



# Isotope Separation

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Most elements exist in nature as a mixture of isotopes differing in mass as a result of differences in the number of neutrons in their atomic nuclei. Isotopes of an element have very similar physical and chemical properties that make their separation difficult, but some possess distinctly different nuclear properties that make those isotopes particularly useful. This article describes those properties of isotopes that underlie various methods used to concentrate the rarer isotopes, as well as the operating characteristics of separation processes that make them especially useful for large-scale production or for the enrichment of isotopes of a particular element.

Enrichment plants for isotopes such as uranium-235 and deuterium are on an industrial scale yielding hundreds of tons per year. Other isotopes are produced at rates ranging only from grams per day to grams per year (1). However, the scale of production does not necessarily reflect the relative importance of the separated isotopes. Uranium-235 and deuterium are important materials for the nuclear power industry. Deuterium oxide (heavy water) is a coolant and moderator in heavy-water reactors, which use uranium at natural isotopic abundance (0.7% U-235) rather than enriched U-235 as fuel. Deuterium is also a key ingredient of fuels for all types of nuclear fusion schemes currently under development. Lithium-6 may be a useful fuel in fusion reactors and is also a starting material for producing tritium. Boron-10 is used in control rods for fission reactors.

Carbon-13, nitrogen-15, and oxygen-17 are produced in laboratory-scale facilities whose typical capacities are grams per day. These isotopes are powerful tracers for various fields of research in the physical and life sciences because they are nonradioactive and thus physiologically harmless. They occur in nature at low abundances. For this reason relatively low enrichments yield significant signals. Their nuclear magnetic moments make it possible to trace their location in molecules by the technique of nuclear magnetic resonance spectroscopy.

Important needs exist for enriched isotopes of virtually every element in the periodic table, although the required quantities of some may only be on the order of grams per year (2). Some highly enriched stable isotopes are vital to fundamental research in nuclear physics and chemistry, solid state physics, geoscience, and biology and medicine. Many separated nonradioactive isotopes are used as nuclear targets in research reactors or particle accelerators to produce particular radioisotopes, which are then used as radiotracers or radiopharmaceuticals. High isotopic enrichment of the target is a key to avoiding possible undesirable physiological side effects because of the presence of other radioisotopes, which may result from isotopic impurities in the target.

A variety of methods has been developed especially adapted to separating isotopes. Some methods are based directly on mass differences; others result from less obvious mass-dependent changes in atomic and molecular properties.

## Basic Principles of Isotope Separation

Although the common principles underlying isotope separation are relatively few, a large variety of processes has been considered. Examination of processes for separating deuterium turned up 98 potential candidates, and one study group evaluated at least 25 known processes other than gaseous diffusion and gas centrifuges (3) for separating uranium isotopes. All the processes have some merit for the separation of isotopes, but evaluating them depends on several factors, the two most important being (1) whether isotopes of light weight (e.g., deuterium), intermediate weight (e.g., nitrogen), or heavy weight elements (e.g., uranium) are to be separated and (2) whether the quantities needed are grams (as in research) or tons (as for use in power reactors). The choice depends on the properties of the element, the degree of separation needed, and the scale and continuity of the demand; even for a given isotope, there is no one best method. For large-scale applications availability of feed materials, capital costs, and power requirements may be the overriding considerations, while for laboratory needs simplicity of operation or versatility may be primary.

More than 30 years ago Manson Benedict and Thomas Pigford (in the first edition of ref 1) drew general conclusions that are still valid regarding isotope separation methods:

1. the most versatile means for the production of small quantities of isotopes is the electromagnetic method;
2. the simplest and most inexpensive means for small scale separation of many isotopes is thermal diffusion;
3. distillation and chemical exchange are the most economical methods for large-scale separation of the lighter elements; and
4. gaseous diffusion and the gas centrifuge are most economical for large-scale separation of the heaviest elements.

In addition, laser-induced isotope separation (LIS) has become an extremely attractive method for separating isotopes of many elements as a result of recent advances in laser technology (4) and probably one of the most economical options for future large-scale production of isotopes of heavy elements such as Pu and U.

Since isotopic molecules have very similar properties, the degree of separation achieved in a single separating unit device (e.g., for distillation, a vessel containing a multicomponent liquid and its vapor phase in equilibrium with each other) is usually extremely small. A *separating unit* for any process can be envisioned as a "black box" (Fig. 1) that separates a single feed stream into a product stream—somewhat enriched in the desired isotope—and a waste stream—somewhat depleted in that component. The degree of separation achieved in such a unit is measured by a parameter called the *elementary separation factor*,  $\alpha$ , which is defined as the abundance ratio of the isotopes in the product stream divided by the same ratio for the waste stream:

$$\text{elementary separation factor} = \alpha = \frac{[x/(1-x)]_{\text{product}}}{[x/(1-x)]_{\text{waste}}}$$

Here,  $x$  is the mole fraction of the desired isotope. If  $\alpha$  is unity, no separation occurs. For typical processes (other than electromagnetic and laser isotope separation, and processes operating at cryogenic temperatures) and for most elements (other than hydrogen),  $\alpha$  is at most only several percent different from unity and often only tenths of a percent away from unity. A single separating stage can thus increase the enrichment by only a few percent or less, relative to the enrichment level of its feed.

To achieve a useful enrichment, it is thus necessary to construct a stack of *separating stages* in which the product stream from a lower stage is fed to the next higher stage, whose product is in turn fed to the stage above, and so on. [The lower stages always contain less enriched material than those above.] In fact, the waste streams from upper stages usually contain desired isotope concentrations higher than the natural abundance, so they are recycled as part of the feed to an appropriate lower stage. Such a stack of interconnected stages is called a *separation cascade*. Another engineering consideration comes into play in designing a cascade. If the streams to be joined to form a feed to another stage in a cascade are of different isotopic compositions, some of the work used to effect isotope separation would be wasted since the isotope mixing undoes the isotope separation. In the most efficient cascade, called an *ideal cascade*, joined streams are always of equal isotope enrichment. Because the enrichment level of the desired isotope in the feed stream to a plant is low relative to that in the product of the plant, the stages of an ideal cascade near the feed point must handle considerably higher material flow rates than those closer to the product end in order to satisfy the material conservation (vide infra) and the no-mixing requirement. The higher flow stages should therefore contain larger flow-capacity separative units or a larger number of small units connected in parallel.

Material conservation at steady state (see Fig. 1) requires that the total amount of material fed into the stage be balanced by the amounts leaving in the product and waste streams and further that the quantities of the desired isotope in the two exit streams equal the amount of the isotope that entered the stage:

$$\text{total material balance: } F = P + W$$

$$\text{isotopic material balance: } Fx_f = Px_p + Wx_w$$

Here  $F$ ,  $P$ , and  $W$  symbolize the molar flows in the feed, product, and waste streams, and  $x$  again represents the mole fraction of the desired isotope. These two material-balance conditions, together with the elementary separation factor, govern the steady-state operation of a separating unit. In fact, a similar set of three equations can be applied to either a separative unit or a stage, and the performance of an entire cascade is governed by the overall material balance equa-

tions and the cumulative effect of the separative capability of the individual units.

More detailed theoretical treatments of cascade parameters will be found in the references (see particularly 1, 3, 5-7). Now to illustrate the principles just outlined, the article will provide brief descriptions of several isotope-separating processes used (or proposed) on the industrial or laboratory scales.

### Separation Processes

#### Gaseous Diffusion (1, 6-9)

Gaseous diffusion was used to produce most of the  $^{235}\text{U}$  separated during World War II. The current  $^{235}\text{U}$  enrichment capacity of the world is still provided mostly by gaseous diffusion plants. In each stage of the process, gaseous uranium hexafluoride ( $\text{UF}_6$ , the only volatile compound of uranium at ambient temperatures) flows through a diffusion barrier with very fine holes from a high-pressure chamber into a lower pressure region. This phenomenon is gaseous effusion, although the process is usually termed gaseous diffusion. In this article we will use the conventional term, gaseous diffusion. [“Diffusion” here is a misnomer. Molecules diffuse through a medium under a uniform pressure and nonuniform composition, like the automobile exhaust thinning out in the air.] The lighter  $^{235}\text{UF}_6$  molecules have a slightly higher mean speed than their  $^{238}\text{UF}_6$  counterparts; therefore, the gas passing through the barrier is slightly richer in  $^{235}\text{U}$  than the portion remaining behind. The mean speeds of the molecules are in inverse ratio to the square roots of the molecular weights of the isotopic molecules:  $(^{238}\text{UF}_6/^{235}\text{UF}_6)^{1/2} = (352/349)^{1/2} = 1.0043$ , the elementary separation factor for  $^{235}\text{U}/^{238}\text{U}$  enrichment by gaseous diffusion.

The low separation factor per stage requires the use of many enriching stages in a countercurrent cascade to produce a useful degree of enrichment. Figure 2 depicts schematically the operation of a stage, and Figure 3 shows the arrangement of three stages in a cascade. The gas in the enriched stream is at a lower pressure, so it must be recompressed before it is fed to the next higher stage. This recompression accounts for the high electrical power usage of such enrichment plants; about 70% of the operating expenses of a gaseous diffusion plant (exclusive of feed material) is for electricity. An “ideal cascade” to separate natural uranium feed containing 0.71%  $^{235}\text{U}$  into a product containing 3%  $^{235}\text{U}$  and waste containing 0.2%  $^{235}\text{U}$  requires 1272 separating stages of varying size and capacity arranged in series as in Figure 3. (To produce product containing 90%  $^{235}\text{U}$ , at the same feed and waste compositions, would require 3919 stages.) Figure 4 shows the arrangement of stages in an “ideal” cascade, one in which the compositions of streams from the upper and lower stages at each enrichment level are equal (Fig. 3).

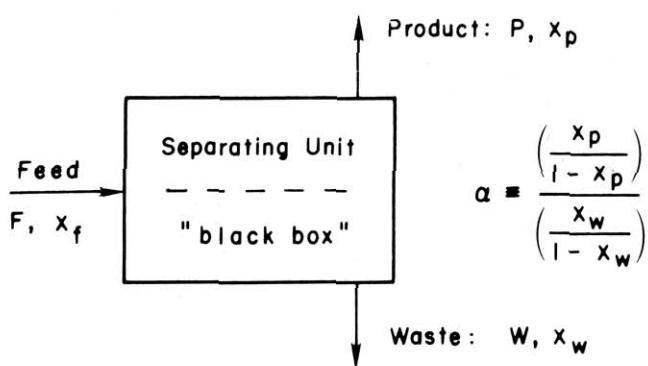


Figure 1. An elementary separation stage.

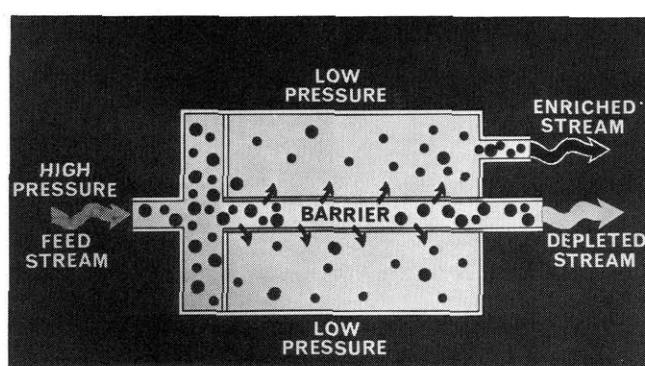


Figure 2. A gaseous diffusion stage.

Many of the operating parameters of an enriching plant that make large contributions to the cost of enriched product (other than the cost of feed material) are proportional to a simple mathematical function of the isotopic abundances and the quantities (moles or kilograms) of the feed, product, and waste streams entering and leaving the plant. This function—applicable to an ideal separating cascade and called the *separative work* (1, 6, 7)—is a measure of the value added by the enriching plant to the material processed. The separative work is proportional to the quantity of the enriched product, and increases with the change in the enrichment levels of product and waste away from that of the feed. It does not, however, depend on the stage separation factor. The cost of an enriched product is proportional to this separative work, which is a measure of the quantity of separation achieved, and an additional factor—a function of the separation factor and thus dependent on the efficiency of the separation process. Thus the relative merits of various separation

processes can be discussed in terms of their costs per *separative work unit (SWU)*. The conventional unit for the SWU for  $^{235}\text{U}$  is kilogram or metric ton of uranium.

For a plant with a single waste, product, and feed stream, there are three mole-fraction variables and three quantity variables, of which only four can be specified independently because of the two material balance requirements. Thus, for instance, two plants each taking the same fixed feed concentration and yielding the same amount of product enriched to the same isotopic concentration and the same waste assay have the same SWU's per year, no matter what separation principle and engineering design they operate on. A plant of a given SWU capacity may be run (a) to produce either a small quantity of material at high enrichment or a larger quantity at lower enrichment and (b) to maintain a given quantity and quality of product by extracting more  $^{235}\text{U}$  from the feed (lower waste assay) when natural uranium is in short supply and allowing a stream of higher  $^{235}\text{U}$  assay to leave the plant when feed material is plentiful.

The gaseous diffusion plants in the world have a combined annual capacity of about 50 million SWU's or 50 thousand metric tons of uranium enrichment, of which the United States and the Soviet Union have, respectively, capacities of 27 million SWU's/yr and about 10 million SWU's/yr (9). Gaseous diffusion plants also exist in France, England, and China.

Overall, the advantages of the gaseous diffusion process are its proven reliability and demonstrated ability (over more than 40 years) to operate at a capacity factor of over 99%. Among its disadvantages are its high energy consumption—about 2200 kilowatt hours per SWU—an inevitable consequence of the need to recompress the gas many times—and its need for large installations to make economical operation possible.

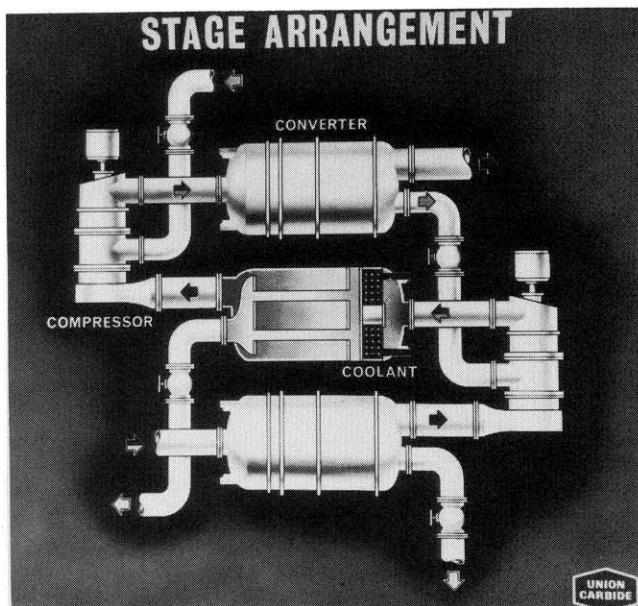


Figure 3. Arrangement of gaseous diffusion stages.

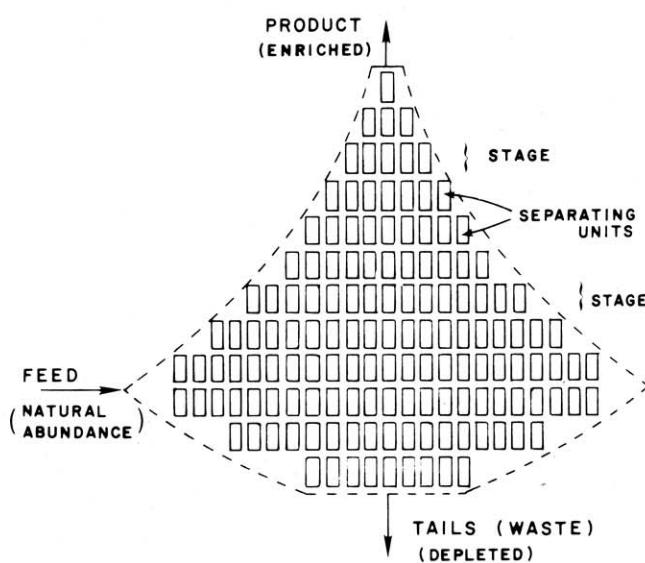


Figure 4. A schematic representation of relative flow rates of an ideal cascade.

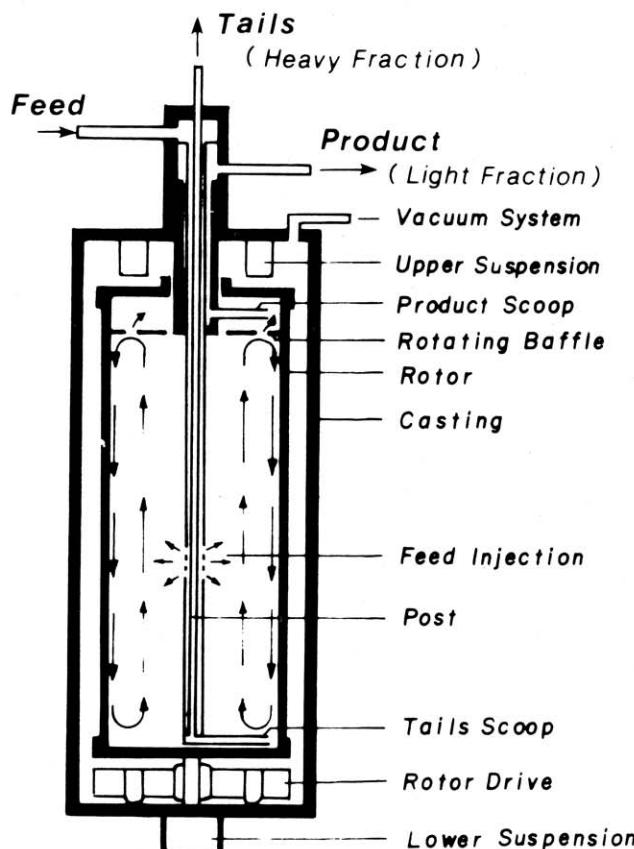


Figure 5. Gas centrifuge.

### Gas Centrifugation (1, 6-11)

When gaseous uranium hexafluoride spins in a centrifuge at a high rotational speed, the heavier  $^{238}\text{U}$  molecules move preferentially toward the periphery, leaving the inner zone enriched in  $^{235}\text{U}$ . Modern developments in this method (see e.g., Fig. 5) are all variants of the countercurrent gas centrifuge design of Gernot Zippe.  $\text{UF}_6$  gas enclosed within a rapidly rotating cylinder is subject to centrifugal acceleration thousands of times greater than gravity. At peripheral speeds above 500 m/s, which would be made possible if current centrifuges use rotors composed of high-performance carbon fiber- or aramide-reinforced polymer composites (7), the  $^{235}\text{U}$  content at the center of the cylinder could be as much as 18% greater than at the periphery. A system of rotating baffles and stationary scoops induces longitudinal countercurrent gas flow with light gas (rich in  $^{235}\text{UF}_6$ ) flowing upward near the axis and heavy gas (depleted in  $^{235}\text{U}$ ) flowing downward near the periphery. This sets up a cascade of multiple separative elements in a single centrifuge and, in a sufficiently tall centrifuge, a  $^{235}\text{U}$  concentration ratio as high as 2 between the top and bottom; the enriched product is then withdrawn from the top of the cylinder. Only seven stages would be needed in an ideal cascade to produce 3%  $^{235}\text{U}$  product and waste at 0.25%.

The intrinsic separation factor in centrifuges is proportional to the difference in the masses of isotopic molecules rather than the ratio (or its square root) of the masses. Therefore, this process is best suited to a system such as  $^{235}\text{UF}_6$ - $^{238}\text{UF}_6$ , which has a mass difference of 3 mass units. Unfortunately, uranium hexafluoride condenses at pressures higher than  $\frac{1}{6}$  atm at room temperature. This, coupled with the fact that at the periphery of a centrifuge the pressure is millions of times the pressure near the axis, necessarily makes the throughput of gas (the amount of material processable in a given time) by an individual centrifuge quite low. Thus, a centrifuge plant with a capacity of 3,000,000 kg SWU/year producing 3%  $^{235}\text{U}$  would need 60,000 centrifuges, each 10 m long, to do the separative work produced by 1200 gaseous diffusion stages. On the other hand, the electrical energy consumed would be only 90 kwh/SWU as opposed to 2200 kwh/SWU for gaseous diffusion.

Among centrifuge plants existing or designed around the world are a plant with a capacity of about 1 million SWU's per year built and operated by a joint British, Dutch, West German venture; a plant with an annual capacity of 2.2 million SWU's per year designed by the U.S. Department of Energy at Portsmouth, Ohio; and in Japan a prototype plant with a 200,000 SWU's per year capacity built and operating, and another with a capacity of 1.5 million SWU's per year scheduled for completion in 1991.

### Laser Isotope Separation (1, 6-9, 12, 13)

This process takes advantage of the small differences in absorption spectra of isotopic species. The electronic absorption spectra of isotopic atoms differ slightly; the electronic-vibrational-rotational interactions of molecules with electromagnetic radiations (i.e., light— infrared, visible, or ultraviolet) are also altered by isotopic substitution. By using sufficiently monochromatic light of an appropriate wavelength, a particular isotopic species is preferentially excited to an upper energy level. The excited species must then be separated from its isotopic partners, before it exchanges isotopes or before it loses excitation, by some physical or chemical process. The technique was successfully used to separate small quantities of mercury isotopes almost three decades ago. Attention has been focused on these methods by the recent development of narrow-band, tunable lasers of high intensity and high repetition rate. Laser methods have been notably successful in achieving separation of isotopes of elements such as hydrogen, boron, chlorine, sulfur, and bromine, but the greatest importance of the

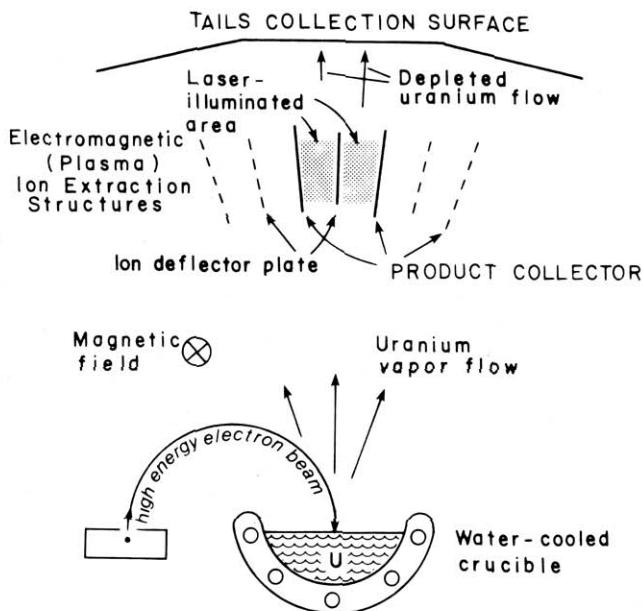


Figure 6. Cross-sectional view of an atomic vapor laser isotope separation module.

method is likely to lie in its potential as a next generation process for uranium isotope separation.

One such process, called atomic vapor laser isotope separation (AVLIS), is illustrated in Figure 6. Atoms of uranium heated in a high vacuum chamber by a high energy beam of electrons vaporize and flow upward through a region between a pair of negatively charged plates. The space between the plates is illuminated by light from a system of lasers passing through in the direction perpendicular to the page. Laser photons with an appropriate wavelength selectively excite  $^{235}\text{U}$  atoms but leave  $^{238}\text{U}$  atoms unexcited. At least one additional laser beam is used to ionize the excited  $^{235}\text{U}$  atoms. The ionizing photons have energies sufficiently high to ionize the already excited  $^{235}\text{U}$  atoms but insufficient to ionize unexcited  $^{238}\text{U}$  atoms. The  $^{235}\text{U}$  ions are then collected by negatively charged plates, while  $^{238}\text{U}$  atoms continue their upward flow until condensed on the ceiling surface. It is a major attraction of the method that under ideal conditions a complete separation of  $^{235}\text{U}$  and  $^{238}\text{U}$  in a single LIS stage is theoretically possible.

The future of the LIS process depends on successful development of laser systems. Since even the largest energy difference between the atoms of  $^{235}\text{U}$  and  $^{238}\text{U}$  corresponds only to a change on the order of 1 in 50,000, the excitation laser photon energy must be tuned more closely than this to avoid accidental excitation of  $^{238}\text{U}$  atoms. Lasers generate pulses (or packets) of photons at a fixed repetition rate. The lasers for the LIS must have a sufficiently rapid repetition rate to catch all the  $^{235}\text{U}$  atoms passing between the collection plates;  $^{235}\text{U}$  atoms left unionized by the lasers will not be collected by the plates, thus reducing the effective separation factor. Only a fraction of laser photons passing through an LIS chamber is actually absorbed by uranium, and it takes one mole of absorbed photons to excite one mole of uranium atoms. Thus, LIS requires a high-power (high photon production rate), rapid-repetition, finely tunable laser. Since a higher density of uranium atoms in the illuminated region increases the likelihood of collision between excited  $^{235}\text{U}$  atoms and  $^{238}\text{U}$  atoms, which can produce excited  $^{238}\text{U}$  atoms at the expense of de-excited  $^{235}\text{U}$ , the throughput of LIS processes is necessarily low.

In spite of these technical difficulties, LIS for  $^{235}\text{U}$  (13) holds high promise because of the theoretical possibility of

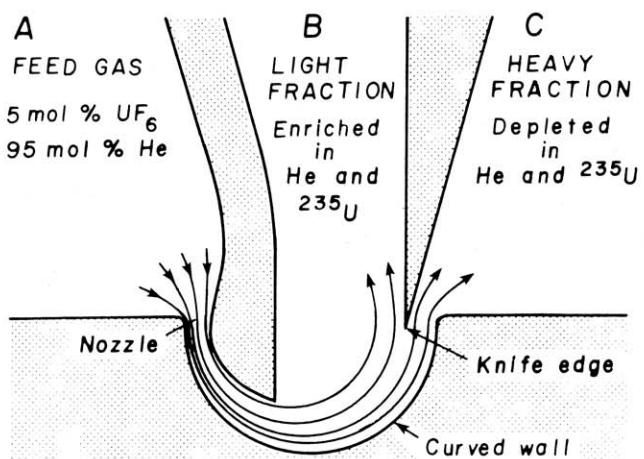


Figure 7. Operating principle of the separation nozzle.

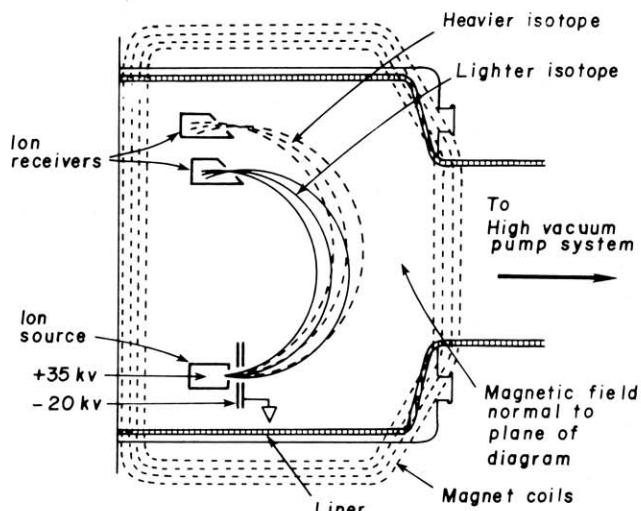


Figure 8. Diagram of a Calutron separator (14).

its extremely high separation factor. The laser isotope separation processes other than the AVLIS for  $^{235}\text{U}$  that have been developed include the molecular LIS for  $^{235}\text{U}$ , in which  $\text{UF}_6$  is working material, and "Special Isotope Separation" for converting fuel-grade [7 to 19%  $^{240}\text{Pu}$ ] into weapon-grade [less than 7%  $^{240}\text{Pu}$ ] by removing unwanted isotopes such as  $^{240}\text{Pu}$  from  $^{239}\text{Pu}$ .

#### Separation Nozzle (1, 3, 6-8, 9)

This aerodynamic process achieves partial separation of isotopes in a flowing gas stream subjected to high linear or centrifugal acceleration, or both. A cross section of an improved separation nozzle developed in 1967 by E. W. Becker and his co-workers in Germany is shown in Figure 7. A feed gas, typically consisting of a mixture of about 5 vol%  $\text{UF}_6$  and 95%  $\text{H}_2$  at a pressure of about 1 atm, passes through a nozzle with first a convergent, then a divergent cross section into a lower pressure region. The change in cross section accelerates the mixture to supersonic speed, and the curved groove produces centrifugal acceleration. The gas adjacent to the curved wall is preferentially enriched in  $^{238}\text{U}$ , and the knife edge downstream divides the stream into a (waste) portion depleted in  $^{235}\text{U}$  (region C) and a portion enriched in the light isotope (region B).

The separation factor increases with the mean speed of the gas molecules and with their centrifugal acceleration. Therefore, a larger pressure ratio between the feed and product gases, a narrower throat width at the entrance, and a smaller radius of curvature of the curved groove all contribute to increasing the separation factor. But the resulting miniaturization of nozzle elements reduces the throughput and makes fabrication of the elements a formidable task. A separation factor of 1.015 has been achieved with a mixture of 5%  $\text{UF}_6$ -95%  $\text{H}_2$  flowing through a pressure ratio of 3.5. The dilution of  $\text{UF}_6$  with a gas of low molecular weight yields (1) a higher sonic velocity and thus a higher separation factor and (2) higher diffusion rates of  $\text{UF}_6$  molecules, which allow operation at higher product pressures and correspondingly increased uranium throughput. The Becker nozzle process offers a higher separation factor than gaseous diffusion, but the 20-fold dilution of  $\text{UF}_6$  also makes power consumption (about 3000 kwh/SWU) higher than for gaseous diffusion. A demonstration cascade of about 0.3 million SWU/yr has been operated in Brazil with technical assistance from West Germany.

#### Electromagnetic Separation (1-3, 13)

In this process, the principle is essentially that of a large-scale mass spectrometer, and its use dates back to the World War II Manhattan District Project when such machines were used to separate  $^{235}\text{U}$  in kilogram quantities. Since the end of World War II, the electromagnetic separators (called Calutrons for California University Cyclotron because they were originally developed at the University of California by E. O. Lawrence) have been used for separating an amazing variety of isotopes, both stable and radioactive. Figure 8 shows a diagram of a Calutron. A retrospective paper by L. O. Love (14) describes activities at Oak Ridge National Laboratory (ORNL) in this area over three decades. See ref 2 for a discussion of needs for various isotopes of practically every element that can be separated by this versatile method, and a description of the current ORNL electromagnetic separation program.

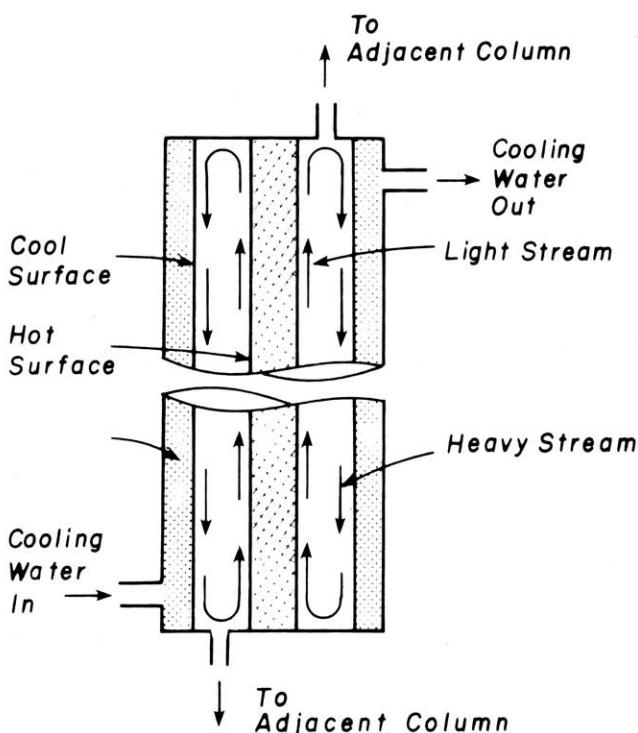


Figure 9. Thermal diffusion column.

### *Thermal Diffusion (1, 3, 6)*

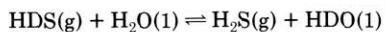
The thermal diffusion effect—namely, that a concentration gradient is produced in a gaseous mixture subjected to a temperature gradient (e.g., in a vessel with walls at different temperatures)—was transformed from a laboratory curiosity into a useful and simple method for separating fluid mixtures (including mixtures of isotopes) by the invention of the thermal diffusion column by Ausius and Dickel in 1938. The operating principle of such a column is illustrated in Figure 9. A fluid is confined in a long vertical cylinder between an inner wall, kept at a higher temperature, and an outer wall, kept at a lower temperature. A counter-current convective flow is set up in the fluid, as indicated in the figure, descending along the cool wall and rising adjacent to the heated wall. Since horizontal slices of the column at different levels along the column length act as unit separation stages, the countercurrent vertical flows multiply the small (less than 1%) isotopic concentration difference between the two walls, so that a single column contains a large number of separating stages.

Laboratory-scale cascades suitable for daily separation of milligram quantities of isotopes in gaseous form are remarkably simple to construct and operate. Notably, the isotopes of the noble gases are separated by this method.

### **Chemical Exchange (1, 3, 5, 6, 15–17)**

Isotopic exchange equilibria, which lead to unequal distribution of isotopes among different exchanging chemical species, result from differences in vibrational frequencies of the isotopic molecules. The magnitude of the separative effect depends on the fractional difference in isotopic masses,  $\Delta m/m$ , and on the difference in free energy (produced by the mass difference) in a pair of different chemical species (3, 5, 15). The first criterion leads to the conclusion that chemical exchange is most effective for separating isotopes of the lighter elements and becomes increasingly difficult as one proceeds to heavier elements [ $>$  sulfur]. The second criterion leads one to expect a large separation effect between two molecules, one in which the isotopic atom is unbonded or weakly bonded, and another in which it is connected by a maximum number of strong bonds. Unfortunately, such compounds do not necessarily undergo isotope exchange rapidly, and exchange processes often require a catalyst to promote the reaction at an effective rate.

Reactions that have been used to produce quantities of separated isotopes include the exchanges:  $\text{H}_2\text{O}(\text{liq})/\text{HDS(gas)}$ ;  $\text{H}_2\text{O}(\text{liq})/\text{HD(gas)}$ ;  $\text{NH}_3(\text{liq})/\text{HD(gas)}$ ;  $\text{H}^{14}\text{NO}_3(\text{aq})/\text{H}^{15}\text{NO(gas)}$ ;  $^{12}\text{CN}^-(\text{aq})/\text{H}^{13}\text{CN(gas)}$ ;  $^{10}\text{BF}_3$ -ether(complex)/ $^{11}\text{BF}_3(\text{gas})$ , and  $\text{H}^{32}\text{SO}_3^-(\text{aq})/\text{H}^{34}\text{SO}_2(\text{gas})$ . For example, the first pair in this list represents an exchange reaction,



for which the separation factor is equal to the equilibrium constant, 2.37 at 25 °C and 1.84 at 125 °C. These values are unusually high for an isotope separation factor. This reaction, and the others in the above list involving exchanges of hydrogen and deuterium, have been and are being used in plants producing thousands of tons of D<sub>2</sub>O annually (16).

The elementary exchange effects are multiplied in long exchange columns similar to those used for distillation. In contrast to distillation, where reflux at the ends is effected by a boiler (at the bottom) to evaporate the liquid, and a condenser (at the top) to liquify the vapor, exchange columns use chemical reactors at each end to interconvert the exchanging species. Figure 10 shows the analogy between the gas-liquid exchange process and distillation. The nitrogen isotope exchange between nitric oxide and nitric acid will be explained in some detail below to illustrate these and other important points concerning chemical exchange methods. The reaction,

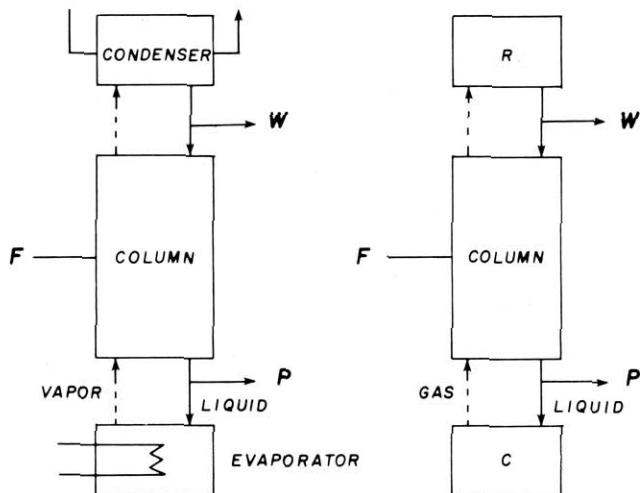
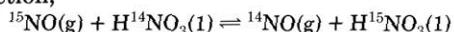


Figure 10. Analogy between distillation and gas-liquid chemical exchange. R = reflux converter; C = chemical reactor or electrolytic cell; F = feed; P = product; W = waste.

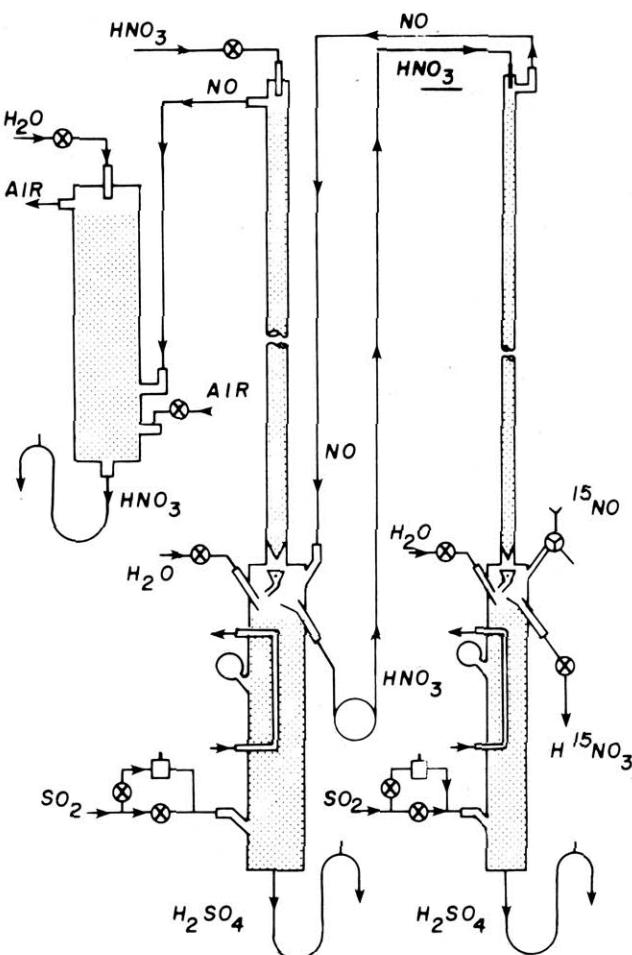


Figure 11. Schematic diagram of a two-section cascade for preparing highly enriched nitrogen-15 by the Nitrox process.

(termed the Nitrox process) has been widely used throughout the world in laboratory-scale cascades to produce grams per day of nitrogen-15 enriched to purities up to 99.8%  $^{15}\text{N}$  from the natural abundance of 0.37%.

Such a two-column Nitrox process (17) is schematically shown in Figure 11. Because the system consisting of nitric oxide and nitric acid in chemical equilibrium also contains several other chemical species such as  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , and  $\text{HNO}_2$ , these molecules also participate in nitrogen isotope exchange and thus contribute to the overall isotope fractionation, making it dependent on temperature, pressure, and acid concentration. The elementary separation factor at 25 °C under 1 atm in 10 M  $\text{HNO}_3$  is 1.055. In Figure 11 the first exchange column (a packed column, 2.5 cm diameter and 5.2 m long) produces 6.8%  $^{15}\text{N}$ , and the second column (0.9 cm diameter and 5.5 m long) brings it up to a maximum concentration of 99.9%  $^{15}\text{N}$  at a rate of 0.5 g/day.

As in distillation, each exchange column contains multiple separative stages, and the  $^{15}\text{N}$  abundance in the exchanging species increases as one goes from the top of each exchange column toward the bottom. Thus, at the lower end of the first column, most of the "nitric oxide" containing approximately 6.8%  $^{15}\text{N}$  has to be returned to the column. This is accomplished by the first reflux column, which reduces the nitric acid of 6.8%  $^{15}\text{N}$  enrichment. The reduction is effected by bubbling  $\text{SO}_2$  up the packed column through which the nitric acid descends. Water is introduced near the top of the reflux column to dissolve and wash down the higher oxides of nitrogen ( $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ) so that they can be further reduced to NO. The  $\text{SO}_2$  is oxidized to sulfuric acid, which leaves the refluxer at the bottom. The needs for chemical feed (e.g.,  $\text{SO}_2$ ) and disposal of the chemical waste (e.g., 10 M  $\text{H}_2\text{SO}_4$ ) are the main drawback of chemical exchange methods. In spite of this, the exchange methods are simple to set up and energetically economical mainly because they use thermodynamically reversible processes.

The use of a two-column system in Figure 11 is a compromise between ideal cascade and reality. Referring to Figure 4, an ideal cascade calls for a smooth decrease in the flow rates from the feed point to the product end. The ideal cascade is most efficient in terms of separative work needed, but an ideal chemical exchange plant would have needed a refluxer for every step-down of the flow rate.

### Distillation (1, 3, 5, 6)

H. C. Urey discovered the heavy isotope of hydrogen, deuterium, in 1932 by concentrating it sufficiently through distillation of liquid hydrogen and detecting it for the first time spectroscopically. The method, which is one of the common chemical engineering processes for separating chemical substances by differences in volatility, has also been used for isotope separation. A compound containing heavier isotopes is usually less volatile than its isotopic counterpart containing lighter isotopes. Deuterium has been concentrated by distilling either liquid hydrogen or water. Isotopes of carbon, nitrogen, and oxygen have been produced by distilling compounds such as carbon monoxide, nitric oxide, and water.

The energy consumed by distilling water to produce heavy water is relatively high, due partly to the fact that heavy

water is less volatile than light water. This makes distillation less competitive than chemical exchange processes for primary enrichment of heavy water. However, the high throughput (the amount of material processed per unit time per unit volume of a separation plant), its reasonably high separation factor (1.027 at 100 °C), design simplicity, and operational reliability make it useful for final enrichment—from several percent deuterium to 99.9% D. This illustrates the comment made earlier in this article that, even for a given isotope, there is no one best separation method.

### Conclusions

Critical needs exist for enriched isotopes of virtually every element in the periodic table. The required quantities vary depending on their applications. The annual requirements for some are tons, while others may only be on the order of grams per year. Highly enriched stable isotopes are vital to the nuclear energy industry, fundamental research in nuclear physics and chemistry, solid state physics, geoscience, and biology and medicine. Many separated nonradioactive isotopes are used as nuclear targets in research reactors or particle accelerators to produce particular radioisotopes, which are then used as radiotracers or radiopharmaceuticals. High isotopic enrichment is a key for most of these applications. Usually, there are several methods available for separation of a given isotope, but choice depends on the enrichment level and quantity required for the separated product, availability of suitable feed material, and numerous other factors.

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