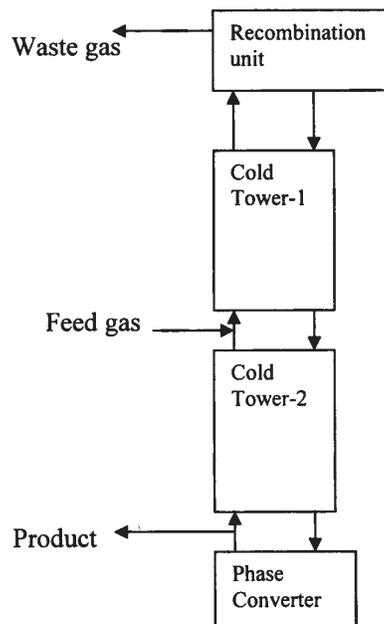
ammonia from hydrogen and nitrogen is relatively low and the conversion of nitrogen and hydrogen into ammonia and its decomposition is an established process.

A schematic of monothermal NH_3-H_2 exchange process is shown in Fig. 2. Feed gas containing deuterium is brought into contact with liquid ammonia in an extraction tower where in deuterium exchange reaction takes place and the deuterium laden liquid is enriched further in the enrichment tower. The reflux requirement of the enrichment tower is met with decomposition of the liquid ammonia into hydrogen and nitrogen in an ammonia-cracking unit. The deuterium depleted feed gas is taken out of the extraction tower and sent to the feed gas generation unit after reflux liquid ammonia is generated in an ammonia synthesis unit. Since the separation factor at -25^{0}C is over 5, a low temperature of around –25^{0}C is employed for the exchange reaction in order to have a good separation.

3. Comparison of Various Processes

For developing a large-scale plant based on a process of chemical exchange for deuterium separation, it is important to look at the general

TABLE 1. Process comparison

	H$_2$S-H$_2$O	NH$_3$-H$_2$	Hydrogen Distillation
Feed	H$_2$O	Syn Gas	H$_2$
Energy GJ/kg D$_2$O	42	30	22
Mass Transfer	Fast	Slow-fast	Fast
Temperature * K	400	258	24
Pressure MPa	2	25	0.25
Separation Factor	1.3	4.8	1.5
Source of energy	Coal	Natural gas	Electrical power

nature and the considerations that go into the design of any isotopic separation process. The isotopic separation process differs substantially from other conventional systems especially due to the low abundance of the isotope there by necessitating a very large number of separating elements. An industrial level heavy water plant is required to handle large amount of feed material and has large number of contacting stages necessitated due to low enrichment factor. The combination of large feed flow and large number of separative elements resulting in the heavy water plants being very large as compared to most of the other chemical plants. Accordingly, a number of conflicting requirements also are to be considered while designing, the most important ones being, ease in operation, minimization of the cascade volume and energy consumption.

The H$_2$S-H$_2$O bi-thermal exchange and NH$_3$-H$_2$ monothermal exchange processes have relatively lower separation factors and higher energy consumption than other processes. However, both these processes are still preferred methods for production due to availability of abundant feedstock for both the processes. While the H$_2$S-H$_2$O process uses water as feed material, the NH$_3$-H$_2$ process uses synthesis gas as feed that is available through large-scale fertiliser plants. The energy consumption of both the processes is at about 30 GJ/kg for NH$_3$-H$_2$ process and 40 GJ/kg for H$_2$S-H$_2$O process. The table below shows the comparison of some of the parameters between the various processes. The sustained operation of the plants with higher on stream hours together with implementation of various systems have helped Heavy Water Board in bringing down the specific energy consumption of heavy water production.

In the counter current gas-liquid deuterium exchange reactions, the arrangement for providing gas-liquid phase conversions at both the ends of the column is different from the conventional distillation column. The phase conversion here is analogous to reboil / reflux arrangement of the conventional distillation. The need for phase conversion is in view of the fact that the gas-liquid components of isotopic exchange reactions are chemically different. There are two different ways with which such reflux / reboil arrangement is provided and this differentiates between monothermal and bi thermal systems.

In monothermal configuration the reflux / reboil is provided by means of chemical conversion. Ammonia-hydrogen deuterium exchange process is most readily adapted to such operation because the heat of formation from hydrogen and nitrogen is relatively low. In this case, ammonia synthesis gas is the deuterium source and hence the feed is a gas to the exchange column. The ammonia liquid reflux is provided at the top of the column through synthesis (to ammonia) of the gas, and the gas reboil is provided at the bottom of the column through decomposition of ammonia liquid. The isotopic exchange reactions take place in the column at a constant temperature, chosen based on thermodynamic and kinetics of the reaction. Therefore, such type of deuterium exchange process is configured on this basis for production of heavy water on an industrial scale.

Practical monothermal processes are unfortunately rare because chemical phase conversion is too energy intensive. In the bi thermal arrangement, the phase converter of monothermal arrangement is replaced by a hot tower that provides the deuterium reflux at the bottom of the cold column. In this case, the gas remains essentially in a closed loop cycle. Thus, a bi thermal arrangement of ammonia-synthesis gas would have two columns operating at different temperatures with synthesis gas in a closed loop circulation. Another example in this category is H_2S-H_2O exchange process used for extracting deuterium from the normal water. The very nature of the chemicals i.e. H_2S and H_2O indicate that monothermal process will be infeasible. However, bi thermal arrangement of this process overcomes the above situation. The hot tower of bi thermal process is analogous to an imperfect reboiler and so, provides gas to the cold tower at a considerably lower deuterium concentration than is achieved by a phase converter of the monothermal process. As a consequence, not only does the hot tower and its associated heating and cooling equipment of the bi thermal process replace the phase converter of the monothermal process, the bi thermal process requires much longer cold tower making the process more complex. The counter current H_2S gas and water flows, if appropriately controlled cause a net transport of deuterium up the hot section and down the cold section to provide enriched water and the gas at the centre of the column. The enriched stream at this point is withdrawn as feed for the subsequent section causing a net extraction of deuterium from the feed liquid.

4. Heavy Water Plant

Ammonia synthesis gas or simply syngas is generated by steam reformation of hydrocarbons-naphtha, natural gas etc- in the front end of the ammonia plant and is subsequently sent to the ammonia synthesis loop consisting of ammonia converter, waste heat recovery and cooling section and the liquid ammonia separation unit of the ammonia plant. Nitrogen and hydrogen combine to form ammonia in the ammonia converter under high pressure and the syngas produced at the generation section is compressed to the required pressure by the syngas compressor. The feed gas to heavy water is tapped from the discharge of the syngas compressor. After recovery of deuterium in heavy water plant, the syngas is returned to the fertilizer plant for production of ammonia. Figure 3 depicts a typical interlinking of the ammonia plant with heavy water plant. Table 2 indicates the heavy water plants with the operating pressures and the ammonia plants to which the plants are interlinked.

The synthesis gas from ammonia plant contains moisture and other oxygenated impurities like CO and CO_2 at trace levels. Though an elaborate purification system is provided in the heavy water plant, it is important that the gas generation section is designed and operated to have minimum levels of CO/CO_2 impurity. By ultramethanation these impurities in ammonia plant are maintained at about 1 ppm.

TABLE 2. HWP – Ammonia.plants and operating pressures

Sl, No	Heavy Water Plant	Fertiliser Plant	Operating Pressure, kg/cm^2
1	Baroda	GSFC	650*
2	Tuticorin	SPIC	250
3	Thal	RCF	200
4	Hazira	KRIBHCO	200

* HWP Baroda operation with GSFC linkage has been discontinued.

The level of deuterium in the synthesis gas varies widely depending on the process employed in the ammonia plant. The deuterium concentration of the hydrocarbon and the steam carbon ratio employed in the reformation process affect the deuterium level in the feed syngas due to the deuterium shift reaction between hydrogen to water taking place in the process. It is hence important to recover and recycle all the steam condensate produced from the process as the deuterium gets accumulated in the water phase. It has been the experience that with effective utilization of the deuterium rich condensate, deuterium concentration level of 115 ppm is possible to be achieved in the feed synthesis gas. The various sections provided in the process scheme are (i) Syngas pressure boosting, (ii) Drying and purification of gas, (iii) Extraction of
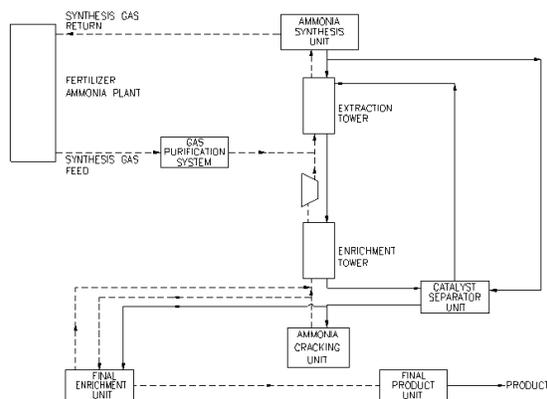
Fig. 3   Flow Scheme of HWP (Monothermal NH$_3$-H$_2$ exchange)

deuterium into liquid ammonia containing potassium amide catalyst, (iv) Synthesis of ammonia from nitrogen and hydrogen, (v) Enrichment of ammonia containing catalyst, (vi) Decomposition of ammonia in an ammonia cracker, (vii) Final enrichment of ammonia , (viii) Heavy water Production and (ix)Heavy water upgradation. The auxiliary units include amide catalyst preparation section, natural gas handling, effluent water circulation and gas vent system, fire water system while the utilities include cooling water, ammonia refrigeration section, nitrogen generation, instrument air etc.

After removing impurities the gas is cooled to –25^{0}C and sent to the extraction tower wherein the deuterium extraction takes place. The deuterium-laden ammonia is further enriched and is sent to the catalyst removal unit for preparing the liquid ammonia for cracking. The deuterium enriched ammonia containing catalyst is heated after reducing the pressure to 25 kg/cm^2 and the liquid ammonia containing less than 1 ppm K$^+$ is sent to the ammonia cracker operating at 130 kg/cm^2 pressure.

Liquid ammonia is cracked into the components in a fired furnace having high nickel alloy tubes filled with iron based catalyst. The catalyst is of special design as the normal catalyst gets nitrided on exposure to high ammonia concentration. The heat requirement for the cracking

of ammonia is supplied by burning naphtha/natural gas.

In order to achieve a closed loop for the system with respect to ammonia, generation of ammonia is required which will be matching to the amount cracked. The ammonia is added to the extraction tower. The feed gas together with the gas coming out of the enrichment tower that is sent to the extraction tower is taken out of the tower and is sent to ammonia synthesis unit. The ammonia synthesis unit comprises mainly of ammonia converter, heat recovery unit and cooling system for condensing the ammonia synthesized. As the ammonia requirement for the process is about 20 % of the syngas sent from the extraction tower to the synthesis unit, the same can be generated through a once through loop converter. The ammonia converter loop in a typical ammonia plant is operated in a recirculating mode in order to convert the syngas produced in the generation section completely. While the cracking process is endothermic, the ammonia synthesis process is exothermic. The heat recovery is done by generation of steam, which find utility for various heating requirement. HWP is self sufficient in its steam requirement. A small quantity of enriched ammonia and syngas is withdrawn from the enrichment section and further contacted for final concentration. The unit is almost same as that of the first enrichment section except for the small size. The synthesis gas enriched to 50 to 60 % deuterium in the unit is burned with air to produce off-grade heavy water, which is further distilled to nuclear purity.

The process employs ejector trays for efficient liquid-gas contacting. The gas is sent through a number of nozzles and the ejector action of the high-speed gas draw the liquid ammonia containing amide catalyst into a reaction chamber. Liquid is dispersed as fine particles and the enhanced area is provided to improve the total exchange. At the end of the reaction chamber, the liquid is separated and added to the liquid pool and the gas depleted in deuterium enters the stage above. The high energy requirement for the gas liquid contactor is reflected in the high pressure drop in the ejector stage and necessitates the liquid to be pumped to the stage below. Thus, a typical exchange tower has a number

Fig. 4   A view of Heavy Water Plant Manuguru

of ejector trays and each have two numbers of canned motor pumps.

Operation of the plant with various pressures and temperature levels demand complex control and the extensive instrumentation is one of the basic features of the plant. Though the earlier plants were having conventional instrumentation, the newer plants had state of the art instrumentation with distributed digital control system. The complexity of HWP can be seen in Figs. 4 & 5 which give the view of HWPs at Manuguru and Hazira.

5.   Conclusion

The story of development of the heavy water technology in India is a true example of self-reliance. Despite the various difficulties, Heavy Water Board took up development of the different processes simultaneously during late sixties and early seventies itself. With the multi-pronged approach taken in seventies HWB has mastered the two processes (H_2S-H_2O bi thermal process and NH_3-H_2 monothermal process). However, the process of NH_3-H_2 bi thermal process could not achieve much

Fig. 5   A view of Heavy Water Plant Hazira

success due to difficulties in getting reliable and sustained supply of inputs from the fertiliser plant. Currently, the plant at Baroda (Gujarat), the first plant based on the Ammonia-Hydrogen monothermal exchange process has been modified with a ammonia-water deuterium extraction system at the front end leading to its de-linking from the fertiliser plant.

Heavy Water Board has developed total expertise in the heavy water technology in all aspects and is meeting all the requirements of the Indian PHWR programme. It has also exported major quantities of heavy water to other countries. The performance of the plants in terms of energy consumption, safety and also environment management aspect also were excellent. Heavy Water Board has also taken up presently development of alternate applications of heavy water in the fields of life sciences and high technology areas of electronics.

Isotopic Enrichment by Thermal Diffusion -Overview

Shri V. K. Tangri, *B.Tech (Chem. Engg) joined BARC in 1970. Now he is the Head, Heavy Water Division. He has been involved in several development activities such as procedure for stelliting of carbon steel in H_2S/H_2O environment, imparting protective coating on carbon steel for smooth commissioning of Heavy Water plants, upgrading vacuum distillation and electrolysis and setting up plants based on these process at various sites, pretreatment of product of exchange units of Heavy Water Plants based on H_2S/H_2O prior to upgrading it to reactor grade product in a vacuum distillation based plant employing phosphor bronze packing and implemented the project for HWP-Manuguru and production of H_2S by synthesis of H_2 and Sulphur which is economical and environment friendly and set up a plant on this process for CAT, Indore. He is a member of Bereau of Indian Standards - MTD 8. He is engaged in initiating activities for using hydrogen as an alternative energy source.*

Dr.(Mrs.) Sadhana Mohan *joined BARCin 1985 through 28th batch of training school. Now she is the head of Process Development Section, Heavy Water Division. She has developed process design and optimization of cryodistillation cascade, isotopic exchange catalyst development and technology for the production of detector grade silicon. Her area of expertise is simulation of reactors, distillation cascade and LPCE columns. Her current activity is the development of new catalysts for isotopic exchange.*

Dr. (Mrs.) Sushama Mishra *has joined Heavy Water Division, BARC in 1985 through 28th batch of Training School. Her field of interest is in basic research in Analytical Chemistry. Her activities include Deuterium analysis using Mass spectrometry, testing the catalytic activity of catalyst, on-line analysis of bio-aerosols using time-of-flight mass spectrometer and analysis of trace element impurities in trichlorosilane.*

Introduction

Life is possible without any need for isotopically altered matter, except in the case of a few elements as ^2H, ^{13}C, ^{15}N and, relatively recently ^{57}Fe, and these too were needed in minute amount for research. A few isotope pools maintained in laboratories met these demands. But atomic age has changed all this. Today vast amounts measured in tones, of highly enriched, sometimes absolutely pure isotopes of certain elements are needed. These include ^2H, ^3H, ^6Li, ^{10}B, ^{233}U, ^{235}U and some others, each account of its certain special nuclear property. Continuous work on perfecting several sophisticated techniques, each specially suited for these isotopes, has been in progress since the second war with excellent results, though at phenomenal cost.

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Isotopes can be separated by various methods

1. Electromagnetic method
2. Physical Method – Gaseous diffusion, Nozzle jet separation, thermal Diffusion, Ultra centrifugation
3. Chemical Methods
4. Electrochemical Method
5. Photochemical Method
6. Biological Method

The advantage of thermal-diffusion process is that large separation factors can be obtained in an apparatus of moderate size and no complex equipment and operation is required. Thermal-diffusion is an attractive method in small-scale experiment.

Development of Process

According to the theory of transport phenomena in gases, diffusion should arise because of non-homogeneity of composition, temperature and pressure [1]. If in a mixture which initially has uniform concentrations, pressure and a temperature gradient is set up, a relative motion of the components may occur which leads to the development of concentration gradients. This type of diffusion is called thermal diffusion. Since the concentration gradients originated by thermal diffusion in turn cause concentration diffusion, a steady state is established which balances these two processes. Thermal diffusion gives rise to a partial separation of the components of the initially uniform mixture. Thermal diffusion in isotopic mixtures is of great interest both from a practical point of view, because it is used as a highly effective separation process, and from a theoretical one, due to the close dependence of this phenomenon on intermolecular forces. The essence of this transport phenomenon is that in the presence of a temperature gradient in a solution or a gaseous mixture there takes place a transport of matter, which produces a concentration gradient such that the light component of the mixture concentrates in the region of higher temperature and the heavy component in the region of lower temperature.

Thermal-diffusion is of importance and interest in four main respects: as a means of studying intermolecular forces; as a means of separating isotopes and normal gas mixtures; as a disturbing influence in experiments on mixed gases in a state of diffusion of non-uniform temperature and in cosmic gases of low density containing multiple ions.

Theoretical Background

For a mixture of two gases, which is non-uniform with respect to composition as well as temperature, the general equation of diffusion may be written in the form (1):

Net Flux of lighter isotope

$$C_1 (V_1-V) = C_1C_2 (V_1-V_2) = C_2 (V-V_2) =$$
$$-[D_{12}\text{grad}C_1 - D_T \text{ grad ln } T] \qquad (1)$$

In this equation, which is sufficient to describe the phenomenon of thermal-diffusion, C_1 is the fractional molar concentration of the first gas (or the lighter isotope) and C_2 is the fractional molar concentration of the second gas (or the heavier isotope); $V1$ and V_2 are the convection velocities of the molecules of the first and the second gas, respectively, and V defined as

$$V = C_1 V_1 + C_2 V_2 \qquad (2)$$

Represents the convection velocity of the whole gas, D_{12} is the coefficient of ordinary diffusion and D_T is the thermal-diffusion coefficient.

$$\text{Thermal diffusion ratio } k_T = D_T/D_{12} \qquad (3)$$

This enables the thermal-diffusion effect to be defined for the steady state, i.e. an equilibrium between the concentration diffusion and the thermal-diffusion effect, which will be approached in a binary mixture in a volume with a temperature gradient present.

For steady-state diffusion the flux is zero. Hence from Eq. (1) it follows that

$$\text{grad } C_1 = k_T \text{ grad ln } T \qquad (4)$$

A temperature gradient leads to a definite concentration gradient. This is the quantitative definition of the thermal-diffusion effect.

Historical Aspect

In many laboratories all over the world the thermal-diffusion effect has been used, particularly for the separation of isotopic gas mixtures, since the

discovery of the separation by Clusius and Dickel [2] in 1939. The isotopes of an element show identical chemical properties and differ in atomic weight. This mass difference is utilized directly or indirectly in all separation processes. The difference in the molecular kinetic qualities of the gas mixture is utilized in the separation of isotopes with thermal-diffusion. The advantage of this process over other separation processes essentially consists in the simple and cheap construction of the separation column, which makes possible smooth continued running for months. In general the separation plant used in the form of a thermal-diffusion column essentially consists of two vertical concentric cylinders as the hot and the cold surface. The annular gap is filled with the mixture to be separated.

The effect of thermal-diffusion is to drive the lighter molecules toward the hot surface, so that they enter the rising convection current, which exists near the inner cylinder due to the force of gravity and buoyancy. This convection current multiplies the thermal-diffusion separation effect. The lighter molecules are thus carried upward and the heavier ones downward, so that a concentration gradient is set up along the column. The total transport through any transverse cross section is zero in this process because the same quantities are carried upward and downward. For the two parts of isotopes this is not so, because the concentration of the lighter isotope is greater at the hot cylinder than at the cold surface. This shows that the lighter isotopes are enriched at the top of the column and the heavier isotopes are transported to the bottom of the column. On the other hand, the two convection currents are essentially mixing processes, which tend to destroy any concentration gradient along the column. The final equilibrium concentration gradient along the tube wall, therefore, results from a compromise among these two effects and a third, the remixing effect of ordinary diffusion along the column. The greater the mass difference of the components the better is the separation effect.

A typical thermal-diffusion column consists of a metal or glass tube kept at a temperature T_1, usually by the help of a water jacket, and a central heater kept at a temperature T_2 ($T_1 \ll T_2$). The temperature

difference ΔT between the two walls of the column is of the order of magnitude of a hundred degrees.

The thermal-diffusion column permits a considerable multiplication of the elementary separation effect as convective effect is superimposed on the thermal-diffusion effect. This ultimately leads to the concentration of the lighter and the heavier component at the top and bottom of the column, respectively.

For any thermal-diffusion column under discontinuous operation the equilibrium separation factor, q is given as (3)

$$q = e^{2AL}$$

Where L is the length of the column and 2A= H/ [K_c +K_d + K_p]
H, K_c, K_d, and K_p are column constants and depend on the transport properties of the gas as well as on the geometry of the separation column.

Uranium Enrichment – Manhattan Project History

The Manhattan Project considered four physical processes for the Uranium enrichment.

1. Gaseous diffusion
2. Electromagnetic separation
3. Liquid Thermal diffusion
4. Centrifugation

First three processes were employed at the Oak Ridge to produce enriched Uranium (>90% U-235) for the Hiroshima bomb. Centrifugation technology was abandoned because the technology required to spin rotator at high speeds was not practical for large- scale separations at that time.

Manhattan project scientist and engineers explored several Uranium enrichment technologies and production plants employing three Uranium enrichment processes- Electromagnetic isotope separation (EMIS), liquid thermal-diffusion and gaseous diffusion were constructed at Oak Ridge Tennessee during the period from 1943-1945. Into the space between two concentric vertical pipes Philip Abelson placed pressurized liquid Uranium hexafluoride with the outer wall cooled by a circulating water jacket and the inner wall heated by high-pressure steam. The lighter U-235 isotope tended to concentrate near the hot wall and the

Production of weapons grade U-235
Oak Ridge, TN - 1944-45
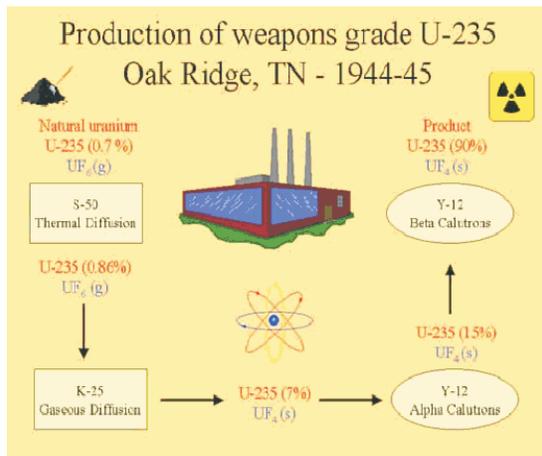
heavier U-238 near the cold wall. Like other enrichment methods liquid thermal-diffusion was at an early stage in 1940. The process was subsequently improved and led to the design and construction of the greatest thermal-diffusion production plant S-50 built at Oak Ridge during World War II. It produced uranium with 0.86% U-235, which was used as feed material for further electromagnetic separation [4].

The thermal-diffusion columns employed consisted of three concentric tubes, the innermost hot-wall tube being of nickel, the middle one of copper and the outside one of iron. The annular space (about 0.025cm) between the nickel and the copper tube was filled with process fluid. To cool the copper tube water was pumped upward between it and the iron tube. The columns were mounted vertically on a steel framework. Saturated steam at high pressure was introduced at the top of the column, condensate being removed at the bottom and returned to the boiler. A cooling-water inlet was at the bottom of the column, with the outlet at the top, and water was circulated through the column by means of a pump. To maintain the desired cooling temperature of about $64\,^0$C some hot water was removed at the top of the column while cold water was added to the ingoing stream.

A large number of columns with spacing of 0.025cm were made and operated using steam at 286 ^{0}C and cooling water at 63 ^{0}C. The highest separation factor obtained was 2.23. It was measured for a product rate of 49 g of uranium per day. By the spring of 1945 oak Ridge had shipped ~132 lbs of enriched uranium (~90%) to Los Alamos New Mexico. This

was used in "Little Boy" the bomb dropped on Hiroshima on Aug 16 1945.

Applications

Clusius and Dickel carried out the earliest application of thermal-diffusion to isotope separation. They used a 2.6 m long column to enrich Ne-22 to 31% from its natural content [5]. Other isotopes separated using thermal-diffusion process were of hydrogen isotopes, ^{3}He, ^{10}B, ^{13}C, ^{15}N, ^{18}O, ^{22}Ne, ^{30}Si, ^{37}Cl, ^{38}Ar, ^{79}Br, ^{124}Xe.

Neon isotope separation- Case study at HWD

For isotopes of noble gases such as helium, neon, argon etc., methods of enrichment are few due to their chemically inactive nature. Thermal-diffusion process utilizes the difference in molecular kinetic qualities of the gas mixture, hence making it the most suitable for the separation of noble gas isotopes. For an increase in efficiency of the thermal-diffusion process to be achieved it is necessary to have a theory of the separation column which does not only take account of constructional features but also of the kinetic properties of the gas mixture used. To meet both requirements neither the geometric structures of the separation column nor the interacting forces between the molecules of the gas mixture should be neglected, because the column constants depend on them in a very important manner.

Neon has three stable isotopes, ^{20}Ne, ^{21}Ne, ^{22}Ne with natural abundance of 90.92, 0.257 and 8.827 at % respectively. In the case of Neon, Neon-22 gets enriched at the bottom end of the column while the lighter isotope Neon-20 gets enriched at the top of the column.

From the values of, gas density (ρ), Viscosity (η), Self-diffusion coefficient (D), Thermal diffusion factor (α), cold-wall radius (r_1), hot-wall radius (r_2), Cold-wall temperature (T_1) , hot -wall temperature (T_2). With $y_o = r_1/r_2$ and $\theta_o = T_2/T_1$ and column length L cm, under total reflux conditions overall equilibrium separation factor is estimated based on the following equations,

The equilibrium separation factor of the column, q defined as

$$q = \frac{C_{bottom}/(1-C_{bottom})}{C_{top}/(1-C_{top})}$$

C_{bottom} being concentration of Neon-22 at bottom and C_{top} at top of column respectively, is given theoretically as

$$\ln q = [2A]L = \frac{H}{Kc+Kd} * L$$

Here,

$$2[A] = \frac{H}{Kc+Kd}$$

With

$$H = \frac{2\pi g}{6!}\left[\frac{\alpha\rho 2}{\eta}\right]_1 r_1^4 h$$

$$K_d = 2\pi[\rho D]_1 r_1^2 k_d$$

$$K_c = \frac{2\pi g^2}{9!}\left[\frac{\rho^3}{\eta^2 D}\right]_1 r_1^8 k_c$$

Subscript 1 outside the brackets in the above equations signify that the gas properties are taken at temperature T_1, h, k_c and k_d known as column shape factors which are complicated functions of y_o, θ_o and $T_1^*\{(T_1/\epsilon/k)$ ϵ is depth of intermolecular potential well and k is the Boltzman constant} for different potential models. These can be computed directly for the column and gas concerned utilizing the temperature variation of transport properties of the gas, of known accuracy. For maximum operational efficiency, theoretically [K_c/K_d] should lie between 5 and 25 and a value of 10 always provides operation at nearly the maximum of efficiency. With T_1 as ambient running water temperature, for the gas obeying a known intermolecular potential, from the appropriate tables of h, k_c and k_d the vales of y_o and θ_o are roughly chosen where h/k_d has a flat maximum.

At these values of Y_o, θ_o and T_1^*, from the available tables h, k_c and k_d can be obtained. Setting [K_c/K_d] = 10 and utilising gas properties at temperature T_1 and atmospheric pressure.

$$\left[\frac{K_c}{K_d}\right] = \frac{g^2}{9!}\left[\frac{\rho^2}{\eta^2 D}\right]_1 r_1^6\left[\frac{k_c}{k_d}\right]$$

Yielding the appropriate value of r_1, radius of the cold-wall for maximum, theoretically efficient operation. Since θ_o and y_o are already chosen, this defines both T_2 and r_2 also. With [2A] known theoretically, one can evaluate the necessary length L of the column for the required final enrichment value of the concerned gas isotope concentration, (C_{bottom}). If the initial concentration of the isotope is $C_{initial}$, and defining

$$q* = \frac{C_{bottom}/(1-C_{bottom})}{C_{top}/(1-C_{top})}$$

Assuming the gas to be a binary isotopic mixture, one gets

$$L = \frac{\ln q}{2A} \qquad And \ln q* = \left[\ln q - \ln\left(\frac{q-1}{\ln q}\right)\right]$$

Having set the column parameters by the above procedure, the actual design will depend on the availability of appropriate tubes and suitability for operational ease of assembly.

A 1m column used in Heavy Water Division for initial experiments was shown in Fig.1. Thermal-diffusion column was designed and fabricated at our division. Column was operated under static condition. Hot wall was formed by a 7.92 mm Kanthal wire. Flow of tap water kept the temperature of the cold wall constant. After getting encouraging results from 1m column a 2m column was fabricated and tested under static conditions. and 2m column were used to test the separation for Neon22. The equilibrium separation factor (q), achieved in 1m column was 2.53 and in 2m column it was 12.93.

Conclusion

The positive aspects of the thermal-diffusion as a process of isotope separation are (i) the extreme simplicity of the equipment involved consisting mainly of coaxial tubes, wires valves and special seals, and (ii) large overall separation factors the process is associated with, leading to high purity
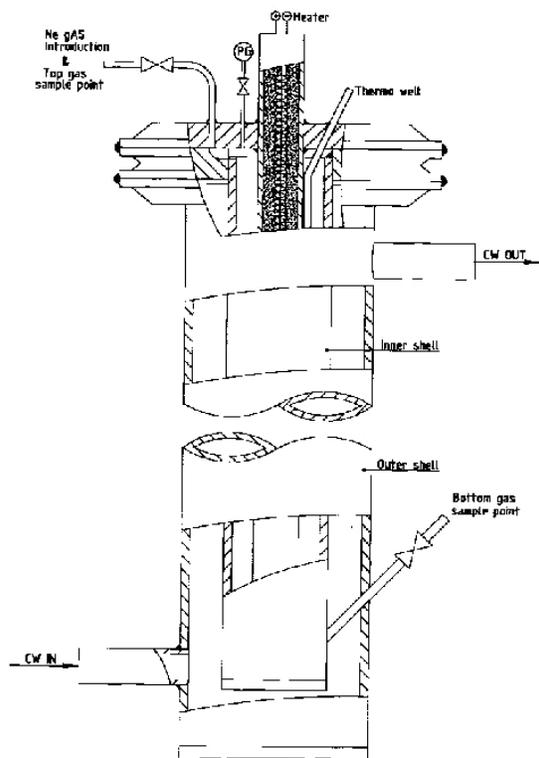
Fig. 1   Test set up for thermal diffusion

separations. As against these advantages of simplicity and performance efficiency, the process proves to be very expensive when account is taken of the heavy input of energy needed to maintain a high temperature gradient across the inner and outer tubes over prolonged periods. The time needed for the attainment of equilibrium is of the order of weeks or even months.

Today, thermal-diffusion remains a practical process to separate isotopes of noble gases (e.g. xenon) and other light isotopes (e.g., carbon) for research purposes.

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NUCLEUS

Element 111 named as Roentgenium

Element 111 was synthesized and characterized by S. Hofmann et al[1,2] at Gesellschaft für Schwerionenforschung mbH (GSI) in Darmstadt, Germany in 1994 using the cold-fusion reaction, $^{209}Bi(^{64}Ni,n)^{272}111$. An accelerated beam of ionized ^{64}Ni atoms was made to impinge on a thin ^{209}Bi foil; the reaction recoils were separated in flight from the incoming beam and from the unwanted products of transfer reactions by a velocity filter consisting of a combination of magnetic and electric fields. This facility is known by the acronym SHIP, i.e. Separated Heavy-Ion reaction Products. In bombardments of ^{209}Bi targets with ^{64}Ni using the velocity selector SHIP facility to discriminate in favor of the fused product, $^{273}111$, three sets of localized alpha-decay chains were observed with position sensitive detectors. The origin was assigned to the isotope $^{272}111$, one neutron removed from the compound nucleus. The product atoms were then implanted in position-sensitive solid-state detectors which recorded up to five -particle decay energies. Time-of-flight was also used to estimate the masses of these particles. These five -particle decay energies could be assigned to the chain:

$^{272}111$ $^{268}109$ $^{264}107$ $^{260}105$ ^{256}Lr ^{252}Md

In all, three atoms of $^{272}111$ were observed during the period 8-17 December, 1994, leading to an average half-life of 1.5 ms (uncertainty: +2.0, -0.5 ms).

In 2003, a joint IUPAC-IUPAP Working Party (JWP)[3] confirmed the discovery of element number 111 by the collaboration of Hofmann et al. In accordance with IUPAC procedures, the discoverers proposed a name and symbol for the element. Following the 80th Meeting of the Bureau in Bled, Slovenia, the proposed name roentgenium for the element of atomic number 111, with symbol Rg was officially approved as of 1 November 2004.

Roentgenium's most stable isotope, roentgenium-280, has a half-life of about 3.6 seconds. It decays into meitnerium-276 through alpha decay

1. S. Hofmann et al., Z. Phys. A 350, 281-282 (1995)
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Super heavy elements with atomic number 100 and above

Atomic number	Name and (Symbol)	Year discovered /synthesized	Mode of discovery /synthesis	No. of isotopes	Mass range	$T_{1/2}$ range
100	Fermium (Fm)	1952	Debris of thermonuclear testing Bombardment of U with oxygen	19	242-260	0.8 ms – 100.5 d
101	Mendelevium (Md)	1955	Bombardment of Es with α particles	14	247-260	3 s – 27.8 d
102	Nobelium (No)	1965	Bombardment of Am with nitrogen	12	250-262	250 μs – 58 m
103	Lawrencium (Lr)	1961-71	Bombardment of Cf with boron	11	252-262	346 ms – 3.6 h
104	Rutherfordium (Rf)	1969	Bombardment of Pu with neon Bombardment of Cf with carbon Bombardment of Cm with oxygen	10	253-262	7 ms – 65 s
105	Dubnium (Db)	1970	Bombardment of Am with neon Bombardment of Cf with nitrogen	9	255-263	1.3 s – 34 s
106	Seaborgium (sg)	1974	Bombardment of Cf with oxygen Bombardment of Pb with chromium	6	259-266	3.6 ms – 30 s
107	Bohrium (Bh)	1981	Bombardment of Bi with chromium	4	260-264	12 ms – 440 ms
108	Hassium (Hs)	1984	Bombardment of Pb with iron	5	263-269	80 μs – 1.8 ms
109	Meitnerium (Mt)	1982	Bombardment of Bi with iron	2	266,268	3.4 ms – 70 ms
110	Darmstadtium (Ds)	1994	Bombardment of Pb with nickel	6	267-273	3 μs – 60 ms
111	Roentgenium (Rg)	1994	Bombardment of Bi with nickel	2	272,280	2 ms – 3.6 s