Title
ISOTOPES

Author
Lederer, C. Michael

Publication Date
1980-10-01

LBL-10124 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

An abridged version of this report will be published in the Encyclopedia of Chemical Technology, ed. by M. Grayson and D. Eckroth, John Wiley and Sons, Inc., New York (1981)

ISOTOPES

C. Michael Lederer

October 1980

NUCLEAR SCIENCE DIVISION

LBL-10124 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-10124

An abridged version of this report
will be published in the Encyclopedia
of Chemical Technology, ed. by M. Grayson
and D. Eckroth, John Wiley and Sons, Inc.,
New York (to be published in 1981).

ISOTOPES

C. Michael Lederer

October 1980

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

*This work was supported by the Director, Office of Energy Research, Division of Nuclear Sciences of the Basic Energy Sciences Program of the U.S. Department of Energy under Contract W-7405-ENG-48.

Isotopes

C. Michael Lederer

Abstract

Ordinary matter consists of the 286 isotopes of 83 elements that are stable or long lived compared to the age of the earth. For most polyisotopic elements, the relative abundances of the isotopes are remarkably constant. Isotopes are usually assayed by mass spectrometry.

Of many isotope separation methods that have been developed, two (electromagnetic and thermal diffusion) are used commonly to produce small quantities of many isotopes for research purposes, and two others (the GS chemical-exchange process for hydrogen, gaseous diffusion for uranium) are used on an industrial scale. The large-scale use of gas centrifuges for uranium is imminent, and laser separation methods appear promising for uranium, deuterium, and expanded-scale production of research materials.

In addition to the applications of ^{235}U and deuterium in nuclear energy, separated isotopes serve as chemical tracers and as targets or beam particles in radioisotope production and nuclear research. Isotope effects on chemical equilibria and reaction rates are well understood; kinetic effects provide a useful tool for the study of reaction mechanisms. Isotopic substitution in living systems has yielded new knowledge in the biological sciences, as has the study of natural isotopic abundance variations in the geosciences.

ISOTOPES

The term isotope, from the Greek ισος τοπος meaning "same place" (in the periodic table), was coined by Soddy to describe members of the natural radioactive series having the same atomic number (element) but different atomic weights. In 1912 J.J. Thompson demonstrated (1) that neon contained two stable isotopes of mass 20 and 22. (A rarer isotope of mass 21 also exists.) The modern definition of an isotope, based on the nuclear theory of the atom, derives from the hypothesis that the atomic nucleus is composed of protons and neutrons (2). The number of protons, or atomic number Z (equal to the number of electrons surrounding the nucleus), is associated with the chemical properties of the element, whereas the nuclear properties are dependent upon both Z and N, the neutron number. The mass number A (= N + Z) is nearly equal to the atomic mass*, the difference ($\lesssim 0.1$ mass unit) arising mainly from variations in the average nuclear binding energy.

Our environment is composed almost entirely of those isotopes that are stable or that have half-lives of the order of the age of the earth (5×10^{9} y) or longer. There are 286 such isotopes of 83 elements (3). In addition, there are small quantities of short-lived isotopes produced continuously, mostly as daughters of natural thorium (Z = 90) and uranium (Z = 92). Many other isotopes are produced in very small quantities by the interaction of cosmic-ray particles on stable matter; at least two of these--^{3}H and ^{14}C--have important applications. Many radioactive isotopes have been produced artificially; a total of about 1965 isotopes (unique A and Z) of 106 elements are known (3).

Table 1 lists the stable and long-lived isotopes. Many of the elements are polyisotopic. Figure 1 displays the frequency of occurrence of elements with 0, 1, 2,... stable or long-lived isotopes. Certain regularities are evident. Most odd-numbered elements consist of one or two isotopes, whereas most even elements have more than two, with the average near five. Only nine naturally occurring isotopes are odd-odd (that is, odd Z and N, even A). The frequencies of occurrence can be understood statistically from the principles underlying nuclear stability.

Table 1 also lists the natural isotopic abundances of the elements (4,3). The earth and the rest of the solar system, to the extent that we have been able to observe it (e.g., via moon rocks, meteorites), display a remarkably uniform isotopic composition. For a majority of the polyisotopic elements, there is no positive evidence for variations in the relative isotopic abundances. The common exceptions are of two kinds:

(1) Isotope effects produce chemical fractionation of different isotopes of the same element, which are pronounced only for the lightest elements. Natural abundances known to display such variations have footnotes b or d in Table 1.

(2) Elements possessing stable isotopes with long-lived, natural radioactive parents will have varying isotopic compositions, depending on the geologic history of the particular sample. These include argon and calcium (^{40}K decay), strontium (^{87}Rb decay to ^{87}Sr), and lead (natural uranium and thorium decay chains beginning with ^{238}U, ^{235}U, and ^{232}Th, ending with ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively). Abundances subject to variation because of radioactive parents have the footnote f in Table 1.

---

* The atomic mass scale is defined by M(^{12}C) $\equiv$ 12.

The causes of the variations are much better understood than the reason for the general lack of variations in the natural isotopic abundances. The synthesis of matter is a nuclear process; it is dependent on nuclear characteristics such as cross sections and nuclear level properties and on ambient conditions such as temperature and density. The classic study of nucleosynthesis (5) hypothesizes that most elements are produced in stars, by processes that are taking place continuously; only hydrogen and helium existed in the primordial material of the universe produced by the "big bang" (6). In order to explain the isotopic (and elemental) abundances, it is necessary to invoke as many as eight processes, which take place under a variety of very different conditions characteristic of different stages of stellar evolution. The implication of this hypothesis, now generally accepted, is a universe with nonuniform abundances, since the relative rates at which the processes are occurring depend on the locally varying populations of stars in different stages. Recent studies (7) have shown the existence of abundance anomalies in meteorites, whose explanation in terms of different nucleosynthetic events has been the subject of some debate (8).

The uniformity of normal terrestrial material is illustrated by the precise measurement of some titanium isotope ratios for several different sources (see Table 2). Because of this uniformity, the atomic weights of most elements are well defined, so that it is possible to do elemental assaying by gravimetry to high precision. Uniform abundances also provide an invariant background against which to measure exceptional effects. As an example, the last row of Table 2 shows the slightly anomalous ratios of titanium isotopes recently observed in material from a meteorite (7). Some additional anomalies are discussed in the section on applications of isotopes.

To summarize, most of the elements are polyisotopic. The abundances of different isotopes of the same element are for the most part uniform. The chemical (and thus the biological) properties of substances are very slightly influenced by the isotopic composition of the elements.*

Nevertheless, isotopes play a significant role in research and technology. Most important, certain isotopes form the basis for nuclear technology. Uranium, plutonium, and hydrogen isotopes head the list; boron and lithium are also important. Second, because chemical properties are little altered by isotopic substitution, isotopes make excellent labels for atoms within compounds. Not only do they provide a convenient way to assay for an element, they also can act as probes of chemical structure and of reaction mechanisms. Third, the high-energy ionizing radiations emitted by radioisotopes have important applications and pose environmental problems in the development of nuclear energy. Isotopes thus play an important role in nuclear technology and in basic and applied science generally.

The primary instrument for detection and measurement of isotopes is the mass spectrometer, in which a substance is vaporized and ionized, accelerated by an electric field, and the resulting ion beam analyzed by a magnetic field or a combination of electric and magnetic fields. The field of mass spectrometry has been reviewed in a number of books (9) and is the subject of several series of international conferences, most recently in 1979 (10). The resolution requirements for isotopic analysis, $\Delta M/M << 1/A$, are not stringent. The measurement of accurate isotope ratios encounters a number of problems including partial fractionation of isotopes in the ion source, which may

---

* Deuterium is an exception. See section 2.5.2.

change the apparent ratios by as much as 1% per mass unit. In order to circumvent such problems, absolute or calibrated measurements--comparison to known standards prepared by mixing separated isotopes--are required. Isotopic ratios have been measured with mass spectrometers with reproducibilities as high as 0.002% and absolute accuracies as high as 0.05% (11).

Nuclear magnetic resonance (NMR) provides in principle a method to detect and assay isotopes that possess a magnetic moment. However, isotopes with spin >1/2 can be difficult to detect because of the broadening of the NMR resonance by quadrupole interactions. Twenty-four elements possess an isotope with spin 1/2, five of them monoisotopic. Only three natural elements are completely undetectable by NMR--argon, cerium, and thorium.

Most isotopes can be detected and assayed by nuclear activation--bombardment with neutrons or charged particles to produce a radioisotope whose characteristic radiations can then be identified and counted. The technique most commonly employed is neutron activation analysis--irradiation in a thermal position of a nuclear reactor followed by analysis of the gamma-ray spectrum. Activation analysis is most commonly used for simultaneous assay of trace elements in a complex sample.

Atomic absorption and emission spectra contain lines characteristic of individual isotopes that may be used for measurement. Most often used are vibrational lines in the infrared region. In cases where the sample consists of a well-established compound, a combination of a stoichiometric method (e.g., titration) and a gravimetric one can be used to determine the isotopic composition of an element with two isotopes.

1. Isotope Separation

The production of isotopically enriched substances generally requires separation of the isotopes of natural elements. There are several alternatives applicable in special cases. ^{3}He is produced as a decay product of radioactive ^{3}H (tritium) by the reactions

$$^{6}Li + n \rightarrow {}^{4}He + {}^{3}H$$

$$^{3}H \xrightarrow[t_{1/2}=12.33\ y]{\beta^{-}} {}^{3}He \quad .$$

In this case the low natural abundance of ^{3}He and the fact that it is an easily separated by-product make its production by a transmutation reaction economic. More generally, the use of nuclear reactions for stable isotope production is not practical; the value of a reactor neutron, the cheapest projectile, is too great, and the separation of a product from radioactive by-products or contaminants entails special, costly processing. The problem of handling radioactivity and the generally low isotopic purity of fission products also makes it impractical to separate stable isotopes from nuclear waste. Natural radioactivity gives rise to stable daughter elements enriched in one or more isotopes. For example, Table 3 shows the composition of two lead samples, one of "common" lead, the other of radiogenic origin, the latter evidently formed mainly by the decay of ^{238}U. Relatively pure ^{87}Sr may be isolated from a rubidium source of low natural strontium content. Of the above alternatives to isotope separation, only the production of ^{3}He by the $^{6}Li(n,\alpha)^{3}H(\beta^{-})$ reaction is commonly used.

Table 4 lists the most important classes of processes that have been used or proposed for isotope separation. With the exception of the electromagnetic and laser processes, all have small intrinsic separation capabilities, and thus require the use of many separations in series to achieve a product of high isotopic purity. Because of this fact, all processes developed to date are expensive, and isotope separation is normally done on a small scale to provide special research materials. Only ^{2}H and ^{235}U, because of their importance for nuclear technology, and ^{6}Li, for nuclear weapons, have been separated on an industrial scale. The requirement for repeated separations introduces a common element into most separation processes, which is the subject of cascade theory.

1.1. General Aspects of the Separation Process

Rayleigh (13) first studied the cascade process for a continuous or differential separation, such as occurs in batch distillation. The urgency of developing suitable processes for separating uranium during World War II spurred the development of a general theory of cascades. The brief summary of the most important aspects given here follows the review of Benedict, Pigford, and Levi (14) and uses their symbols and terminology.

In any isotope separation process, one (or more) input or *feed* stream(s) is converted to two (or more) output streams--the *heads* enriched in the desired isotope, and the *tails*, depleted in the desired isotope. Such a process is shown schematically in Figure 2. There are six external variables:

Z	The *feed* flow rate (input stream)
M	The *heads* flow rate (stream partially enriched in the desired isotope)
N	The *tails* flow rate (stream partially depleted in the desired isotope)
z	The composition of the feed stream
y	The composition of the heads stream
x	The composition of the tails stream

The composition variables z, y, and x are usually given as the mole fraction of the desired component. Material balance imposes constraints on the total flow and on the isotope in question*:

$$Z = M + N \tag{1.1}$$

$$Zz = My + Nx \tag{1.2}$$

---

* For the general case, with multiple input and output streams, the balance equations take the form

$$\Sigma S_i = 0$$

$$\Sigma S_i x_i = 0$$

where S_i is a flow rate (positive for an output stream, negative for an input stream),
and x_i is the fraction of the desired isotope in the stream i.

The effectiveness of the separation is measured by the enhancement of the desired isotope. The *separation factor*

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \tag{1.3}$$

is a useful measure; for many processes, α is independent of concentration. The total flow rate Z is limited by the nature of the process and the specifics of the implementation (size of separation unit(s), speed of mixing, etc.) With this constraint, the constraints imposed by equations (1.1-1.3) and a given feed composition z, only one of the six parameters is adjustable. A useful parameter is the *cut*, the ratio of heads flow to feed flow:

$$\theta = M/Z \tag{1.4}$$

Another useful quantity, the *recovery* or fraction of the desired isotope transferred from the feed to the heads stream, is given by

$$r = \theta\ y/z. \tag{1.5}$$

By analogy with equation (1.3), the degree of separation of the desired isotope between the heads or tails stream and the input stream is given by

$$\beta = \frac{y/(1-y)}{z/(1-z)} \qquad \textit{(heads separation factor)} \tag{1.6}$$

$$\gamma = \frac{z/(1-z)}{x/(1-x)}\ (=\alpha/\beta) \qquad \textit{(tails separation factor)} \tag{1.7}$$

The heads separation factor is related to the cut by

$$\beta - 1 = \frac{(\alpha-1)(1-\theta)}{1 + \theta(\alpha-1)(1-y)} \tag{1.8}$$

This equation shows that there is a tradeoff between enrichment and the rate of production; the heads separation factor varies from $\beta = \alpha$ at $\theta = 0$ (no product) to $\beta = 1$ (no enrichment) at $\theta = 1$ (no waste product). Different types of separation processes are characterized by convenient values for θ; in many processes, the cut may be adjusted (within limits) in order to obtain a desired value of β. Note that the weak dependence of β on y in equation (1.8) implies that, at high enrichment ($y \to 1$), a slightly lower cut is required to obtain a specified heads separation factor.

The above equations apply to any separation process. Since the separation factors for most single-step processes are close to unity, significant enrichment requires many steps. The theory of *separation cascades* deals with the manner in which the individual separation units are interconnected and are operated (i.e., the value(s) of β). There are many types of cascade; the present brief description covers mainly the major features of the *ideal cascade*, which is approximated by most large separation plants.

A single unit of a cascade is referred to as a *separating unit*. It is the smallest unit capable of performing some separation: a single diffusion barrier, a gas centrifuge, or one plate of a distillation column, for example.

An ensemble of separating units in parallel (that is, operating in the same manner upon a common feed stream or streams of like composition) constitutes one *stage* of the cascade. The number of separating units in a given stage and the manner in which the output (heads and tails) from one stage are connected to the feed of other stages can be varied. In the *simple cascade*, stages of equal size are connected in series, with the heads of each stage feeding the next (Figure 3). If the cut of each stage is adjusted so that β is constant, the overall separation factor is:

$$\omega = \frac{y_P/(1-y_P)}{z_F/(1-z_F)} = \beta^n \tag{1.9}$$

where n is the number of stages,

and y_P, z_F refer to the heads of the final stage (the product) and the feed to the first stage, respectively.

The minimum number of stages required to achieve a desired separation factor is

$$n_{min} = \ln \omega / \ln \alpha \tag{1.10}$$

The *recovery*, or fraction of the desired isotope recovered from the input,

$$r = \left(\frac{\alpha-\beta}{\alpha-1}\right)^n = \left(\frac{\alpha-\omega^{1/n}}{\alpha-1}\right)^n \quad , \tag{1.11}$$

is zero for $n = n_{min}$ $(\beta=\alpha)$, and increases to a limit

$$r = \omega^{-1/(\alpha-1)}$$

as $n \to \infty$.

The simple cascade is wasteful in that the tails, which are progressively richer in the desired isotope with each succeeding stage, are discarded. As a result, it has a low recovery and large material flows (hence, large energy use and equipment volumes) per unit of product. A more efficient *reflux cascade* uses the tails from each stage as input to a preceding stage. The *ideal cascade* is approximated by all large-scale plants based on processes for which the separation factor is close to unity. It has the following properties:

1) The heads separation factor β is constant.
2) There is no mixing of streams of different composition. (An ideal cascade is sometimes referred to as a *no mixing cascade*.)
3) The total interstage flow required to produce a product and waste with specified compositions is minimized.

In the large gaseous diffusion uranium separation plants, the heads from each stage feed the following stage, while the tails feed the preceding stage. This type of cascade, illustrated in Figure 4, is referred to as the *one-up one-down cascade* or as the *standard ideal cascade*. It has the following additional properties:

1) $\beta = \gamma = \sqrt{\alpha}$
2) The number of stages is given by

$$n = \frac{\ln\left(\frac{y_P/(1-y_P)}{x_W/(1-x_W)}\right)}{\ln \beta} - 1 \quad , \tag{1.12}$$

where y_P and x_W are the product and waste compositions, respectively.

3) The cascade is tapered, with the largest sized stage at the feed point; Figure 5 illustrates the shape of such a cascade. Stages at and above the feed point constitute the *enriching section*, those below, the *stripping section*.

An important quantity is the total flow through the cascade. The total flow is proportional to the number of separating units required and is thus proportional to the power required to operate a plant. For a large plant, the number of separating units will be nearly proportional to the capital and operating costs of the plant. (Since an ideal cascade minimizes the total flow rate for a specified separation task, it minimizes cost and energy use.) For a standard ideal cascade, the total flow is given by:

$$\text{Total flow} = \frac{\beta+1}{(\beta-1)\ \ln\beta}\sum X_k \phi(x_k) \tag{1.13}$$

where X_k are the *external* flows (positive for an output, negative for an input),*

$$\text{and } \phi(x_k) = (2x_k - 1)\ \ln \frac{x_k}{1-x_k} \tag{1.14}$$

The first factor in equation (1.13) depends only on the heads separation factor and is thus a characteristic of the process. The second factor (the summation) is called the *separative capacity* or *separative power* (15), with the symbol D. It depends only on the flow rates and compositions of external streams and is a measure of the relative difficulty of performing a given separation task, independent of the process used. Separative capacity is quoted in units of quantity of material *separative work units* (SWU) per unit time; for example, moles SWU/day, kg U (kg of uranium) SWU per year.** A closely related quantity, the *separative work*, is defined by replacement of the flow rates (X_k) with amounts of material (E_k)

$$S = \sum E_k \phi(x_k) \tag{1.15}$$

---

* Equation 1.13 is generalized to cover more than three flows (feed, product, and waste). For example, one may want to extract several products of different enrichment.

**The quantity ϕ in equations 1.14 and 1.15 is dimensionless; the designation SWU distinguishes separative capacity or work from a flow rate or quantity of material.

Separative work measures the relative effort required to separate a given quantity of starting material into a product of specified enrichment and waste of specified depletion. It is given in units of quantity SWU; for example, kg U SWU.

The separative capacity of an ideal cascade is the sum of the separative capacities of the individual separation units. Since a large separation plant consists of many units, whose interconnections may be changed rather flexibly, equation (1.13) may be used to calculate the effect of a change in the mode of operation. For example, if it is desired to make a more highly enriched product by adding more stages, taking the added separation units from existing stages, this equation gives the sacrifice in product rate necessary to increase the enrichment. The separative work defines the relative economic value of a specified separation task or of a specified product.

The brief discussion of cascades presented above omits many facets of isotope separation, a few of which should be at least mentioned. *Differential stage separation* occurs when the heads or tails stream is removed continuously as the separation takes place. Continuous removal of heads is typified by the gaseous diffusion process; batch electrolysis of water, with hydrogen depleted in ^2H continuously removed as hydrogen gas, is an example of the continuous removal of tails. Either type of differential separation results in a separation factor that is somewhat larger than the *local value*. The *reflux ratio* is the ratio of tails feeding a given stage to the rate of product flow. In the enriching section of a standard ideal cascade (see Figure 4):

$$\text{reflux ratio} = N_{i+1}/P \qquad (1.16)$$

where N_{i+1} is the tails flow from the $i+1^{st}$ stage.

A *close separation cascade* is one for which $\alpha - 1 \ll 1$; this restriction simplifies some of the equations describing the cascade. An isotope separation plant has an *inventory* of material tied up in the cascade; if the plant is initially started with uniform material of the feed composition in all stages, the isotopic composition of this inventory and the product and waste flow rates all vary with time. A product may be drawn off only after the upper end of the cascade has reached the desired enrichment. The *equilibrium time* required to start up a plant may introduce a significant delay and may in some cases be so long as to make a process impractical. A plant operating at equilibrium contains, in addition to its material inventory, an inventory of separative work equal to the work required to produce its own steady-stage concentration gradient.

Other types of cascades are of interest. In a *square cascade*, all stages are of the same size. In spite of its inefficiency compared to an ideal cascade, the square cascade is often mandated by design considerations, as in the case of a distillation column, for which any other shape would require external heat exchange. A *squared off cascade* is tapered stepwise. An example of this type of cascade is several banks of distillation columns or thermal diffusion columns in series, where each column constitutes a number of stages. This type of cascade has been treated by Cohen (15). Other types of ideal cascades have been studied; for example, Olander (16) has developed cascade equations for a two-up, one-down cascade.

The discussion above has assumed mixture of just two isotopes. The separation of mixtures of more than two isotopes entails additional complications, which have been treated by several authors (17-19). For a specified set of feed, product, and waste compositions (in terms of the mole fraction of the desired isotope), the presence of a third isotope increases the amount of separative work required. There is no way to avoid the loss of some separative work due to mixing of streams of different composition. A cascade which mixes streams so as to match the abundance ratio of the two principal components has nearly ideal properties so long as the fraction of the other components is small. The additional components will tend to fractionate in the product or waste stream, depending on the relative separation factors from the two principal isotopes. For example, in the separation of ^{235}U from ^{238}U by gaseous diffusion, another uranium isotope will tend to concentrate in the product (^{235}U) fraction if its atomic weight is less than the arithmetic mean or *key weight* (236.5). It is not possible to fractionate out a third component from both product and waste in a single cascade optimized for the separation of the other two; a second cascade, optimized for this purpose, is required.

1.2. Isotope Separation Processes

Many processes have been proposed for isotope separation, a significant fraction of which have been tried at least on a small scale. A survey carried out in 1953 identified 98 potential processes for the production of heavy water alone (20). The factors which dictate the choice of a process for use in the laboratory or a small-scale plant, where flexibility and low capital cost are important, are very different from the factors governing industrial scale plants, in which low energy and materials use, ease of operation, and high reliability tend to be more important. Over twenty years ago, Manson Benedict stated some generalizations (21) whose validity was affirmed more recently by Spindel (22):

1) The most versatile means for the production of research quantities of isotopes is the electromagnetic method.
2) The simplest and most inexpensive means for small-scale separation of many isotopes is the Clusius thermal-diffusion column.
3) Distillation and chemical exchange are the most economical methods for the large-scale separation of the lighter elements.
4) Gaseous diffusion and the gas centrifuge are most economical for the large-scale separation of the heaviest elements.

The following sections cover some of the most important processes currently in use or anticipated to become important.

1.2.1. Electromagnetic Separation

Electromagnetic separators are high-current mass spectrometers, in which the ion-current detector is replaced by a collector. In 1943, a very large facility known as Y-12 was constructed at Oak Ridge to separate ^{235}U for the war effort. When the process was abandoned in 1946 in favor of gaseous diffusion, some of the more than 1100 units were saved and used in a program to produce stable isotopes of many elements for research.* The war effort and the conversion of the plant to peacetime use form a colorful chapter in the history of modern science (23,24). Among other things, many of the magnet coils and busbars were fabricated from 15,000 tons of silver borrowed from the U.S. Treasury (23).

The separators at Y-12, designed by E.O. Lawrence and known as calutrons, are 180^0 magnetic focusing devices of radius 24 or 48 inches. Figure 6 is a partial cutaway view of a smaller "beta" calutron, showing the ion orbits. According to electromagnetic theory, the orbital radius is

$$r = \sqrt{2mV/e}\Big/B \tag{1.17}$$

where m and e are the charge and mass of the ion,
V is the accelerating potential, and
B is the magnetic field strength.

The spatial separation between two isotopes at the focal plane is thus

$$2\Delta r = r\Delta m/m; \tag{1.18}$$

values for r = 24 inches range from 0.1 inch for adjacent isotopes of plutonium to 3.7 inches for lithium isotopes. Since the beam spread is quite small, the electromagnetic method (almost uniquely) provides a good separation in a single stage; in the calutrons the enrichment factor** ranges from 30 to as high as 80,000 (23). A major limitation is the restriction of beam current necessary to prevent the loss of beam quality or stability. The maximum current of the calutron beams, about 0.01-0.1 A, depending on the element, is equivalent to 0.009-0.09 moles/day for a singly ionized beam. The corresponding separative capacity, assuming a separation factor $\beta = 100$, is about 0.04-0.4 moles SWU/day. Since the throughput limitation applies to the total beam current, the production rate for a pure isotope is inversely proportional to its abundance in the feed material. The beam intensity is high, however, in terms of its energy dissipation (3.5 kW for a 0.1 A beam), which necessitates careful collector design and cooling in order to avoid the loss of the product by vaporization or sputtering. Special collector design (and, in some cases, special ion source design) are required for each element. The electrical power consumption of the calutrons is roughly 0.1 MW per tank, so that roughly 10^5 to 10^6 MJ of energy are required to separate one mole of material in a single pass, or 2-20 x 10^4 MJ per mole SWU.

A number of innovative technical improvements were made in the course of the post-war program; Love (23) has described the plant and the program in more detail. Table 5 lists the elements separated from 1966 through 1972, which include reactor-produced plutonium, americium and curium, several other irradiated elements containing radioisotopes, and all natural polyisotopic elements

---

*Two of the larger "alpha" units and 72 of the "beta" units, a maximum of 30 of which were operated at one time, were retained for general isotope production.

**The enrichment factor, as defined by Love (23), is equivalent to a heads separation factor β (See equation 1.6.) The separation factor α (equation 1.3) is approximately the square of β.

except hydrogen and the noble gases. A total of almost 3 x 10^6 tank hours at average currents ranging from 6 to 65 mA, were logged during this period, resulting in the production of about 200 kg of separated isotopes (over 250 isotopes), most of them of high purity (90 to 99+%). The program has been partially subsidized by the U.S. Department of Energy and its predecessors. Separated isotopes are sold or loaned from a pool*; sales for the period 1966-1972 were close to $1 million per year, with the equivalent value of new loan materials in the range $3-7 million per year. Production was cut back to eight tanks in 1974 and, at current production rates, the inventories accumulated in previous years are decreasing. Isotopes are presently priced to recover separation costs, with the cost for a new separation allocated to the isotope for which the separation was requested. A Soviet program of electromagnetic separation was begun around 1968. Pricing is competitive with Oak Ridge, and Soviet sales to European customers in the last few years have been significant. An electromagnetic separator at Harwell (U.K.), Hermes, has been used mainly to separate plutonium and other radioactive or toxic substances (25).

1.2.2. Thermal Diffusion

The existence of the thermal diffusion effect, the tendency of the light components of a fluid subject to a temperature gradient to concentrate in the hotter region, has been known since 1916 (26). The concentration difference in a temperature gradient results in a separation factor (14):

$$\alpha = \frac{y_2/(1-y_2)}{y_1/(1-y_1)} = (T_2/T_2)^{\gamma} \approx 1 + \gamma \ln(T_2/T_1) \tag{1.19}$$

The *thermal diffusion constant* γ is dependent on the intermolecular potential, but is on the order of 0.3 m/m or less. Some representative measured values are 0.059 for ^{3}He-^{4}He at 398 K, 0.00085 for ^{131}Xe-^{132}Xe at 448 K(14). Although γ is independent of temperature at high temperatures, at practical values it is temperature dependent and may vanish or become negative.

The thermal diffusion effect is small, so that practical applications awaited the invention of the countercurrent thermal diffusion column by Clusius and Dickel in 1938 (27). Figure 7 illustrates the type of column used today. In earlier designs, the inner (hot) tube was replaced by a hot wire. Lighter isotopes tend to concentrate near the hot wall, heavier ones near the cold wall. Due to convection, the hot fluid near the inner wall rises and the cold fluid falls. The combined effect of the radial thermal diffusion gradient and axial convection creates a countercurrent flow and produces a concentration gradient in the vertical (axial) direction; in practical sized columns, a separation factor equivalent to several hundred stages can be obtained (28). The theory of thermal diffusion columns, as developed by Furry, Jones, and Onsager (29) and modified by Rutherford and others, is in satisfactory

---

* Information on prices and availability is contained in the catalog Research Material, Separated Isotopes and Radioisotopes, and Special Preparations, available free from Oak Ridge National Laboratory Isotope Sales, P.O. Box X, Oak Ridge, TN 37830, U.S.A.

agreement with the measured performance of precisely constructed columns (28). References (28, 30, and 14) provide a review of theoretical and experimental aspects, as well as additional references to the extensive literature on the subject.

Since 1938, laboratory-scale separations have been used to produce highly enriched isotopes of chlorine, bromine, oxygen, nitrogen, carbon, sulfur, and the noble gases. In 1944 a large thermal diffusion plant was constructed to enrich liquid UF_6 slightly as feed for the calutrons. This plant, whose characteristics are described in references (31 and 14), was shut when the first gaseous diffusion plan began operation. Mound Laboratory, operating under a U.S. Department of Energy contract, currently produces isotopes of carbon and the noble gases in columns like that illustrated in Figure 7. Up to 19 columns, located in a common water jacket, are interconnected in series/parallel to form an appropriate squared-off cascade. Figure 8 shows several arrangements used to separate krypton isotopes. Based on the data presented (33), the single-column separation factor for ^{84}Kr-^{86}Kr is about 2.6, and the separative capacity of one column is about 1 g Kr SWU per day. Commercial distribution of separated isotopes by Mound was begun in 1960; a summary of 1978 sales is given in Table 6*. Since 1975 Mound has also sold isotopes separated by thermal diffusion in liquids; currently sulfur and chlorine isotopes are separated in this manner (32,33). The method suffers from the inherently lower diffusion rates for liquids but has the advantage of thermal diffusion constants that are typically 3-5 times larger than for gases, making it practical to use smaller columns and lower temperature differences ($\Delta T \approx 100^oC$, vs. 700^oC for gases) (33).

Energy consumption by thermal diffusion columns is very high. For example, the columns used to separate UF_6, which had a separative capacity of 2.46 kg U SWU per year, consumed about 93 kilowatts of power in the form of steam at 559 K (14). The power consumption was thus about 10^6 MJ per kg U SWU. Hoglund, Schachter, and Von Halle have reviewed the thermal diffusion column in greater detail (34); they give a formula for energy consumption as the sum of conductive and radiative heat transfer between the hot and cold walls.

1.2.3. Distillation

In the distillation of a mixture of compounds differing by isotopic substitution, the lighter components tend to concentrate in the vapor phase. When only two isotopic compounds are present, the separation factor is closely approximated by the ratio of vapor pressures of the pure compounds:

$$\alpha = \pi_A/\pi_B \tag{1.20}$$

Deviations from this Raoult's Law value are important only for ^3He-^4He and H_2-HD-D_2 mixtures; with these two exceptions, the value of ln α predicted by equation 1.20 is accurate to better than 10% (14). Compounds containing n equivalent atoms of the element in question will have n + 1 isotopic species:

---

* Information on prices and specifications may be obtained by contacting Monsanto Research Corporation, Stable Isotope Sales, Mound Facility, Miamisburg, Ohio 45342, U.S.A.

$$XA_n, XA_{n-1}B, XA_{n-2}B_2, \ldots \quad XAB_{n-1}, XB,$$

where A and B are the two isotopes,
and X is the rest of the molecule.

Under the assumption that the isotopes A and B are distributed randomly among the n + 1 species, the separation factor for isotopes A and B is the nth root of the ratio of vapor pressures of the isotopically pure compounds:

$$\alpha = \sqrt[n]{\pi(XA_n)/\pi(XB_n)}, \qquad (1.21)$$

where the mole fractions in the definition of the separation factor (equation 1.3) refer to the total concentration of the isotope A or B, irrespective of the chemical form, i.e.,

$$x(A) = n\ x(XA_n) + (n-1)\ x(XA_{n-1}B) + \ldots \qquad (1.22)$$

Table 7 gives some examples of separation factors estimated by equation 1.21. The temperature for distillation is, of course, confined to the range between the triple point and the critical point; the separation factor decreases with increasing temperature, so that low temperatures are generally advantageous.

Because of the rapid decrease of the separation factor with increasing mass, distillation is a suitable method only for separation of light elements. The most important application today is as the final step in the separation of deuterium, where distillation of water is the preferred method. Of the nine deuterium plants with capacities over 1 Mg (metric ton) of D_2O per year operating or planned, all but two use water distillation as the final stage (14). The use of water distillation for low-enrichment portions of the process is generally unfavorable because of the large columns required (35). Three small water distillation plants were operated during World War II but were abandoned in 1945 (36,14). However, primary enrichment of deuterium using low-grade waste heat has been proposed recently (37).

Hydrogen (H_2) distillation has the advantage of a large separation factor (see Table 7) but poses problems because of the very low temperatures required. Five plants employing hydrogen distillation have been built, of which one of fair size is still operating. The plants and the process are described in reference (14) and references contained therein. Like all deuterium plants whose feed is elemental hydrogen, they are parasitic to synthetic ammonia production, which sets a limit on deuterium production rates.

Ammonia distillation is often preferred as the final stage of enrichment of deuterium plants whose primary enrichment is based on ammonia-hydrogen exchange (14). The comparative merits of different deuterium separation methods is considered below, under chemical exchange.

Several other isotopes are separated on a small commercial scale by distillation. Cryogenic distillation of carbon monoxide is the preferred method for separation of ^{13}C in quantities greater than 500 grams per year (33); Mound Laboratory currently produces ^{13}C in part by this method (33,32). CO distillation and the distillation of nitric oxide to separate isotopes of both oxygen and nitrogen is carried out at Los Alamos Scientific Laboratory (38,33).

1.2.4. Chemical Exchange

The exchange of two isotopes ($^1A, ^2A$) between two compounds (AX, AY) is a chemical reaction

$$^1AX + ^2AY \rightleftarrows ^2AX + ^1AY$$

whose equilibrium constant is

$$K = \frac{a(^2AX)\ a(^1AY)}{a(^1AX)\ a(^2AY)} \tag{1.23}$$

To the approximation that the activities a(AX), a(AY) of the substances are proportional to the concentrations [AX], [AY], the separation factor is equal by definition to K. For compounds containing more than one atom of element A, the concentrations of ^1A and ^2A entering into the definition of α (equations 1.3) are given by equation 1.22, and the equivalence of α and K is no longer valid. In the more general case, there can be exchange between compounds of the form A_nX and A_mY, for which there are m x n reactions of the form

$$^1A_i{}^2A_{n-i}X + ^1A_j{}^2A_{m-j}Y \rightleftarrows ^1A_{i-1}{}^2A_{n-i+1}X + ^1A_{j+1}{}^2A_{m-j-1}Y \quad ;$$

the separation factor α is then a function of the m x n equilibrium constants and is not independent of concentration. However, in the case where the isotope of interest (say ^1A) is dilute, such that

$$^2A_nX >> ^1A^2A_{n-1}X >> ^1A_2{}^2A_{n-2}X \ldots$$

and $$^2A_mY >> ^1A^2A_{m-1}Y >> ^1A_2{}^2A_{m-2}Y \ldots.$$

the separation factor is given by

$$\alpha \simeq \frac{n}{m} K \tag{1.24}$$

Equation 1.24 is a reasonable approximation to the true separation factor for most systems of actual interest.

Practical isotope separation must be based on systems in which the two compounds are concentrated into different phases (heterogeneous reactions) or can be separated readily into different phases following equilibration. In the former case, the separation factor is the product of the separation factors for the reaction and for the phase separation. For example, the water-hydrogen exchange reaction

$$H_2O(\ell) + HD(g) \rightleftarrows HDO(\ell) + H_2(g) \qquad \alpha \simeq K$$

is equivalent to the sequential reactions

$$H_2O(\ell) + HDO(g) \rightleftarrows HDO(\ell) + H_2O(g) \qquad \alpha = \alpha^*$$

$$H_2O(g) + HD(g) \rightleftarrows HDO(g) + H_2(g) \qquad \alpha \simeq k$$

The first of these steps is simply the vapor-liquid exchange or distillation, for which the separation factor is given by equation 1.21 as

$$\alpha^* = \sqrt{\pi_{H_2O}/\pi_{D_2O}}$$

whereas the separation factor for the second reaction, homogeneous steam-hydrogen exchange, is approximately equal to k, the equilibrium constant for this reaction, according to equation 1.24. The net separation factor for the (heterogeneous) reaction is thus

$$\alpha \simeq K \simeq k\alpha^* \qquad (1.25)$$

Table 8 lists separation factors for some heterogeneous reactions, most of which have been used for isotope separation. α decreases rapidly with increasing atomic number. Although chemical exchange methods have been studied for many elements including carbon, nitrogen, sulfur, calcium, and even uranium, they are presently the methods of choice only for hydrogen, lithium, and boron. Nevertheless, the importance of heavy water lends a special significance to the subject of chemical isotopic exchange. Of the hundreds of methods that have been studied for heavy water production (35), most involve chemical exchange.

1.2.4.1. Bithermal Exchange Processes: the GS Process

Ever since the construction of large plants at Dana, Indiana, and Savannah River, South Carolina, in 1952, the exchange reaction between water and hydrogen sulfide has been the dominant heavy-water process. One of the factors in favoring what has become known as the GS (for Girdler Sulfide) process is the use of a bithermal exchange mechanism to avoid the once-through use of costly reagents. To see why this is important, consider the exchange of deuterium from a hydrogen sulfide stream flowing through a reactor countercurrent to a stream of water (Figure 9). Because of the separation factor for the exchange reaction, deuterium will be transferred from the upflowing H_2S to the downflowing water. In order to get significant enrichment, it is necessary to convert most of the enriched hydrogen emerging from the bottom of the column as water to the form of hydrogen sulfide for recycle through the column. The sulfur required may be reclaimed from the depleted H_2S emerging from the top of the column by partial oxidation:

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S$$

This reaction uses no scarce materials and is exothermic. However, the transfer of hydrogen from water to hydrogen sulfide is costly. Benedict, Pigford, and Levi (14) illustrate one way this could be done:

$$S + \frac{2}{3}\,Al \rightarrow \frac{1}{3}\,Al_2S_3$$

$$\frac{1}{3}\,Al_2S_3 + H_2O \rightarrow \frac{1}{3}\,Al_2O_3 + H_2S$$

In this hypothetical process, the net penalty for the phase conversion is the degradation of aluminum to aluminum oxide (less a credit for the heat produced by the partial oxidation of H_2S). Since reflux ratios for the production of D_2O are large, due to its low natural abundance (0.015%), the penalty for phase conversion is large. For the system illustrated in Figure 9, the ratio is at least (14)

$$\frac{1}{z_F} \times \frac{\alpha}{\alpha - 1} = \frac{1}{0.00015} \times \frac{2.32}{1.32} \simeq 11{,}700 \quad ,$$

so that at least $11{,}700 \times \frac{2}{3} = 7800$ moles of aluminum are consumed per mole of D_2O produced.

The phase conversion step, which is analogous to reboiling in distillation and is required for any monothermal process, is usually costly in materials and/or energy. Dual-temperature processes substitute thermal reflux for phase conversion, by making use of the decrease of the separation factor with increasing temperature. Consider the reaction of natural water with a large volume of cold H_2S whose deuterium content y relative to natural water is between $1/\alpha_c$ and $1/\alpha_h$:

$$\frac{1}{\alpha_c} < \frac{y_{H_2S}}{z_{H_2O}} < \frac{1}{\alpha_h} \quad *$$

The resultant water will have a deuterium concentration $\alpha_c y$. A portion of this enriched water is now reacted with the same depleted gas at a higher temperature, restoring the gas to its original deuterium concentration. Because $\alpha_h < \alpha_c$, less than the original amount of water is required, and this water is depleted below its natural abundance to a concentration $\alpha_h y$. The hydrogen sulfide has now been restored to its original state, and the water has been separated into an enriched fraction with $x_p = \alpha_c y$ and a depleted fraction with $x_W = \alpha_h y$, equivalent to a single-stage separation process with an effective separation factor

---

* The separation factors are expressed here as concentration ratios, since $1-x \simeq 1-y \simeq 1$.

$$\alpha = \frac{x_p}{x_W} = \frac{\alpha_c}{\alpha_h} \tag{1.26}$$

The temperature dependence of the separation factor, upon which any bithermal process relies, is illustrated in Figure 10 for some exchange reactions of hydrogen. The data are fitted to curves of the form

$$\ln\alpha \simeq \ln K = \frac{b}{T} + a \quad , \tag{1.27}$$

where the constants b and a have a simple interpretation in terms of the thermodynamics of the exchange reaction:

$$b = \frac{\partial \ln K}{\partial(1/T)} = -\frac{\Delta H}{R} \tag{1.28}$$

$$a = \ln K - \frac{b}{T} = -\frac{\Delta F}{RT} + \frac{\Delta H}{RT} = \frac{\Delta S}{R} \tag{1.29}$$

For comparisons with the principal hydrogen-exchange reactions, a boron-exchange reaction also is shown in Figure 10. The small temperature dependence of the separation factor precludes the use of bithermal processes for elements other than hydrogen.

Figure 11 shows a simplified flow diagram for the bithermal H_2O-H_2S system. This system has been analyzed by Benedict, Pigford, and Levi (14). Variables in the system are the number of stages in the cold and hot towers (n_c, n_h), the rate of product withdrawal $P = F - W$, and the ratio of gas to liquid flow G/F. The system operates between $T_c = 32^oC$, below which H_2S hydrates tend to precipitate out, and $T_h = 138^oC$, above which the partial pressure of steam in the gas phase becomes excessive. Other characteristics of the system are given by the analysis in reference (14). The performance is very sensitive to the ratio G/F, with optimum recovery of deuterium from the feed water occurring for

$$G = \sqrt{FW\alpha_c\alpha_h} \; (\simeq F\sqrt{\alpha_c\alpha_h}) = 2.03\ F \quad . \tag{1.30}$$

Less than 15% of the deuterium content of natural water is recovered; recovery in the GS process is limited by the value

$$r \leqq 1 - \frac{\alpha_h}{\alpha_c} = 0.22 \tag{1.31}$$

This is not a serious problem, since the feed material is abundant and cheap. However, the low effective separation factor also results in a high reflux ratio:

$$G/Px_p \simeq \frac{\alpha_c\alpha_h}{x_F(1-\alpha_c/\alpha_h)} \simeq 61{,}000 \text{ moles of gas per mole of } D_2O \text{ produced.} \tag{1.32}$$

The large flows and resultant large volumes are offset by the high pressure at which the GS process can be operated; a practical limit around 300 PSI (2 MPa) is set by the solubility of H_2S and, mainly, by the availability of process equipment. The process is driven by mechanical (electric) energy for pumping and heat (steam) to raise both phases from T_c to T_h, part of which is recovered in the heat exchangers. Additional complexity in the GS process results from the presence of steam in the gas phase and dissolved H_2S in the liquid. Gas leaving the hot towers is passed through condensers to remove deuterium-rich water; the gas is rehumidified upon re-entry to the hot tower. H_2S must be stripped from the waste water before discharge.

Reference (14) describes the Savannah River plant and gives further references to the literature on its design. This plant uses two stages (each comprised of multistage towers) to enrich water from 0.0147% to about 15% D_2O. Further concentration to reactor-grade (99.75%) D_2O is accomplished by water distillation and electrolysis. (The reliability and simplicity of these processes outweigh their inefficiencies since, according to equation 1.15, only a fraction of a percent of the separative work is expended in the "finishing" step.) Production of the Savannah River plant has been cut back from 480 to 69 Mg (metric tons) of D_2O per year; the Dana plant, with a similar capacity, was shut down in 1958. The Canadian plants, for which detailed information is scarcer, are described in references (35 and 41). They employ three stages to enrich water from 0.014% to about 20% D_2O, followed by water distillation. Although their flow diagrams are different, their operating characteristics are similar to those of the Dana and Savannah River plants. Three large plants are currently fully operational: Port Hawkesbury and Glace Bay, Nova Scotia, each with a capacity of 400 Mg/y, and Bruce A, Ontario, with a capacity of 800 Mg/y (14,35). Bruce B is scheduled to be in service by the end of 1979* (41) and two more plants are planned. The addition of these three 800 Mg/y plants is expected to meet demand until about 1990 (35).

1.2.4.2. Ammonia-hydrogen Exchange

This reaction has both a larger separation factor (Table 8) and a larger temperature dependence (Figure 10) than the H_2O-H_2S exchange reaction. Thus, processes based on the reaction are favored by columns with fewer theoretical stages, lower reflux rates, and higher deuterium recovery from the source. There are, however, several disadvantages. The reaction proceeds at a sufficient rate only in the presence of a catalyst of 1-2 mole percent potassium amide (KNH_2). Even with a catalyst the reaction is slow, and specially designed gas-liquid contactors, high pressures, and large tower heights are required. The catalyst is dissolved in the liquid (ammonia) fraction with which it is in isotopic equilibrium, necessitating the separation of catalyst from the product and (in the case of the monothermal process) a further stripping operation to recover deuterium before recycling of the catalyst. The catalyst is also very reactive, combining with CO_2, CO, H_2O, and O_2 to form solid impurities and with O_2 to form KN_3, which is explosive; concentrations of these impurities in the feed gas must therefore be reduced to less than a part per million. The process is fed by ammonia synthesis gas (N_2 + $3H_2$). In the monothermal process, chemical reflux (phase conversion) is

---

* Bruce B has in fact been completed. However, the Canadian plants are not operating at full capacity, due in part to lack of demand.

accomplished by dissociation of ammonia rich in deuterium and by recycling part of the ammonia made from synthesis gas that is depleted in D_2. A 26 Mg/y plant utilizing the monothermal exchange process was built in 1968 at Mazingarbe, France. (The plant was closed in 1972 by an explosion.) Several additional plants with capacities around 70 Mg/y, have been planned for India. Based on partial information (42-44), Benedict, Pigford, and Levi (14) have constructed a flow diagram for the Mazingarbe plant. The plant operates at $T = -25^oC$, at which temperature $\alpha = 5.2$. Friedrich Uhde GmBH has developed a dual-temperature process, with $T_c = -25^oC$, $T_h = 60^oC$ ($\alpha_h = 3.0$), or $\alpha_{effective} = 5.2/3.0 = 1.7$. The UHDE process (45) eliminates the dissociation of ammonia and the synthesis of additional ammonia for reflux, and also the catalyst stripping step. However, it requires far more internal stages, larger columns, and more reflux. A flowsheet, based on a partial description of the process (44), is given in reference (14). UHDE is constructing a plant at Talcher, India, with a capacity of 63 Mg/y (45).

1.2.4.3. Amine-hydrogen Exchange

Potential advantages of this reaction over ammonia-hydrogen exchange include higher separation factors (and larger temperature dependence) and a faster reaction rate, permitting the use of a lower temperature. The reaction, which is catalyzed by potassium methylamide (CH_3NHK), has an interesting process chemistry (46). A side reaction, unexpected on the basis of experience with the similar ammonia-hydrogen exchange reaction, is the production of insoluble potassium hydride:

$$CH_3NHK + H_2 \rightleftarrows CH_3NH_2 + KH\downarrow$$

The solution to this problem was the use of a mixture of potassium and lithium methylamides, which form a complex $K_2Li_2(NHCH_3)_4$ (46). The AECL-Sulzer Amine process, which is described in references (14 and 47), employs this catalyst and operates between $T_c = -50^oC$ ($\alpha_c = 7.9$) and $T_h = 40^oC$ ($\alpha_h = 3.6$), $\alpha_{effective} = 2.2$. Sulzer Brothers Ltd. have generated a complete design package for a 65 Mg/y plant attached to an ammonia synthesis plant in Alberta (47).

1.2.4.4. H_2O-H_2 Exchange, Electrolysis, and the CECE Process

The relatively large separation factors obtainable by the exchange of hydrogen with steam or water (Table 8 and Figure 10) are in part offset by the slow reaction rate. Additional difficulties are the high chemical reflux energy required to decompose water for a monothermal system and the absence (until recently) of a catalyst whose activity is not destroyed by liquid water. However, the combination of H_2O-H_2 exchange with water electrolysis offers gains over either process by itself. Until 1943, all commercial-scale production of heavy water was by electrolysis, the heavy water being a by-product of hydrogen gas. Separation factors for electrolysis are in the range about 5-13, depending on the temperature, the electrolyte and cathode material, and the cell construction. (Electrolysis has the highest separation factor of any commercial process and also requires the largest energy input.) Hydrogen from some of the early stages of an electrolytic cascade, whose deuterium concentration is in excess of natural abundance but is not of sufficient value to be worth recycling (by burning the hydrogen), can be exchanged with H_2O (steam) to recover most of the deuterium without sacrifice of hydrogen gas production. Norsk Hydro electrolysis plants at Rjukan and Glomfjord, Norway, were converted to the combined process after World War II. (Conversion was interrupted during the war by a commando raid.) These plants, with a combined capacity of 12 Mg/y (14), are still operating. A similar plant, with a capacity of 6 Mg/y, was built by the Manhattan District at Trail, B.C., Canada, in 1944 (36).

Steam-hydrogen exchange suffers from the relatively large volume required for the vapor-phase reaction and from the added energy input and the complex tower structure required to separate water from steam at each internal stage of the tower. These problems may be solved by the invention of a catalyst that is not wetted by and that retains its activity in the presence of liquid water (48). Electrolysis with heterogeneous-phase water-hydrogen exchange, which has come to be known as the CECE (for Combined Electrolysis and Chemical Exchange) process, would appear to be the best method to produce heavy water as a by-product of hydrogen, provided a catalyst of sufficient activity can be prepared (49). A pilot heavy water plant is planned at Chalk River National Laboratory (Canada). Another application of the process is the recovery of tritium from reactor moderator water (either heavy or light water); a pilot plant is planned at Mound Laboratory (50). A combination of vapor-phase catalytic exchange and hydrogen distillation has been used at Grenoble to purify heavy water moderator from a research reactor of both tritium and light water (51).

Miller and Rae (52) have suggested the use of a bithermal water-hydrogen exchange process using the same hydrophobic catalyst. Because of the larger effective separation factor, resulting in lower gas and liquid flow rates, this process might compete favorably with the GS process if a catalyst of sufficient activity could be produced at a low enough cost. H_2O-H_2 exchange might also provide a transfer mechanism between water as a feed and H_2-based processes.

1.2.4.5. Comparison of Processes for Production of Heavy Water

The high cost of heavy water and its importance as a reactor moderator have generated an active competition for the best production methods. Table 9 gives some of the factors that are relevant to this competition. Rae (35) has discussed these factors and concluded that two of the fundamental parameters define limits of acceptable processes: an economic process must have a separation factor of at least 1.1-1.2 and use less than about 40-50 Gigajoules per kilogram of D_2O. This criterion eliminates distillation or crystallization of water (α too low), or hydrogen diffusion, centrifugation, and electrolytic separation undertaken purely for heavy water production (excessive energy use). Two additional processes considered by Rae, H_2 adsorption on Pd and hydrogen/methane exchange followed by hydrogen distillation (the Gulf process), are marginally too energy consumptive. All processes above the line of Table 9 are economic by the above criterion.

Figure 12a shows the cumulative world heavy-water production and the breakdown by process to May 1977. By country, the breakdown is U.S. 59%, Canada 35%, Norway 4%, and India and France 1% each (35). The present world capacity (Figure 12b) shows a similar dependence on the GS process, but most of the heavy water is now being produced in Canada, reflecting Canadian dependence on the natural-uranium, heavy-water-moderated CANDU reactor, as contrasted with the U.S. reliance on enriched-uranium, light-water reactors.

For the same reason, India has become the second largest producer of heavy water. The picture projected for the near future (Figure 12c) does not look very different; plants utilizing ammonia-hydrogen exchange are expected to come on line in India, but the planned construction of three very large GS plants in Canada means that the GS process will remain the most important one for at least 10 or 20 years (35). The almost complete dominance of the GS process is largely due to the fact that it is the only practical process that is fed by water as the deuterium source. The only other sources of sufficiently large amounts of deuterium are natural gas and petroleum. Synthesis gas ($3H_2$ + N_2), produced from these hydrocarbons by reaction with steam and air, is an abundant source for hydrogen-fed processes. The total world synthesis gas production, about 10^8 Mg per year, could satisfy over 10 times the present heavy-water requirements, assuming recovery of 80% of the deuterium; however, the largest single plant, with a capacity of about 5 x 10^5 Mg/y of ammonia, would yield only about 100 Mg/y of deuterium (45). The use of electrolytic processes (including CECE) is prohibitively expensive in terms of energy consumption if undertaken for deuterium production alone; in locations where excess hydroelectric capacity makes it profitable to produce electrolytic hydrogen, deuterium can be obtained as a by-product at almost no cost.

The price charged for heavy water from Savannah River by the U.S. Department of Energy, $215/kg in 1977 (53), reflects a diseconomy of scale for this plant, which has been partially shut down; the Department would have been willing to negotiate a lower price for quantities large enough to require operation at a higher capacity (14). The Canadian price in 1977 was around $150/kg (54), of which 60% is allocated to return on capital, 25% to energy, and 15% to other operating expenses (52). (Energy consumption in the Canadian GS plants is 6800 kwh thermal plus 700 kwh electric per kg of D_2O. Assuming an efficiency of 0.4 for conversion of heat to electricity, the average price of power reflected in the cost estimates is about 1¢/kwh electric. Comparison of this figure with typical U.S. energy prices (≃3¢/kwh) suggests that energy may account for considerably more than 25% of the true cost of heavy water.) The capital cost of Canada's La Prade plant was predicted to be $375 per kg D_2O/year in 1974, not including escalation and interest during construction (55).

1.2.4.6. Chemical Methods for Other Elements

Lithium isotopes are separated by exchange between lithium amalgam and aqueous lithium hydroxide (56,14). A plant utilizing this reaction to produce 1000 kg per year of 99.99% ^{7}Li at a price of about $3/g is being built at Quapaw, Oklahoma (14).* The reaction, numbered 9 in Table 8, has some advantages over a similar exchange (57) between LiBr or LiCl in an organic solvent and Li(Hg) (reaction 8 in the table). D.A. Lee discusses the use of cation exchange resins and gives references to some other methods that have been explored for the separation of ^{6}Li-^{7}Li (58). The separation of boron isotopes by exchange distillation (reaction 10 in Table 8 and others) has been discussed by Palko and Drury (39). A plant at Quapaw based on reaction 10 has

---

* The amount of ^{6}Li separated for use in nuclear weapons must be much larger than this figure suggests; as a rough estimate, based on estimates of the U.S. stockpile, on the order of 10^2 Mg of ^{6}Li have been produced.

been operated since 1973; it is being expanded to a capacity of 1000 kg per year of ^{10}B, to be sold at a price of $5-15/g (14). Processes for separation of ^{14}N-^{15}N based on reaction 14 of the table have been proposed (59-61,14). An unusual advantage of these processes obtains from the fact that chemical reflux (reduction of ^{15}N-enriched HNO_3 to NO) is effected by oxidation of SO_2 to H_2SO_4, a more valuable substance. With ^{15}N produced as a by-product of sulfuric acid at a cost estimated in 1958 as $4 per gram (60,14), the method would appear to compete favorably with NO distillation, by which Los Alamos Scientific Laboratory produced ^{15}N sold in 1978 at an average price of $95 per gram (32).

The enrichment of carbon isotopes by CO_2-carbamate exchange has been studied and appears to be uneconomic compared to CO distillation for quantities above 0.5 kg per year (33). Mound Laboratory has also studied (33) the enrichment of sulfur isotopes by SO_2-$NaHSO_3$ exchange and the enrichment of Ca and other metals by extraction with organic solvents containing crown ethers, with which they form a complex (reaction 17 in Table 8). Uranium separation by reactions 18 and 19 of Table 8 has been studied (14,40); the low separation factors make it highly unlikely that any chemical process will compete with the industrial-scale methods described below.

1.2.5. Gaseous Diffusion

Since the first gaseous diffusion plant, known as K-25, began operation at Oak Ridge in 1944, almost all of the world's enriched ^{235}U has been produced by this method. Although other processes are expected to compete in the future, over 98% of the present uranium separation capacity is embodied in diffusion plants. The principle underlying diffusion of a gas through a porous barrier (effusion, or molecular flow) is the dependence of the average velocity of a molecule on the inverse square root of its mass, which results in a local separation factor

$$\alpha_0 = \sqrt{m_2/m_1} = \sqrt{352/349} \text{ for } ^{235}UF_6\text{-}^{238}UF_6 \qquad (1.33)$$

The separation factor for an actual barrier is reduced by the occurrence of collective flow of the gas (viscous or "laminar" flow) by incomplete mixing of the bulk of the undiffused gas with the layer adjacent to the barrier and by back diffusion, due to nonzero pressure downstream of the barrier.

$$\alpha - 1 = 1.386\, E_M E_B(\alpha_0 - 1) \qquad (1.34)$$

where E_M is the mixing efficiency,
E_B is the efficiency due to viscous flow and backpressure,
and the factor 1.386 (= 2 ln2)* is the enhancement due to the differential separation process.

---

* For a cut $\theta = 0.5$. For other values of θ, the enhancement is $-\dfrac{\ln(1-\theta)}{\theta}$.

The dependence of E_B on the upstream (fore-) and downstream (back-) pressure can be approximated (62) by:

$$E = \frac{1 - P'/P''}{1 + \frac{P''-P'}{P_c}} \qquad (1.35)$$

where P'' is the upstream pressure,
P' is the downstream pressure, and
P_c is the *characteristic pressure* at which E_B is equal to 0.5 when $P' = 0$ and $P'' = P_c$.

Since the separation factor decreases with pressure due to the increase in viscous flow relative to molecular flow, a good barrier is one that has a high characteristic pressure. Barriers are further characterized by a permeability, which is the ratio of flow rate per unit area to the pressure difference. The permeability is proportional to the fraction of the area that is holes and inversely proportional to the barrier thickness; high permeability is desirable, since the energy required to force gas through the barrier at a given pressure is inversely proportional to the permeability. The fabrication and performance of barriers is still subject to security classification. Open literature on French work (63,14) gives optimum properties of $P_c = 0.20$ MPa and a permeability (for air) of 7.5×10^{-3} kg moles/(s$\cdot$m$^2\cdot$MPa).

A previous article in this series (34) gives a more complete review of the technical and economic aspects of the gaseous diffusion process. Reference (14) derives in some detail the optimum operating pressures and the resulting capital and operating costs per unit of separative work, based on the characteristics of French barriers noted above. The present combined uranium separation capacity of the three U.S. plants is 17.23×10^6 kg U SWU per year (64). At full capacity, these plants consume about 6.1×10^3 MW of electric power, the equivalent of that produced by six large nuclear reactors. The power usage per unit of separative capacity or energy per unit of separative work (0.352 kW/kg U SWU per year or 11 GJ/kg U SWU) and the anticipated 1980 price ($100/kg U SWU) are close to the figures calculated in reference (14). Improvements currently being implemented will add another 10.5×10^6 kg U SWU per year to the capacity and reduce energy consumption to about 8.4 GJ/kg U SWU. (Olander states (65) that in 1978 the energy consumption of U.S. gaseous diffusion plants was 9.0 GJ/kg U SWU.) Additional diffusion plants are operating in the U.S.S.R. (7-10 x 10^6 kg U SWU per year), in France and the U.K. (about 0.5 x 10^6 kg U SWU per year each), and in China (capacity unknown). Eurodif, a European consortium, is constructing a plant in France with an initial capacity of 10.8×10^6 kg U SWU per year and a planned expansion by 50% in the late 1980s.

The U.S. Department of Energy enriches uranium for the nuclear power industry on a toll basis. According to equations 1.1, 1.2, and 1.14, the production of 1 kg of enriched uranium (mole-fraction y) from natural uranium (mole-fraction $z = 0.00720$) requires:

$$E_F = \frac{y-x}{z-x} \text{ kg of natural uranium and} \qquad (1.36)$$

$$S = \theta_P - \theta_F - \frac{y-z}{z-x}(\theta_F - \theta_W) \text{ kg U separative work units} \qquad (1.37)$$

where x is the mole-fraction of ^{235}U in the tails,

$$\theta_P = (2y - 1) \ln \frac{y}{1-y},$$

$$\theta_F = (2z - 1) \ln \frac{z}{1-z},$$

and $$\theta_W = (2x - 1) \ln \frac{x}{1-x}.$$

The total cost of 1 kg of enriched uranium is the sum of the toll for enrichment and the cost of the natural uranium feed:

$$\text{Cost} = S\, C_S + E_F\, S_F \tag{1.38}$$

where C_F is the cost of 1 kg of natural uranium and
C_S is the cost of 1 kg U SWU.

In 1977, the U.S. Department of Energy (then ERDA) set the tails assay at 0.2% ^{235}U. With x = 0.002, the production of 1 kg of 3% ^{235}U, a typical enrichment for light-water reactors, requires 5.385 kg of natural uranium and 4.253 kg SWU. With C_S = \$100 per kg SWU and a recent price of about \$89 per kg for natural uranium, the cost of 3% ^{235}U is about \$905 per kg. By setting the derivative of equation 1.39 with respect to the variable equal to zero, one can derive an optimum tails composition, at which the total cost of enriched uranium is a minimum. The optimum is a function of C_F/C_S; x approaches 0 for very high values of this ratio and approaches z for very low values. There are several interesting consequences of the dependence of the optimum tails composition on C_F/C_S (14). In the future, it is likely that the customer will be allowed to define the tails composition. For the present ratio $C_F/C_S = 0.89$, $x_{opt} = 0.0024$, and the minimum cost is \$897 per kg of 3% ^{235}U, so that a utility will choose a higher tails composition than the ERDA value of 0.2%. The development of more efficient methods for enrichment and the scarcity of uranium suggests a long-term trend toward an increasing ratio and, consequently, a lower value for x_{opt}. An increasing ratio would also make it economic to reuse the tails from previous separation as feedstock. If these tails are assigned a zero value, their use becomes economic when the value of x_{opt} falls below their ^{235}U content.

1.2.6. The Gas Centrifuge

A gas subject to an acceleration a in the direction x will have a local density or pressure distribution given by

$$\frac{d\ln\rho}{dx} = \frac{d\ln P}{dx} = \frac{m}{RT}\frac{d^2x}{dt^2} \tag{1.39}$$

where m is the molecular weight of the gas,
R is the gas constant, and
T is the absolute temperature.

In a mixture of gases, the partial pressures follow equation 1.39; the dependence on m is the basis of isotope separation by the gas centrifuge. In a centrifugal field ($-\frac{d^2r}{dt^2} = v^2/r = \omega^2 r$), the density or pressure distribution is given by

$$\frac{\rho(r)}{\rho_a} = \frac{P(r)}{P_a} = e^{-mv_a^2(1-r^2/a^2)/2RT} \qquad (1.40)$$

where r is the radius,
a is the radius of the outer wall of the centrifuge, and
v_a is the peripheral speed of the outer wall;

the local separation factor is given by

$$\alpha = \frac{x/(1-x)}{x_a/(1-x_a)} = e^{\Delta m v_a^2(1-r^2/a^2)/RT} \qquad (1.41)$$

where $\Delta m = m_2 - m_1$.

Figure 13 shows the pressure (or density) and the local separation factor for $^{235}UF_6$-$^{238}UF_6$ in a centrifuge with v_a = 400 m/s. Due to the large separation factor (1.10 between r = 0 and r = a), the centrifuge appears to have a great advantage compared to the gaseous diffusion barrier ($\alpha \simeq \sqrt{m_2/m_1}$ = 1.00429). However, because of the very small fraction of the gas present at small radii, it is not possible to utilize the full separative effect. Furthermore, a practical stage design requires a means for continuous extraction of the enriched and depleted portions of the gas. The solution to both problems is the countercurrent gas centrifuge, whose principle of operation is similar to that of the thermal diffusion column (Figure 7). In the thermal diffusion column convective axial flow is driven by the temperature gradient that also effects the radial separation; in the gas centrifuge, axial flow is imposed by external pumps, by heating and cooling opposite ends of the rotor, by imposition of an axial temperature gradient along the rotor wall, or by an internal system of stationary scoops and rotating baffles. Scoops at the top and bottom also serve to remove the product and tails; feed gas is introduced near the middle of the centrifuge via a stationary tube at the axis. The rotor is surrounded by a housing that maintains a vacuum and provides protection against high-speed debris that can result from failure of the rapidly spinning rotor assembly.

Reviews of developmental work on the gas ultracentrifuge through about 1960 are given in references (14,34,65,66) and references contained therein. In 1960 secrecy was imposed upon the U.S. and European research effort; details of the design and performance of more recent machines are thus unavailable. The more modern machines are descendants of the centrifuge developed by Zippe (67). Expected performance figures, based on the characteristics of earlier machines, theoretical considerations, and a general notion of their size, are given by May (68) and discussed in reference (14).

The primary goal of the mechanical design is to operate a long, narrow rotor at the maximum possible speed. Various metal alloys can be spun at maximum peripheral speeds of 400-500 m/s, above which they fly apart. Glass fiber composite materials have maximum peripheral speeds over 500 m/s; carbon fiber composites can hold together at speeds up to about 700 m/s but are probably too expensive. A second mechanical problem is the occurrence of vibrational resonances at which the rotor or its bearings can be damaged. For rotors operated near their maximum speeds, the first resonance occurs at a length-to-radius ratio around 13; longer rotors must be operated off resonance and must be accelerated and braked rapidly across resonances in order to avoid damage. The rotor speed and the induced pattern of the axial countercurrent flow determine the operating characteristics. The flow pattern is radially asymmetric and more complex than that depicted for the thermal diffusion column. Figure 14 shows the calculated performance (14,68) of a long-bowl centrifuge with v_a = 400 m/s. The effective radial separation factor is equal to 1.021 and is nearly independent of v_a. The optimum separative capacity varies approximately as $v_a^{2.02}$.

URENCO-Centec, a combination of British, Dutch, and German interests, currently operates three pilot plants with a total capacity of 0.12 x 10^6 kg SWU per year and plans expansion (some of it already under construction) to about 10 x 10^6 kg SWU per year. The capacity of the URENCO machines is estimated as "from 2 to 20" (66) and as "around 5" (69) kg SWU per year. Japan is completing a pilot plant and is considering a 6 x 10^6 SWU per year plant to be built in 1985. The U.S. is committed to an expansion of uranium separation facilities; after completion of improvements in the three gaseous diffusion plants, further additions to capacity will be the form of centrifuges. A test facility is operating at Oak Ridge National Laboratory, and a plant with a capacity of 8.8 x 10^6 SWU per year is to be built at Portsmouth, Ohio, by 1988. U.S. centrifuges have been estimated to have 10 times the capacity of the URENCO machines (66). Although the number of machines required is small compared to the number of barrier tubes in a diffusion plant of comparable capacity, the centrifuges are more expensive than barriers and associated equipment. The net cost associated with a centrifuge plant is thought to be comparable or lower; Letokhov and Moore state (70) that the costs may be lower by 10-30%. The big advantage of the centrifuge is its lower energy consumption; the energy per unit separative work has been estimated as about 4% of that required for gaseous diffusion (71,14) or about 0.4 GJ/kg U SWU. The CONAES report (72) cites a factor of 10 reduction in energy use compared to gaseous diffusion and an estimated unit capital cost of about $500/kg SWU per year.

1.2.7. Laser Isotope Separation

The conditions for laser separation of isotopes have been reviewed by Letokhov and Moore (70):

1) There must be at least one absorption line of the isotope separated that does not overlap significantly any absorption lines of other isotopes in the mixture;
2) Radiation at the chosen frequency must be available with the characteristic power, duration, divergence, and monochromaticity necessary for the separation method chosen;
3) There must be a primary photophysical or photochemical process that permits easy separation of the excited species from the mixture;
4) The selectivity for the desired isotope must be maintained against all competing photophysical or photochemical processes.

Laser separation is applicable to atoms or molecules. Either may be excited to a state (a) that undergoes a photochemical reaction with another atom or molecule, (b) that can be deflected in an external field (or by the pressure of the laser beam), or (c) that can be ionized by a second photon. Additionally, a molecule can be excited to a state that isomerizes to a different compound or that dissociates, either spontaneously or upon absorption of a second photon. Dissociation upon absorption of a single photon can be isotopically selective only if the excited state is quasi-stable, with a lifetime long enough to yield a sufficiently narrow line-width (predissociation). A well-studied example is the photochemical dissociation of formaldehyde,

$$H_2CO + h\nu(350\text{-}340\ \text{nm}) \rightarrow H_2 + CO$$

which, under appropriate conditions, yields stable products with a quantum efficiency close to unity.* The reaction can separate ^{1}H-^{2}H-^{3}H, ^{12}C-^{13}C-^{14}C, and ^{16}O-^{17}O-^{18}O; the highest enrichment factors obtained experimentally are 180 for hydrogen-deuterium (73), 80 for ^{12}C-^{13}C (74), 9 for ^{16}O-^{17}O, and 17 for ^{16}O-^{18}O (73). The practicality of separation methods based on this reaction, as for all laser methods, depends on the cost and energy efficiency of the laser. Typical figures are around $2 per watt of input electrical power and an efficiency around 1% for visible or near-ultraviolet lasers, 10% for infrared lasers (70). With a 1% laser efficiency, the dissociation of formaldehyde by a uv laser thus requires about 34 MJ per mole of a product partially enriched in one pass. More generally, the energy required per mole is

$$E = \frac{n_\nu hcN_o}{E_\nu E_\ell \lambda} = 1.196 \times 10^8 \frac{n_\nu}{E_\nu E_\ell \lambda} \text{ joules/mole} \qquad (1.42)$$

where n_ν is the number of photons required,
h is Planck's constant,
c is the speed of light,
E_ν is the overall quantum efficiency of the separation process,
E_ℓ is the laser efficiency,
λ is the wavelength of the laser light in nanometers, and
N_O is Avagadro's constant.

The factor $\frac{n_\nu}{E_\nu E_\ell}$ in equation 1.43 should be replaced by a summation for processes involving several photons of different wavelength and/or several lasers. Note that the energy calculated by this equation is only the energy of the laser excitation process; it does not include the energy required to separate the excited species from the mixture, to convert the feed material to a chemical or physical form suitable for separation, to convert the product to the desired form, or to drive the material flows involved. The capital cost of the laser is given by

$$\text{Cost} = \frac{E}{3.156 \times 10^7 \text{ s/y}} C_W \text{ \$/g-mole per year} \qquad (1.43)$$

where C_W is the cost per electrical watt for the laser.

---

* The reaction mechanism is more complex than indicated here. Both the quantum yield and the isotopic selectivity are functions of the temperature, the pressure, and the presence of other substances, such as radical scavengers.

For the dissociation of formaldehyde at λ = 350 nm with a 1% efficient laser, a quantum yield of 100%, and an assumed capital cost and amortization rate of \$2 per watt and 20% per year, the capital cost is about 43¢ per mole, and the power cost at 3¢ per kwh is 28¢. Thus, ^{13}C of high (>90%) enrichment could be prepared in two stages at a cost of about 12¢ per gram for the laser and power, compared to an average price around \$69 per gram in 1978 for ^{13}C enriched by CO distillation (33). Although the overall costs are much higher than those associated with the laser, it appears that separation of carbon and perhaps oxygen isotopes by this method already has a strong economic advantage over existing small-scale commercial processes. The separation of deuterium by predissociation of formaldehyde has a comparative disadvantage due to the low natural abundance of deuterium and the low cost and energy efficiency of existing, large-scale industrial processes. A research effort aimed at a 1 ton per year pilot plant in 1983 is under way (75); isotopic selectivities of 10^3-10^4 and laser efficiencies approaching 2 or 3% are needed to make the process competitive.

Several schemes for separation of uranium isotopes are under active investigation. The most well-developed one (76) involves the selective ionization of ^{235}U atoms in a beam of uranium metal vapor and removal of the ions in an electric field. This is accomplished by selective excitation of ^{235}U to an intermediate bound state, followed by nonselective ionization by a second photon, where the energy of each photon separately is less than, but the sum of their energies is greater than, the ionization energy. Uranium metal is vaporized in a long trough; ^{235}U atoms selectively ionized by the two-step process are deflected from the beam by an electric field. The density of uranium vapor must be very low in order to avoid charge-exchange collisions between ^{235}U ions and neutral ^{238}U atoms, which would destroy the selectivity. Because of the resulting low optical density, a long optical path is employed in order to utilize the laser light fully. Product concentrations of 6% ^{235}U have been obtained from natural uranium in a single stage, with nearly complete stripping of the tails. The process has the capability of producing enriched uranium for light-water reactors ($\simeq$3% ^{235}U) economically from the large stockpiles of tails from gaseous diffusion plants. Jersey-Nuclear-Avco-Isotopes, Inc. (JNAI) is constructing a pilot separation plant based on this method. The economics are not well established (14): Janes, et al. (76) estimate that a full-scale plant would cost \$195/kg SWU per year and use about 0.6 GJ of energy per kg SWU. The capital cost is much lower than for gaseous diffusion or the gas centrifuge, and the energy consumption is comparable to that expected for the centrifuge.

Another type of process of recent interest is the use of isotope-selective multiple vibrational excitation of molecules. The excitation can cause dissociation of the molecule or induce a photochemical reaction with another molecule. A potential advantage of the method is the use of low-energy infrared photons--on the order of 200-2000 cm^{-1} (50,000-5,000 nm) or 0.025-0.25 eV, vs about 5 eV for dissociation by electronic excitation. The method requires very high instantaneous power densities in short pulses, on the order of 10^7 to 10^9 W/cm^2 in pulses of <1 μs. A combination of two frequencies, one to provide the isotope-selective multiple excitation (but with fewer photons per excitation), the second to further excite the same molecule to the energy at which it will react or dissociate, makes it possible to utilize intensities of 10^4 to 10^5 W/cm^2 (77,70). The dissociation of SF_6 has been studied extensively (78-80) using wavelengths around 10,600 nm, obtained from A CO_2 laser. The dissociation yields lower fluorides, which are less volatile and thus easily separated from unreacted SF_6. Because several photons are involved, the quantum yield in such a process increases with the laser intensity, so that the total energy required to excite a molecule decreases with intensity.

Although the net efficiency for use of photons must be lower than for single-step processes, the higher efficiencies of infrared lasers (10%, vs 1% for visible or uv lasers) can more than compensate. For the case of SF_6, the decrease is approximately linear and, at a power density of 200 W/cm^2, the dissociation of an SF_6 molecule requires only 12 eV of absorbed energy (70). This is equivalent to the energy required for a typical electronic excitation with a quantum yield of $\approx$50%. The separation factor varies from 3.5 at a pressure of 210 Pa to 10 at 27 Pa (70), and high enerichments can be obtained practically by "burning out"* the undesired isotopes (79). The Soviets are currently producing small quantities of the rare (0.017%) isotope ^{36}S at enrichments of 70% at a price around $180,000 per gram, presumably by this method (81); they also are producing several grams per day of 95% ^{13}C by multiple-photon disssociation of CF_3I (82). A similar method is under consideration for separation of uranium by dissociation of UF_6, by multiple vibrational excitation alone, or by vibrational excitation plus electronic excitation at another wavelength (14). In either case, the absorption bands are too broad to permit good selectivity; it is necessary to cool the molecules by expansion through a nozzle in order to obtain a high separation factor (83).

To summarize:

1) The subject of photochemistry is a very rich one; it may be thought of as having two dimensions (substance, wavelength), compared to one for ordinary chemistry. The number of potential isotope separation methods is correspondingly large. Furthermore, the most important characteristics of the process, the isotopic selectivity and the quantum yield, depend on the temperature and pressure, the presence of additional substances, and in some cases on the power level, in addition to the wavelength(s) and the substance undergoing separation. For these reasons and because laser photochemistry and photophysics are relatively young subjects under active study, it is likely that new and better methods of laser isotope separation will be discovered at a rapid rate. The first method to go into commercial production likely will not be the final one (70).
2) The low energy use and capital cost estimated for present separation methods make the use of laser separation very attractive. Applications to the small-scale production of research materials are particularly advantageous, since the laser requirements are not stringent, and the equipment is relatively inexpensive and readily available. Laser separation may reduce the cost of isotopes such as ^{13}C or ^{15}N to the point where their use in much greater quantities is practical. Competition with the large-scale, capital-intensive separation methods used for heavy-water and uranium enrichment is more severe. In the case of uranium, economic processes may be at hand; for deuterium, the selectivity of present processes is one to two orders of magnitude too low.

---

* A differential process similar to the enrichment of deuterium by electrolysis (continuous removal of the tails stream).

3) For large-scale operations, the most important factors limiting the use of laser separation are the characteristics of existing lasers. The requirements include a suitable spectrum (in most cases, a tunable laser), high efficiency, and high total power. For example, a plant to produce 2000 Mg of 3% ^{235}U per year, approximately equivalent to the output of a large diffusion plant (9×10^6 kg SWU per year) would require several tens of kW of continuous power, whereas existing tunable lasers in the visible or uv region have optical outputs of a few watts (70). Economically viable lasers for deuterium separation must be 100 times larger than those needed to separate uranium (70).

1.2.8. Other Methods for Isotope Separation

Only one other method, the aerodynamic or nozzle process, has been considered for commercial-scale enrichment. This process, which depends on the centrifugal acceleration of a high-speed stream of gas molecules, is discussed in references (14 and 34) and references contained therein. Work by Becker and collaborators at Karlsruhe (84,85) has resulted in a conceptual design for a 5×10^6 kg SWU per year plant (86); the UCOR process developed in South Africa is the basis for a 5×10^4 kg SWU per year prototype plant under construction (87). Although capital costs for plants based on the aerodynamic process may be somewhat lower, the energy consumption is estimated as 16 GJ/kg SWU for the German plant and 13 GJ/kg SWU for the UCOR plant vs 9.0 GJ/kg SWU for the U.S. gaseous diffusion plants and about 0.4 GJ/kg SWU estimated for a gas centrifuge plant. The high energy consumption makes it unlikely that the separation nozzle will compete strongly with the gas centrifuge or with laser-based processes in developed countries.

Many other interesting effects have been shown to have some degree of isotopic selectivity, although they are not competitive with processes described above. Adsorption of hydrogen on surfaces at low temperatures is selective both for isotopes and for ortho-para hydrogen (88). Biological systems demonstrate a selectivity for the abundant isotopes of light elements--^1H, ^{12}C, and ^{16}O, for example. Mass and sweep diffusion--diffusion of a gaseous isotopic mixture into another gas--has been used to separate isotopes on a laboratory scale (34,14).

2. Applications of Stable Isotopes

Since ordinary matter is composed of stable or long-lived isotopes, "applications" could be interpreted broadly to encompass all of chemistry. At the other extreme, one might consider only applications of artificially enriched isotopes. The latter viewpoint is closer to the spirit of the present article but somewhat too restrictive; also of interest are applications that are dependent on the characteristics of a specific isotope or upon differences between isotopes of the same element. Even without this addition the number of applications is very large. Therefore, this section describes, for the most part, general classes of applications and gives a few examples of specific ones. For isotopes important to the nuclear power industry, the economic aspects are emphasized; for other applications only a brief description of the underlying principle is given.

2.1. Nuclear Power

Because it is based on the fission chain reaction, a purely nuclear phenomenon, nuclear electric power generation involves a number of isotope applications and accounts for most of the separated isotope production. Materials whose nuclear properties are important in a reactor include the fuel, moderator, control elements, and other materials (e.g., structural) present within the nuclear reaction zone. Nuclear fuel consists of a fissionable isotope--one that fissions upon absorption of a neutron, yielding approximately 200 MeV per atom (1.9×10^{13} J per g mole) of energy and more than two additional neutrons. Only one natural substance, ^{235}U, is a suitable fuel; two others, ^{233}U and ^{239}Pu, can be "bred" by capture of neutrons by natural ^{232}Th or ^{238}U and subsequent β^- decay. Most power reactors in use today (light-water-moderated reactors) require uranium enriched from its natural concentration (0.720 atom percent) to about 3% ^{235}U. High-temperature gas-cooled reactors, naval reactors, and some research and isotope-production reactors utilize uranium of higher enrichment. $^{238}U/^{239}Pu$ serve as the fertile/fissile materials in fast breeder reactors currently under development; $^{232}Th/^{233}U$ is under study as a fuel system for a thermal breeder reactor.

Thermal reactors presently in use require a moderator to slow the fission neutrons from an average energy of about 2 MeV to thermal energies ($\simeq 0.05$ eV). Ordinary water is used as a moderator in all commercial U.S. power reactors. Heavy water, which has a lower neutron capture cross section, is used in research and isotope production reactors, in which a high neutron flux or a high energy density is important, and in the CANDU power reactor, which uses natural uranium as a fuel. These reactors require large amounts of heavy water. Carbon (graphite), mixed with fuel particles, serves as the moderator in gas-cooled reactors. The isotopic constitution of other materials within the neutron field of a reactor is important. The coolant and structural materials must have a low probability for neutron absorption, whereas high neutron absorption is required for control elements. Special neutron-absorbing materials include cadmium in control rods, gadolinium as a "burnable neutron poison" in fuel-rod positions, and boron as an alternative control-rod material. The effective isotopes are ^{113}Cd, ^{155}Gd, ^{157}Gd, and ^{10}B, and the average cross sections for the natural elements (the sum of the isotopic cross sections weighted by the isotopic abundances) are Cd: $(2.42 \pm 0.03) \times 10^3$ b, Gd: $(4.91 \pm 0.10) \times 10^4$ b, B: $(7.6 \pm 0.3) \times 10^2$ b (1 b = 10^{-24} cm^2). In some reactors boron may be added to the moderator in an emergency to aid in stopping the chain reaction. Enriched ^{10}B is sometimes used in applications where high neutron absorption per unit volume is important, since ^{11}B, which comprises 80 atom percent of natural boron, has a negligible neutron cross section. Fuel cladding is made of alloys of zirconium with low capture probabilities. Other low-absorption materials include ^7LiOH used to control the acidity of the coolant, since ^6Li has a high cross section and other alkali metals have high cross sections and also activate strongly.

Most of the uranium required in the next 30 years will serve as fuel in power reactors, predominantly light-water reactors utilizing 2-4% enriched ^{235}U. The amount of uranium required per unit power depends on a number of factors: the concentration of ^{235}U in the tails from the enrichment process, the type of reactor and the specifics of its design, the operating and refueling schedule, and whether the fuel is used "once through" or is reprocessed to recycle fissionable material (^{239}Pu, ^{241}Pu, and unused ^{235}U). A 1000 MWe light-water reactor operated at typical capacity factors*, requires approximately 4000 to 6000 Mg (metric tons) of natural U_3O_8 over a 30-year lifetime, the higher figure corresponding to a once-through fuel cycle and a higher tails assay (0.3% vs 0.2%). For the purpose of the present discussion, it is adequate to use a mean figure of 5000 Mg U_3O_8 for the lifetime uranium requirement, with an initial core load of about 710 Mg** and additional yearly consumption at a rate of 143 Mg per year. The corresponding enrichment services are about 0.5×10^6 SWU plus 0.10×10^6 SWU per year of operation. When the enrichment is performed in a gaseous diffusion plant, the energy required is equivalent to 0.25 y of the reactor's power production for the initial core load plus 5% of its continuing output.

The need for enrichment worldwide is dependent on the future growth of nuclear power. At present, that future is somewhat uncertain, and projections have been reduced sharply in the last few years. Figure 15 shows the recent CONAES projections for the U.S. (72,90), along with earlier projections for the U.S. and the "world outside communist countries (WOCA)" (91) and a very recent U.S. projection by the Department of Energy (92). Figure 16 compares the separative capacity that would be required, based on these estimates, with that actually in existence, under construction, or planned.† The U.S. Department of Energy presently has contract commitments, domestic and foreign, that exceed the U.S. separative capacity in the mid-1980s, although it appears that some of these contracts may overstate the utilities' actual requirements (72,93). It is clear from Figure 16 that the U.S. has adequate separative capacity to meet domestic needs. Whether the world capacity is sufficient to meet demand depends on whether even the "minimum likely" WAES estimate may be too high, as appears to be the case for their U.S. estimate. In any case, the scarcity of uranium resources is probably a more important economic limitation than a lack of separative capacity to the expansion of nuclear power based on the present generation of reactors. For example, the CONAES report (72,90) estimates the U.S. resource base as 1.8×10^6 Mg, or enough to fuel about three hundred 1000 MWe reactors over their lifetime. (This figure is also consistent with the WAES estimate (91) of 1.81×10^6 Mg "reasonably assured" and 1.68×10^6 Mg "estimated additional" resources worldwide.)†† Since the more fuel-efficient breeder or advanced converter reactors also require much less separation, it seems unlikely, even in the event the higher projections prove correct, that a serious shortage of separative capacity will occur.

The total heavy-water inventory of a representative 600 MWe CANDU reactor is about 460 Mg (89) or about 770 Mg per 1000 MWe. Yearly make-up requirements are only about 6-10 Mg per 1000 MWe (45) so that the heavy-water requirement

---

* I have assumed here an average capacity factor of 67%. Nero (89) uses a 40-year lifetime with a variable capacity factor, producing the same total energy over its lifetime.

**An average figure. Reference 89 gives 550 Mg for a pressurized water reactor, 870 Mg for a boiling-water reactor.

† I have dropped the WAES "maximum likely" projections from the following discussion of uranium separation, since they appear to be too high.

††However, these estimates of the size of the uranium resource base have been disputed as being too low; see reference (94).

is nearly proportional to the amount of new generating capacity being built. The present world heavy-water capacity of about 1700 Mg/y supports a construction rate of about 2200 MWe per year; by 1982, if the new heavy-water plants are completed on schedule, the world capacity will support a growth rate of about 5700 MWe/y. With the assumption that heavy-water reactors will account for 5% of the total nuclear power in 1985, growing to 7% in the year 2000 (91), WAES projections are equivalent to a D_2O requirement between 2100 and 4500 Mg/y in 1985 and between 2900 and 6300 in the year 2000. (Inclusion of the make-up requirement for existing reactors adds 600 to 1200 Mg/y to the estimates for year 2000.)

Compared to the amount of deuterium used as a moderator, the deuterium requirement for a fusion reactor would be very small; at 30% overall efficiency, a 1000 MWe (d,t) reactor would require less than 0.8 Mg/y of D_2O. The required tritium presumably would be bred in the reactor's neutron-absorbing blanket by the reaction $^6Li(n,\alpha)t$.

2.2. Stable Tracers

The use of isotopes as tracers is a powerful method for following the path of an element through a chemical, biological, or physical system. Radioisotopes are most commonly employed as tracers because they are easily detected, can be used in small quantities, and often can be detected remotely through intervening material, due to the emission of penetrating gamma rays of characteristic energy. (A forthcoming article in this edition will discuss Radioisotopes (95).) On the other hand, there are a number of reasons for using stable isotopes as tracers:

1) There may be no radioisotope of the desired element with a convenient half-life or with easily detected radiations. Both short and long half-lives can present problems. Although the definition of a "convenient" half-life depends on the application, half-lives less than one hour are often inconvenient, and a half-life of less than about one day may be a problem if the isotope is produced commercially and transported to the site of use. Isotopes with long half-lives may be difficult or costly to produce with sufficient activity. The problem of inappropriate half-lives is particularly serious for the light elements that are important in biological systems. Table 10 lists the light elements for which stable tracers are often preferred or required.
2) There may be constraints on the use of radioactivity because of damage to the chemical or biological system under study, to a medical patient, to the experimenter, or to the environment. Long-lived isotopes, especially isotopes of elements with a long residence time in the body, are especially a problem.

The restrictions noted above apply especially to medical and agricultural applications of tracers. These applications account for much of the ^{13}C and ^{15}N used and form a large potential market for cheaper, laser-enriched isotopes. These isotopes are also convenient tracers for use in chemistry laboratories, where IR or NMR spectrometers are often available as detectors.

2.3 Production of Radioisotopes

Radioisotopes are produced by bombardment of a stable isotope with neutrons or charged particles. Enriched isotopic targets, while not essential, may be used because

1) Other isotopes of the target element yield radioisotopes that interfere with the application or produce excessive or long-lasting radiation;
2) The target isotope is a rare one, and high yield and/or high specific activity (in the case where the radioisotope and target material are of the same element and thus cannot be separated chemically) are desired.

Both reasons are often important for nuclear physics experiments, in which high radiochemical purity is usually important, and high yield or high specific activity ("massless" sources) may be necessary to obtain the desired sensitivity or resolution.

In medicine, radiochemical purity may lower dosage to the patient. For example, ^{123}I is preferred over the more commonly used ^{131}I for measurement of the uptake of iodine by the thyroid, because of its shorter half-life (13.0 h vs 8.040 d (3)). ^{123}I is best made by the reactions ^{122}Te(d,n), ^{123}Te(p,n), or ^{124}Te(p,2n). However, the use of a natural target results in production of 60.2 d ^{125}I and 13.0 d ^{126}I via the reactions ^{124,125}Te(d,n), ^{125,126}Te(p,n), and ^{126}Te(p,n); with these contaminants, which are greatly reduced by the use of enriched targets, the total dose to the patient can be larger than with ^{131}I. Kamen (96) has reviewed the use of isotopes in medicine.

Separated isotopes can be used also as projectiles in a charged-particle accelerator, as described in the next section.

2.4 Nuclear Physics Research

In addition to the study of radioisotopes (which has lost much of its standing as a respectable activity), nuclear scientists study nuclear reactions *in beam*: target foils are bombarded with charged particles or neutrons, and the properties of emerging particles (particle type, energy, intensity, angular distribution, polarization, particle-particle correlations) are measured with electronic detectors and/or magnetic spectrometers. Whether in-beam or out, the nuclear characteristics measured, in particular the nuclear structure properties, are specific to the nucleus; i.e., to the nuclear physicist, different isotopes of the same elements are as dissimilar as different elements. Thus, separated isotopes are used routinely as targets. Although most accelerators and/or associated beam transport systems provide good mass discrimination*, separated isotopes whose natural abundance is low are used as beam particles in order to obtain a higher beam intensity. Of particular

---

* The cyclotron is the best "mass spectrometer" for detection of a trace amount of one isotope in the presence of an abundant one. It has been used to assay directly ^{14}C and other radioactive isotopes present in traces in natural samples (97).

importance is ^{3}He. Because of its cost, accelerators using ^{3}He beams have recovery systems to recycle the gas. Other separated isotopes used as beam particles include ^{13}C, ^{15}N, ^{17,18}O, ^{48}Ca, and ^{136}Xe.

2.5 Chemistry Applications

Tracers play a major role in chemistry research. Several additional phenomena related to isotopes are treated here.

2.5.1. Structural Chemistry

The usefulness of nuclear magnetic resonance (NMR) to determine chemical structure is enhanced by the substitution of isotopes that have easily observed resonances for ones that do not. There are three reasons for isotopic substitution in NMR experiments:

1) The abundant isotope(s) has no magnetic moment, i.e., its spin is zero. This is true of all even-even nuclei; all other stable or long-lived isotopes have nonzero spin. Of the 83 elements listed in Table 1, 41 consist entirely of isotopes with nonzero spin; of these 19 are monoisotopic. As mentioned in the introduction, three elements have no NMR-detectable isotopes--argon, cerium, and thorium. For the remaining 39 elements with even Z, detectable (odd-mass) isotopes tend to have low abundances; 11 elements have no detectable isotopes of abundance greater than 5%. For such elements, the use of enriched isotopes enhances the sensitivity of NMR measurements in proportion to the enrichment, $x_{enr.}/x_{nat.}$.
2) The abundant isotope has a quadrupole moment ($J \quad 1/2$), which perturbs the NMR resonances. The quadrupole interaction is the basis for interesting applications of NMR to the study of internal atomic fields. However, in addition to splitting NMR resonances, it may broaden them due to short relaxation times, thus making it difficult to detect resonances or to interpret their structure. For example, the ^{14}N-H coupling is not observed in peptide bonds; the substitution of ^{15}N allows discrimination between hydrogen bonds involving amide groups or hydroxyl groups in deuterated proteins (98).
3) Selective isotopic substitution at specific sites of a molecule permits examination of the electron-nucleus interaction at those sites without interference from the same element at other sites.

Table 11 lists the spin-1/2 isotopes and their magnetic moments, together with their natural abundances. Several isotopic substitutions are especially useful in NMR: ^{13}C($J = 1/2$) for ^{12}C ($J = 0$), ^{15}N ($J = 1/2$) for ^{14}N ($J = 1$). Isotopic substitution can be used similarly in electron spin resonance (esr) measurements to produce a fine structure identifiable with a particular site in a molecule.

2.5.2. Isotope Effects

Isotope effects include the exchange of isotopes between two compounds or phases, and the change in properties of a chemical compound or reaction upon substitution of one isotope for another. They may be classed broadly as thermodynamic effects (the equilibrium isotope effect), or as rate changes (the kinetic isotope effect). The former are of particular interest for isotope separation.* The latter provide a useful tool for the study of reaction mechanisms, and play an important role is isotope biology.

The basic theory of isotope effects, developed by Bigeleisen and Mayer (100), describes the fundamental isotope effect in terms of the *reduced partition function ratio*** for a substance:

$$\frac{s_2}{s_1} f = \frac{(Q_2/Q_1)_{qm}}{(Q_2/Q_1)_{cl}} \qquad (2.1)$$

where s_1, s_2 are symmetry numbers of the isotopic molecules (which always cancel like factors in the partition functions),
Q is the total partition function of the substance,
the subscripts 1, 2 refer to one of two isotopes, and
the subscripts qm, cl denote the quantum mechanical or classical partition function ratios.

Translational and (at ordinary temperatures) rotational components of this function cancel, since these motions are classical. Within the Born-Oppenheimer approximation, the electronic energy is unaffected by isotopic substitution. Thus, only the vibrational degree of freedom is involved, and the effect can be written as (99)

$$\frac{s_2}{s_1} f = \left[\prod \frac{u_{2i}}{u_{1i}}\right] \exp[\textstyle\sum (u_{1i} - u_{2i})/2] \left[\prod \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}\right] \qquad (2.2)$$

where $u_{ni} = \frac{h\nu_{ni}}{kT}$

and ν_{ni} is the frequency of the i^{th} vibrational mode for the substance containing isotope n (n = 1,2).

Several generalizations follow from this formulation (99):

1) Isotope effects are vibrational in nature; they depend only on the isotopic masses and force constants for bonds to the isotopic atom. Isotopic effects for exchange between different compounds occur only if the isotope exchanged is subject to different forces in the two compounds. There is an effect of isotopic substitution upon the equilibrium or rate of a reaction (other than isotopic exchange) only if the bonding forces on the substituted atom undergo a change in the reaction.

---

* Most chemical methods for isotope separation are based on equilibrium effects. However, the separation in electrolysis is due to a kinetic effect (99).

**-RT $\ln(\frac{s_2}{s_1} f)$ is equal to the Gibbs free energy difference between the substance with and without isotopic substitution.

2) Isotopic substitution is additive and cumulative; that is, the logarithms of the partition function ratios add upon isotopic substitution for more than one atom, either in nonequivalent or in equivalent positions.
3) Equivalent isomers (e.g., ortho, meta, para dideuterobenzene) have the same isotope effect.

Several useful approximations to equation 2.2 have been derived. At low temperatures, the third term approaches 1, and:

$$\frac{s_2}{s_1} f \simeq \left[\prod \frac{u_{2i}}{u_{1i}}\right] \exp[\textstyle\sum(u_{1i} - u_{2i})/2] \quad ; \qquad (2.3)$$

furthermore, the first term in equation 2.3 is often neglected (the zero-point energy approximation). At high temperatures (100-103):

$$\ln\left(\frac{s_2}{s_1} f\right) \simeq \frac{1}{24} \sum (u_{1i}{}^2 - u_{2i}{}^2) \qquad (2.4)$$

This formula has been modified for use at lower temperatures (101,104):

$$\ln\left(\frac{s_2}{s_1} f\right) = \frac{\overline{\gamma}}{24} \sum (u_{1i}{}^2 - u_{2i}{}^2) \qquad (2.5)$$

where $\overline{\gamma} = \frac{12}{\overline{u}}\left(\frac{1}{2} - \frac{1}{\overline{u}} + \frac{1}{e^{\overline{u}} - 1}\right)$,

and $\overline{u} = h\overline{\nu}/kT$, where $\overline{\nu}$ is some mean frequency characteristic of the chemical species and the isotopic substitution considered.

Evaluation of equations 2.2-2.5 can be done from spectroscopic data on the actual vibrational energies $h\nu$ or from calculated bond force constants and reduced masses. In the former case, it is necessary only to know the frequencies of one of the isotopic forms, since the others can be calculated from the reduced masses. Examples of the use of bond force constants are given in references (99,103). Further approximations and calculational methods are discussed in references (99,105,106).

2.5.2.1. Equilibrium Isotope Effects

The separation factor for an exchange reaction between compounds AX, AY:

$${}^2AX + {}^1AY \rightleftarrows {}^1AX + {}^2AY$$

is given by:

$$\alpha = \phi(AY)/\phi(AX) \quad , \qquad (2.6)$$

where $\phi = \frac{S_1}{S_2} f$ (in one of the above forms (eqns. 2.2-2.5)).

The effect of isotopic substitution on an ordinary reaction $AX + B \rightleftarrows AY + C$:

$$^1AX + B \rightleftarrows {}^1AY + C \qquad K = K_1$$

$$^2AX + B \rightleftarrows {}^2AY + C \qquad K = K_2$$

is simply given by

$$K_2 = \alpha K_1 \tag{2.7}$$

where α is defined by equation 2.6,

since the second reaction is the sum of the first plus the isotopic exchange reaction. Similarly, equation 2.7 is valid for dissociation reactions of the form $AX \rightleftarrows AY + C$. For dissociation into the atom itself ($AX \rightleftarrows A + X$), the effect of isotopic substitution is given by

$$K_2/K_1 = 1/\phi(AX) \tag{2.8}$$

The above formulae apply to noninteracting molecules; in the condensed state intermolecular forces on the isotopic atom must be considered. This problem and the related subject of solvent effects have been discussed by Van Hook (107). A particularly simple case is the distillation (or sublimation) of a monatomic substance, for which in the high-temperature approximation (99):

$$\ln(P_2/P_1) = \frac{1}{24}(h/kT)^2\left(\frac{1}{m_2} - \frac{1}{m_1}\right)\langle\nabla^2U\rangle \tag{2.9}$$

where $\langle\nabla^2U\rangle$ is the mean value of the Laplacian of the interaction potential in the condensed phase. For a harmonic oscillator potential $\langle\nabla^2U\rangle$ is the force constant; for a Debye solid it is equal to $(k\Theta_D/h)^2m$.

2.5.2.2. Kinetic Isotope Effects

Kinetics are determined by the relationship between the state of the reactants and the transition state. Since the partition function for this state is poorly known, the estimation of kinetic isotope effects is in general difficult. In several circumstances kinetic isotope effects are particularly easy to estimate. In the dissociation of the isotopic atom, $XA \rightleftarrows X + A$, the transition state is equal (to the extent that there is no potential barrier) to the final state, and the change in rate upon substitution of ^2A for ^1A should be given by

$$\frac{k(^1A)}{k(^2A)} = \frac{\nu_{1d}}{\nu_{2d}}\phi(AX) \tag{2.10}$$

where ν_{nd} is the vibrational contribution in the direction of dissociation (i.e., in the stretching mode),
and $\phi(AX)$ is defined by one of the equations 2.2-2.5.

(The factor ν_{1d}/ν_{2d} is the familiar frequency factor in the kinetic rate expression.)

When an isotopic atom (A) is transferred from one compound to another,

$$BA + C \rightleftarrows CA + B,$$

the stretching-mode coordinate ($B \leftrightarrow A$) becomes the reaction (translational) coordinate, as the restoring force nearly vanishes. In this case, the effect of isotopic substitution on the rate constant is given approximately by (108,109):

$$k(^1A)/k(^2A) = \exp[(u_2 - u_1)/2] \frac{1 - e^{-u_1}}{1 - e^{-u_2}} \qquad (2.11)$$

$$= \sinh(u_1)/\sinh(u_2)$$

where $u_n = h\nu_n/kT$,

and ν_n is the stretching-mode frequency of the molecule ^nAB.

For example (108), in the transfer of a hydrogen atom bonded initially to a carbon atom ($\bar{\nu}_{C-H} \simeq 3015\ cm^{-1}$, $\bar{\nu}_{C-D} \simeq 2212\ cm^{-1}$), $k_H/k_D = 7$.

Changes in reaction rates in which the rate-determining step involves the bond to the isotopic atom are called *primary isotope effects*. Secondary isotope effects are further classified as α, β, ... effects according to the separation between the isotopic atom and the bond undergoing reaction. The maximum possible secondary effect is about 10% of the maximum primary effect calculated by equation 2.10 (110). Observation of an effect larger than this demonstrates the involvement of a bond to the isotopic atom; the actual size of the effect further characterizes the transition state. Further review of the use of kinetic isotope effects to elucidate reaction mechanisms is given in references (108,111).

2.6. Isotope Biology

Because of the large isotope effects on biochemical reactions when deuterium is substituted for hydrogen, deuterium (heavy water) was considered toxic to all living organisms prior to 1960. Although moderate quantities of heavy water can be ingested, replacement of more than about 1/3 of the hydrogen in a higher organism with deuterium is lethal (112).* However, in a remarkable experiment in 1960, Chorney and co-workers (113) found that the green algae *Chlorella Vulgaris* and *Scenedesmus obliquus* could be grown in pure (99.7%)

---

* Since replacement of such a large fraction of the body's hydrogen is necessary, deuterium is considered toxic only in large quantities. Mice survive for 12 days on 75% D_2O, indefinitely when drinking 30% D_2O (114). Toxic effects are apparent when ^2H levels reach 10-15% in tissue fluids (98).

heavy water after a period of adaptation. This experiment launched a new field of deuterium biology, which has been reviewed by Katz and co-workers (98,114).

Algae require only CO_2, water, inorganic salts, and light to sustain growth. Since they synthesize all their own organic compounds, with water as the sole source of hydrogen, they serve as factories for a whole spectrum of biochemicals fully substituted with deuterium. Because of interest both in deuterated living systems and in the complex molecules extracted from them, the group at Argonne National Laboratory has developed systems for mass cultivation of algae on a scale of 20-40 grams per day (114). (The growth rate exhibits an isotope effect $k_H/k_D = 3.5$ (114).) Other fully deuterated organisms have been grown in heavy water, using deuterated organic substances extracted from algae as nutrients: bacteria, yeasts and molds, protozoa, and viruses. The effects of varying degrees of deuteration on higher plants and on mammals has been studied. Multiple isotopic substitution, including combinations of deuterium, ^{13}C, ^{15}N, and O^{17} or O^{18} has been studied in algae.

The observed morphological, physiological, and biochemical changes that accompany deuteration (and, to a lesser extent, isotopic substitution for other elements) are not fully understood. Deuteration interferes with cell division; in mammals, it impairs renal function, disturbs the central nervous system, causes cardiac irregularities, and affects enzyme and hormone levels. Effects on the genetic apparatus appear to be small, but D_2O inhibits sexual reproduction at levels too low to affect body weight or life span.

In contrast to the difficulty of interpreting the complex effects of deuterium on living systems, the study of biochemical compounds and reactions by conventional techniques is simplified greatly by isotopic substitution. For example, by study of normal and deuterated compounds in water and heavy water, it is easy to distinguish exchangeable amide or hydroxyl hydrogen atoms from nonexchangeable hydrogen atoms attached to carbon and to distinguish slowly exchangeable amide hydrogen from more rapidly exchangeable hydroxyl hydrogen.

2.7. Isotope Geology

The many subtle variations (and a few dramatic ones) in the isotopic composition of natural materials are the basis for a number of applications to the geosciences. The isotopes ^{40}K, ^{87}Rb, ^{176}Lu, ^{187}Re, ^{232}Th, ^{235}U, and ^{238}U have half-lives that are within a factor of 10 of the age of the earth and are therefore useful as geologic clocks. The somewhat longer lived isotopes ^{138}La, ^{144}Sm, and possibly ^{190}Pt might also serve as clocks. More recent events can be measured by shorter-lived isotopes that occur in trace quantities as the result of cosmic ray bombardment or as daughters of long-lived isotopes. References (115-120) discuss some isotope dating applications.

Small variations in the stable isotope abundance ratios (R) have been exploited to yield information about a number of underlying causes. These variations are expressed conventionally by the quantity

$$\delta(‰) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad . \tag{2.11}$$

Water is of particular interest because it is ubiquitous. The abundance variations of hydrogen (including tritium), oxygen, and carbon (dissolved as CO_2/bicarbonate) in groundwater are related to the origin, sources of recharge, and the temperature (121-125). Meteoric water is characterized by an oxygen isotope ratio that is dependent linearly on precipitation temperature (126) and related linearly to the hydrogen ratio (127):

$$\delta(^{18}O/^{16}O) \simeq 0.69(T-19)$$

$$\delta(D/H) \simeq 8 \ (^{18}O/^{16}O) + 10 \quad .$$

Both correlations are the result of differential separation that occurs when water condenses from vapor with which it is in isotopic equilibrium and is removed continuously as raindrops (Rayleigh condensation). Deviations from these relationships indicate the occurrence of other processes. For example, geothermal waters generally have a D/H ratio characteristic of local precipitation, which is their original source, but elevated $^{18}O/^{16}O$ ratios, due to the exchange of oxygen with deep-lying rock. The temperature dependence of the equilibrium constant for rock-water exchange reactions (either isotopic or chemical) is the basis for several *geothermometers*, from which temperatures at depth can be estimated from the analysis of the composition of surface hot springs.

$^3He/^4He$ abundances can vary over eight orders of magnitude (128,129); the main cause of the variations is the admixture of primordial helium with pure ^4He from the decay of natural alpha emitters. (See Table 12.) Variations in stable isotope abundances have many causes in addition to those described above, including fractionation in biologic systems. References (130-132) offer general treatments of this extensive subject.

Several new sources of isotopic anomalies have been the subject of considerable recent interest. As mentioned in the introduction, there are abundance variations in meteorites (7,8, and references therein); such variations may contain information on nucleosynthesis and the state of primordial matter of the solar system. A striking recent discovery is the onetime existence, about 1.8 billion years ago (133), of a natural nuclear reactor in Gabon, Africa. At that time, the ^{235}U content would have been about 3.1%, sufficient to sustain a chain reaction with water as the moderator. Evidence for the reactor includes anomalously low ^{235}U abundances and certain elements, such as neodymium, whose isotopic compositions are characteristic of fission products rather than terrestrial material. Isotopic aspects of the Oklo phenomenon are discussed in references (134,135).

Acknowledgements

I am indebted to Manson Benedict and Thomas H. Pigford for the use of materials from chapters 12-14 of the second edition of their classic text prior to publication, to C. Bradley Moore for material on laser isotope separation, and to Maynard C. Michel for helpful discussions. Additional information was provided by Jack M. Hollander, Walter Haubach, John Burnett, Eugene Newman, and Richard Vallee. The assistance of the Library Department and of Claire Grevin, Jeanne Christie-Sehr, and Jeanne Hassenzahl of Lawrence Berkeley Laboratory is gratefully acknowledged. This work was supported by the Director, Office of Energy Research, Division of Nuclear Sciences of the Basic Energy Sciences Program of the U.S. Department of Energy under Contract W-7405-ENG-48.

References

1. J.J. Thompson, *Rays of Positive Electricity and their Application to Chemical Analyses*, Longmans, Green and Co., Ltd., London (1913).

2. J. Chadwick, Proc. Roy. Soc. A136, 692 (1932).

3. *Table of Isotopes,* 7th edition: C.M. Lederer and V.S. Shirley, eds.; E. Browne, J.M. Dairiki, and R.E. Doebler, principal authors; A.A. Shihab-Eldin, L.J. Jardine, J.K. Tuli, and A.B. Buyrn, authors, John Wiley and Sons, Inc., New York (1978).

4. N.E. Holden, Brookhaven National Laboratory Report No. BNL-NCS-50605, 1977 (unpublished).

5. E.M. Burbidge, G.R. Burbidge, W.A. Fowler, and F. Hoyle, Rev. Mod. Phys. 29, 547 (1957).

6. Arno A. Penzias, Science 205, 549 (1979).

7. H.R. Heydegger, J.J. Foster, and W. Compston, Nature 278, 704 (1979).

8. R.V. Ballad, L.L. Oliver, R.G. Downing, and O.K. Manuel, Nature 277, 615 (1979), and references therein.

9. G.P. Barnard, *Modern Mass Spectrometry,* The Institute of Physics, London, 1953; Robert W. Kiser, *Introduction to Mass Spectrometry and its Applications,* Prentice-Hall, Inc., Englewood Cliffs, N.J. (1965).

10. *Recent Developments in Mass Spectrometry,* ed. by K. Ogata and T. Hayakawa, University Park Press, Baltimore (1969); *Advances in Mass Spectrometry,* vols. 7a and 7b (Proc. 7th Intl. Mass Spectrometry Conf., Florence, Aug. 30-Sept. 3, 1976), ed. by N.R. Daly, Heyden and Son, Ltd., London (1978); Proc. 8th Intl. Mass Spectrometry Conf., Oslo, Summer 1979 (to be published).

11. Paul de Bievre, *ibid.,* p. 395 (1978).

12. E. Roth, R. Bir, and B. Hageman, in *Recent Developments in Mass Spectroscopy*, ed. by K. Ogata and T. Hayakawa, p. 403, University Park Press, Baltimore (1969).

13. Lord Rayleigh, Phil. Mag. 4, 521 (1902).

14. M. Benedict, T.H. Pigford, and H.W. Levi, *Nuclear Chemical Engineering* (2nd edition), McGraw-Hill Book Co., New York, to be published (1980).

15. Karl P. Cohen, *The Theory of Isotope Separation as Applied to the Large-scale Production of* ^{235}U National Nuclear Energy Series Div. 3, vol. 1B, McGraw-Hill Book Co., New York (1951).

16. D.R. Olander, Nucl. Tech. 29, 108 (1976).

17. A. de la Garza, G.A. Garrett, and J.E. Murphy, USAEC report K-1455, July, 1960; Chem. Eng. Sci. 15, 188 (1961).

18. A. de la Garza, Chem. Eng. Sci. 18, 73 (1963).

19. H.R.C. Pratt, *Countercurrent Separation Processes,* Chapt. 10, Elsevier Publ. Co., New York (1967).

20. F.T. Barr and W.P. Drews, Chem. Eng. Prog. 56, 49 (1960).

21. M. Benedict and T.H. Pigford, *Nuclear Chemical Engineering* (1st edition), McGraw-Hill Book Co., New York (1957).

22. William Spindel, Chapt. 5 in *Isotopes and Chemical Principles,* ed. by Peter A. Rock, ACS Symposium Series no. 11, American Chemical Society, Washington, D.C. (1975).

23. L.O. Love, Science 182, 343 (1973).

24. Herbert Childs, *E. O. Lawrence, An American Genius* , Chapt. XIII, E.P. Dutton and Co., Inc., New York (1968).

25. Stelio Villani, *Isotope Separation,* American Nuclear Society, Washington, D.C. (1976).

26. S. Chapman, Phil. Trans. Roy. Soc. London, Ser. A 216, 279 (1916); 217, 115 (1917).

27. K. Clusius and G. Dickel, Naturwiss. 26, 546 (1938).

28. W.M. Rutherford, Separation and Purification Meth. 4, 305 (1975).

29. W.H. Furry, R.C. Jones, and L. Onsager, Phys. Rev. 55, 1083 (1939); R.C. Jones and W.H. Furry, Rev. Mod. Phys. 18, 151 (1946).

30. G. Vasaru, G. Muller, G. Reinhold, and T. Fodor, *The Thermal Diffusion Column,* VEB Deutscher Verlag der Wissenschaften, Berlin (1969).

31. P.H. Abselson and J.I. Hoover, in Proc. Intl. Symp. on Isotope Separation, Amsterdam, p. 483, Wiley Interscience Publishers, Inc., New York (1958).

32. A.H. Ruwe, Jr., Mound Laboratory Report MLM-2594, March 1979 (unpublished).

33. R.A. Schwind and W.M. Rutherford, in *Radiopharmaceuticals and Labeled Compounds,* International Atomic Energy Agency Report IAEA-SM-171/47, vol. II, p. 255 (1973).

34. R.L. Hoglund, J. Shacter, and E. Von Halle, in *Encyclopedia of Chemical Technology,* ed. by M. Grayson and D. Eckroth, vol. 7, p. 639, John Wiley and Sons, Inc., New York (1979).

35. Howard K. Rae, chapt. 1 in *Separation of Hydrogen Isotopes,* ed. by Howard K. Rae, ACS Symposium Series no. 68, American Chemical Society, Washington, D.C. (1978).

36. G.M. Murphy, H.C. Urey, and I. Kirshenbaum, *Production of Heavy Water,* McGraw-Hill Book Co., New York (1955).

37. G.M. Keyser, D.B. McConnell, N. Anyas-Weiss, and P. Kirkby, chapt. 9 in ref. 35.

38. R.E. Schreiber, *ICONS at LASL,* Los Alamos Scientific Laboratory Report LA-4759-MS, 1971 (unpublished).

39. A.A. Palko and J.S. Drury, chapt. 3 in *Isotope Effects in Chemical Processes,* ed. by Robert F. Gould, ACS Advances in Chemistry Series no. 89, American Chemical Society, Washington, D.C. (1969).

40. J. Shimokawa, G. Nishio, and F. Kobayashi, p. 397 in ref. 12.

41. G.D. Davidson, chapt. 2 in ref. 35.

42. B. Lefrancois in Proc. Conf. Techniques and Economy of Production of Heavy Water, Turin, Italy (1970), p. 197, Comitato Nazionale Energia Nucleare, Rome (1971).

43. P. Elwood, Chem. Eng., July 1, 1968, p. 274.

44. E. Nitschke, Atmowirt., June 1973, p. 274.

45. E. Nitschke, H. Ilgner, and S. Walter, chapt. 6 in ref. 35.

46. W.J. Holtslander and W.E. Lockerby, chapt. 3 in ref. 35.

47. N.P. Wynn, chapt. 4 in ref. 35.

48. J.P. Butler, J.H. Rolston, and W.H. Stevens, chapt. 7 in ref. 35.

49. M. Hammerli, W.H. Stevens, and J.P. Butler, chapt. 8 in ref. 35.

50. M.L. Rogers, P.H. Lamberger, R.E. Ellis, and T.K. Mills, chapt. 13 in ref. 35.

51. P.H. Pautrot and M. Damiani, chapt. 12 in ref. 35.

52. A.I. Miller and H.K. Rae, Chem. in Canada 27, 25 (1975).

53. U.S. Federal Register 42, 14768, March 16, 1977.

54. J.B. Marling, J.R. Simpson, and M.M. Miller, chapt. 10 in ref. 35.

55. L.R. Haywood and P.B. Lumb, Chemistry in Canada 27, 19 (1975).

56. E. Saito and G. Dirian, British patent no. 902,755, January 19, 1960.

57. E. Saito, U.S. Patent no. 3,105,737, Oct. 1, 1963; L. Perret, L. Rozand, and E. Saito, in The 2nd Intl. Conf. on Peaceful Uses of Atomic Energy, vol. 4, p. 595, United Nations, New York (1958).

58. D.A. Lee, chapt. 4 in ref. 39.

59. T.I. Taylor and W. Spindel, p. 158 in ref. 31; W. Spindel and T.I. Taylor, J. Chem. Phys. 24, 626 (1956).

60. G.A. Garrett and J. Shacter, p. 17 in ref. 31.

61. M. Jeevandam and T.I. Taylor, chapt. 8 in ref. 39.

62. G.J. Kynch, United Kingdom Atomic Energy Agency Reports MS 118, MS 119.

63. C. Frejacques et al., in Proc. Intl. Conf. on Peaceful Uses of Atomic Energy, vol. 4, p. 418 (1958).

64. U.S. Atomic Energy Commission Report ORO-684, Jan. 1972 (unpublished).

65. Donald R. Olander, Adv. Nucl. Sci. Tech. 6, 105 (1972).

66. Donald R. Olander, Sci. Amer. 239, no. 2, 37 (1978).

67. G. Zippe, Report EP-4420-101-60U, University of Virginia, July 1960 (unpublished).

68. W.G. May, Am. Inst. Chem. Eng. Symposium Series no. 169, 73, 30 (1977).

69. Nuclear Fuel, Oct. 31, p. 15 (1977).

70. V.S. Letokhov and C. Bradley Moore, chapt. 1 in *Chemical and Biochemical Applications of Lasers,* vol. III, ed. by C. Bradley Moore, Academic Press, New York (1977).

71. U.S. Department of Energy: United States Gas Centrifuge Program for Uranium Enrichment (1978).

72. Energy in Transition 1985-2010, *Final Report of the Committee on Nuclear and Alternative Energy Systems,* National Academy of Sciences/ National Research Council, W.H. Freeman and Co., San Francisco (1979).

73. Jack Marling, J. Chem. Phys. 66, 4200 (1977).

74. J.H. Clark, Y. Haas, P.L. Houston, and C.B. Moore, Chem. Phys. Lett. 35, 82 (1975).

75. J.C. Vanderleeden, Laser Focus 13, no. 6, 51 (1977).

76. G.S. Janes, H.K. Forsan, and R.H. Levy, Am. Inst. Chem. Eng. Symposium Series no. 169, 73, 62 (1977).

77. R.V. Ambartzumian, N.P. Furzikov, Yu.A. Gorokhov, V.S. Letokhov, G.N. Makarov, and A.A. Puretzkii, Opt. Commun. 18, 517 (1976).

78. R.V. Ambartzumian, Yu.A. Gorokhov, V.S. Letokhov, and G.N. Makarov, ZhETF Pis'ma Red. 21, 375 (1975). [Engl. transl: JETP Lett. 21, 171 (1975)].

79. R.V. Ambartzumian, Yu.A. Gorokhov, V.S. Letokhov, and G.N. Makarov, Zh. Eksp. Teor. Fiz. 69, 1956 (1975). [Engl. transl: Sov. Phys. JETP 42, 993 (1975)].

80. R.V. Ambartzumian, N.V. Chekalin, Yu.A. Gorokhov, V.S. Letokhov, G.N. Makarov, and E.A. Ryabov, Kvantovaya Elektron. (Moscow) 3, 802 (1976). [Engl. transl: Sov. J. Quantum Electron. 6, 437 (1976)].

81. S. Raman, private communication (Nov. 1979).

82. C. Bradley Moore, private communication (Dec. 1979).

83. R.J. Jensen, J.G. Marinuzzi, C.P. Robinson, and S.D. Rockwood, Laser Focus 12, no. 5, 51 (1976).

84. E.W. Becker, Prog. Nucl. En. 1, 27 (1977).

85. E.W. Becker, W. Bier, K. Schubert, R. Shütte, D. Seidel, and U. Sieber, Am. Inst. Chem. Eng. Symposium Series no. 169, 73, 25 (1977).

86. H. Geppert, et al., in Proc. Intl. Conf. on Uranium Isotope Separation, London, March 5-7, 1975, British Nuclear Engineering Society (1975).

87. A.J.A. Roux and W.L. Grant, *Uranium Enrichment in South Africa,* paper presented at the European Nuclear Conf., European Nuclear Society, Paris, April 1975, and discussion following the presentation, reported in ref. 14.

88. W.J. Haubach, P. Radhakrishna, A. Katorski, R. Wang, and D. White, chapt. 6 in ref. 39.

89. Anthony V. Nero, Jr., *A Guidebook to Nuclear Reactors,* University of California Press, Berkeley, California (1979).

90. H. Brooks and J.M. Hollander, Ann. Rev. Energy no. 4, 1 (1979).

91. *Report of the Workshop on Alternative Energy Strategies,* Carroll L. Wilson, Director, McGraw-Hill Book Co., New York (1977).

92. Inside DOE, Oct. 19, 1979.

93. Nuclear Fuel, Oct. 31, 1977.

94. K.S. Deffeyes and I.D. MacGregor, Sci. Amer. 242, no. 1, 66 (1979).

95. *Radioisotopes,* in *Encyclopedia of Chemical Technology,* ed. by M. Grayson and D. Eckroth, John Wiley and Sons, Inc., New York, to be published.

96. Martin Kamen, *Isotopic Tracers in Biology,* 3rd edition, Academic Press, New York (1957); for more recent information on stable isotopes in medicine, see Proc. First Intl. Conf. on Stable Isotopes in Chem., Biol., and Medicine, ed. by P.D. Klein and S.V. Peterson, May 9-11, 1973, Argonne National Laboratory, Argonne, Illinois (1973).

97. R.A. Muller, Science 196, 489 (1977).

98. J.J. Katz, R.A. Uphaus, H.L. Crespi, and M.I. Blake, chapt. 9 in ref. 22.

99. Jacob Bigeleisen, chapt. 1 in ref. 22; J. Bigeleisen, M.W. Lee, and F. Mandel, Ann. Rev. Phys. Chem. 24, 407 (1973).

100. J. Bigeleisen and M.G. Mayer, J. Chem. Phys. 15, 261 (1947).

101. J. Bigeleisen, p. 121 in ref. 31.

102. H.C. Urey, J. Chem. Soc., p. 562 (1947).

103. E.U. Monse, W. Spindel, and M.J. Stern, chapt. 9 in ref. 39.

104. J. Bigeleisen and M. Wolfsberg, Adv. Chem. Phys. 1, 15 (1958).

105. Max Wolfsberg, chapt. 10 in ref. 39; chapt. 6 in ref. 22.

106. T. Ishida, W. Spindel, and J. Bigeleisen, chapt. 11 in ref. 39.

107. W. Alexander Van Hook, chapt. 6 in ref. 22.

108. Vernon Jack Shiner, Jr., chapt. 8 in ref. 22.

109. Lars Melandar, *Isotope Effects on Reaction Rates,* Ronald Press, New York (1960).

110. E.K. Thornton and E.R. Thornton, chapt. 4 in ref. 111.

111. *Isotope Effects in Chemical Reactions,* ed. by C.J. Collins and N.S. Bowman, ACS Monograph No. 167, Van Nostrand Reinhold Co., New York (1970).

112. J.J. Katz, H.L. Crespi, D.M. Czajka, and A.J. Finkel, Am. J. Physiol. 203, 907 (1962).

113. W. Chorney, N.J. Scully, H.L. Crespi, and J.J. Katz, Biochem. Biophys. Acta 37, 280 (1960).

114. J.J. Katz and H.L. Crespi, chapt. 5 in ref. 111.

115. Proc. Symp. on Radioactive Dating, Athens, Nov. 19-23, 1962, International Atomic Energy Agency, Vienna (1963).

116. W.F. Libby, *Radiocarbon Dating,* 2nd edition, University of Chicago Press, Chicago (1955).

117. Stephen Moorbath, Sci. Amer. 236, no. 3, 92 (1977).

118. M.A. Lanphere, G.J.F. Wasserburg, A.L. Albee, and G.R. Tilton, in *Isotopic and Cosmic Chemistry,* ed. by H. Craig, D.L. Miller, and G.J. Wasserburg, p. 269, North-Holland Publ. Co., Amsterdam (1964).

119. Clair Patterson, p. 244 in ref. 118.

120. R. Dallmeyer, p. 77 in ref. 132.

121. D.E. White, Econ. Geol. 69, 954 (1974).

122. D.E. White in Proc. 1st U.S. Symposium on the Development and Utilization of Geothermal Resources, Pisa, Fall 1970 (Geothermics 1, Special Issue 2), p. 55 (1970).

123. Alfred H. Truesdell in Proc. 2nd U.N. Symposium on the Development and Utilization of Geothermal Resources, San Francisco, May 1975, p. liii, U.S. Government Printing Office, Washington (1976).

124. Various authors, Section III (p. 687 ff) in ref. 123.

125. W.G. Mook, Geol. Mijnbouw 51, 131 (1972).

126. H. Craig, Science 133, 1702 (1961)

127. W. Dansgaard, Tellus 16, 436 (1964).

128. V.I. Kononov and B.G. Polak, p. 767 in ref. 123.

129. L.K. Gutsalo, p. 745 in ref. 123.

130. J. Hoefs, *Stable Isotope Geochemistry,* Springer-Verlag, Berlin (1973).

131. J. Pilot, *Les Isotopes en Geologie (Methodes et Applications)*, Doin, Paris (1974).

132. *Lectures in Isotope Geology (Course)*, Dept. of Geology, University of Georgia, Springer-Verlag, Berlin (1979).

133. G.A. Cowan, E.A. Bryant, W.R. Daniels, and W.J. Maeck, p. 341 in ref. 135.

134. George A. Cowan, Sci. Amer. 235. no. 1, 36 (1976).

135. *The Oklo Phenomenon* (Proc. Symp. on the Oklo Phenomenon, Libreville, Gabon, June 23-27, 1975), Sessions 3-5 (Isotopic Geochemistry), IAEA-SM-204/35, International Atomic Energy Agency, Vienna (1975).

General References

Table of Isotopes, 7th edition: C.M. Lederer and V.S. Shirley, eds.; E. Browne, J.M. Dairiki, and R.E. Doebler, principal authors; A.A. Shihab-Eldin, L.J. Jardine, J.K. Tuli, and A.B. Buyrn, authors, John Wiley and Sons, Inc., New York (1978).

E.M. Burbidge, G.R. Burbidge, W.A. Fowler, and F. Hoyle, Rev. Mod. Phys. 29, 547 (1957).

M. Benedict, T.H. Pigford, and H.W. Levi, *Nuclear Chemical Engineering* (2nd edition), McGraw-Hill Book Co., New York, to be published (1980).

Isotopes and Chemical Principles, ed. by Peter A. Rock, ACS Symposium Series no. 11, American Chemical Society, Washington, D.C. (1975).

R.L. Hoglund, J. Shacter, and E. Von Halle, in *Encyclopedia of Chemical Technology*, ed. by M. Grayson and D. Eckroth, vol. 7, p. 639, John Wiley and Sons, Inc., New York (1979).

Separation of Hydrogen Isotopes, ed. by Howard K. Rae, ACS Symposium Series no. 68, American Chemical Society, Washington, D.C. (1978).

Isotope Effects in Chemical Processes, ed. by Robert F. Gould, ACS Advances in Chemistry Series no. 89, American Chemical Society, Washington, D.C. (1969).

V.S. Letokhov and C. Bradley Moore, chapt. 1 in *Chemical and Biochemical Applications to Lasers*, vol. III, ed. by C. Bradley Moore, Academic Press, New York (1977).

Proc. Intl. Conf. on Uranium Isotope Separation, London, March 5-7, 1975, British Nuclear Engineering Society (1975).

Martin Kamen, *Isotopic Tracers in Biology*, 3rd edition, Academic Press, New York (1957).

Proc. First Intl. Conf. on Stable Isotopes in Chem., Biol., and Medicine, ed. by P.D. Klein and S.V. Peterson, May 9-11, 1973, Argonne National Laboratory, Argonne, Illinois (1973).

J. Bigeleisen, M.W. Lee, and F. Mandel, Ann. Rev. Phys. Chem. 24, 407 (1973).

Isotope Effects in Chemical Reactions, ed. by C.J. Collins and N.S. Bowman, ACS Monograph No. 167, Van Nostrand Reinhold Co., New York (1970).

J. Hoefs, *Stable Isotope Geochemistry*, Springer-Verlag, Berlin (1973).

Table 1

Stable and Long-lived, Naturally Occurring Isotopes(a)

Z	Element Symb.	Element Name	A	Natural abund., atom %	Notes
1	H	hydrogen	1	99.985	b
			2	0.015	
2	He	helium	3	1.38×10^{-4}	b,e
			4	99.99986	
3	Li	lithium	6	7.5	b,c
			7	92.5	b,c
4	Be	beryllium	9	100	
5	B	boron	10	19.8	b
			11	80.2	b
6	C	carbon	12	98.89	b
			13	1.11	b
7	N	nitrogen	14	99.63	
			15	0.366	b,e
8	O	oxygen	16	99.76	
			17	0.038	b,e
			18	0.204	b,e
9	F	fluorine	19	100	
10	Ne	neon	20	90.51	c,d,e
			21	0.27	c,d,e
			22	9.22	c,d,e
11	Na	sodium	23	100	
12	Mg	magnesium	24	78.99	d
			25	10.00	
			26	11.01	d
13	Al	aluminum	27	100	
14	Si	silicon	28	92.23	
			29	4.67	
			30	3.10	b
15	P	phosphorus	31	100	
16	S	sulfur	32	95.02	b
			33	0.75	b
			34	4.21	b
			36	0.017	b
17	Cl	chlorine	35	75.77	
			37	24.23	
18	Ar	argon	36	0.337	b,e
			38	0.063	b,e
			40	99.60	b,e,f
19	K	potassium	39	93.26	
			40	0.0117	g
			41	6.73	
20	Ca	calcium	40	96.94	f
			42	0.647	
			43	0.135	
			44	2.09	
			46	0.0035	
			48	0.187	
21	Sc	scandium	45	100	
22	Ti	titanium	46	8.2	
			47	7.4	
			48	73.7	
			49	5.4	
			50	5.2	
23	V	vanadium	50	0.250	d
			51	99.750	
24	Cr	chromium	50	4.35	
			52	83.79	
			53	9.50	
			54	2.36	
25	Mn	manganese	55	100	
26	Fe	iron	54	5.8	
			56	91.8	
			57	2.15	
			58	0.29	

	Element			Natural abund., atom %	
Z	Symb.	Name	A		Notes
27	Co	cobalt	59	100	
28	Ni	nickel	58	68.3	
			60	26.1	
			61	1.13	
			62	3.59	
			64	0.91	
29	Cu	copper	63	69.2	b
			65	30.8	b
30	Zn	zinc	64	48.6	
			66	27.9	
			67	4.10	
			68	18.8	
			70	0.62	
31	Ga	gallium	69	60.1	
			71	39.9	
32	Ge	germanium	70	20.5	
			72	27.4	
			73	7.8	
			74	36.5	
			76	7.8	
33	As	arsenic	75	100	
34	Se	selenium	74	0.87	
			76	9.0	
			77	7.6	
			78	23.5	
			80	49.8	
			82	9.2	h
35	Br	bromine	79	50.69	
			81	49.31	
36	Kr	krypton	78	0.356	c
			80	2.27	
			82	11.6	
			83	11.5	
			84	57.0	
			86	17.3	
37	Rb	rubidium	85	72.17	
			87	27.83	i

	Element			Natural abund., atom %	
Z	Symb.	Name	A		Notes
38	Sr	strontium	84	0.56	
			86	9.8	
			87	7.0	f
			88	82.6	
39	Y	yttrium	89	100	
40	Zr	zirconium	90	51.5	
			91	11.2	
			92	17.1	
			94	17.4	
			96	2.80	
41	Nb	niobium	93	100	
42	Mo	molybdenum	92	14.8	
			94	9.3	
			95	15.9	
			96	16.7	
			97	9.6	
			98	24.1	
			100	9.6	
43	Tc	technetium	(no stable isotope)		
44	Ru	ruthenium	96	5.5	
			98	1.86	
			99	12.7	
			100	12.6	
			101	17.0	
			102	31.6	
			104	18.7	
45	Rh	rhodium	103	100	
46	Pd	palladium	102	1.0	
			104	11.0	
			105	22.2	
			106	27.3	
			108	26.7	
			110	11.8	
47	Ag	silver	107	51.83	
			109	48.17	

	Element			Natural abund., atom %	Notes
Z	Symb.	Name	A		
48	Cd	cadmium	106	1.25	
			108	0.89	
			110	12.5	
			111	12.8	
			112	24.1	
			113	12.2	j
			114	28.7	
			116	7.5	
49	In	indium	113	4.3	
			115	95.7	k
50	Sn	tin	112	1.01	
			114	0.67	
			115	0.38	
			116	14.8	
			117	7.75	
			118	24.3	
			119	8.6	
			120	32.4	
			122	4.56	
			124	5.64	
51	Sb	antinomy	121	57.3	
			123	42.7	
52	Te	tellurium	120	0.091	
			122	2.5	
			123	0.89	
			124	4.6	
			125	7.0	
			126	18.7	
			128	31.7	l
			130	34.5	m
53	I	iodine	127	100	
54	Xe	xenon	124	0.096	c
			126	0.090	
			128	1.92	
			129	26.4	
			130	4.1	
			131	21.2	
			132	26.9	
			134	10.4	
			136	8.9	

	Element			Natural abund., atom %	Notes
Z	Symb.	Name	A		
55	Cs	cesium	133	100	
56	Ba	barium	130	0.106	
			132	0.101	
			134	2.42	
			135	6.59	
			136	7.85	
			137	11.2	
			138	71.7	f
57	La	lanthanum	138	0.089	n
			139	99.911	
58	Ce	cerium	136	0.190	
			138	0.254	f
			140	88.5	
			142	11.1	
59	Pr	praseodymium	141	100	
60	Nd	neodymium	142	27.2	
			143	12.2	
			144	23.8	o
			145	8.3	
			146	17.2	
			148	5.7	
			150	5.6	
61	Pm	promethium (no stable isotope)			
62	Sm	samarium	144	3.1	
			147	15.1	p
			148	11.3	q
			149	13.9	
			150	7.4	
			152	26.6	
			154	22.6	
63	Eu	europium	151	47.9	
			153	52.1	
64	Gd	gadolinium	152	0.20	r
			154	2.1	
			155	14.8	
			156	20.6	
			157	15.7	
			158	24.8	
			160	21.8	

	Element			Natural abund.,	
Z	Symb.	Name	A	atom %	Notes
65	Tb	terbium	159	100	
66	Dy	dysprosium	156	0.057	
			158	0.100	
			160	2.3	
			161	19.0	
			162	25.5	
			163	24.9	
			164	28.1	
67	Ho	holmium	165	100	
68	Er	erbium	162	0.14	
			164	1.56	
			166	33.4	
			167	22.9	
			168	27.1	
			170	14.9	
69	Tm	thulium	169	100	
70	Yb	ytterbium	168	0.135	
			170	3.1	
			171	14.4	
			172	21.9	
			173	16.2	
			174	31.6	
			176	12.6	
71	Lu	lutetium	175	97.39	
			176	2.61	s
72	Hf	hafnium	174	0.16	t
			176	5.2	f
			177	18.6	
			178	27.1	
			179	13.7	
			180	35.2	
73	Ta	tantalum	180	0.0123	
			181	99.9877	
74	W	tungsten	180	0.13	
			182	26.3	
			183	14.3	
			184	30.7	
			186	28.6	

	Element			Natural abund.,	
Z	Symb.	Name	A	atom %	Notes
75	Re	rhenium	185	37.40	
			187	62.60	u
76	Os	osmium	184	0.018	
			186	1.6	v
			187	1.6	f
			188	13.3	
			189	16.1	
			190	26.4	
			192	41.0	
77	Ir	iridium	191	37.3	
			193	62.7	
78	Pt	platinum	190	0.013	w
			192	0.78	
			194	32.9	
			195	33.8	
			196	25.3	
			198	7.2	
79	Au	gold	197	100	
80	Hg	mercury	196	0.15	
			198	10.0	b
			199	16.8	
			200	23.1	
			201	13.2	
			202	29.8	b
			204	6.9	
81	Tl	thallium	203	29.5	
			205	70.5	
82	Pb	lead	204	1.42	
			206	24.1	f
			207	22.1	f
			208	52.3	f
83	Bi	bismuth	209	100	
84-89[aa]	(no stable isotopes)				
90	Th	thorium	232	100	x
91	Pa	protactinium (no stable isotope)			
92	U	uranium	235	0.720	y,c,d
			238	99.275	z,c,d

a) Data taken from refs. (3,4). Natural abundances are given in atom percent, rounded so that the uncertainty in the last place is $\lesssim 5$ units. (Note that, because of the rounding, the abundances for an element do not always add to 100%.)

b) Natural isotopic composition of "normal" terrestrial matter varies.

c) Isotopic composition of some commercially available sources has been altered by processing.

d) Natural isotopic composition can vary for some "anomalous" sources.

e) Atmospheric sources.

f) Isotopic composition can vary due to the existence of a radioactive parent.

g) radioactive, $t_{1/2} = 1.28 \times 10^{9}$ y

h) slightly radioactive, $t_{1/2} = 1.4 \times 10^{20}$ y

i) radioactive, $t_{1/2} = 4.8 \times 10^{10}$ y

j) slightly radioactive, $t_{1/2} = 9 \times 10^{15}$ y

k) slightly radioactive, $t_{1/2} = 5.1 \times 10^{14}$ y

l) slightly radioactive, $t_{1/2} = 1.5 \times 10^{24}$ y

m) slightly radioactive, $t_{1/2} = 2 \times 10^{21}$ y

n) radioactive, $t_{1/2} = 1.1 \times 10^{11}$ y

o) slightly radioactive, $t_{1/2} = 2.1 \times 10^{15}$ y

p) radioactive, $t_{1/2} = 1.06 \times 10^{11}$ y

q) slightly radioactive, $t_{1/2} = 8 \times 10^{15}$ y

r) slightly radioactive, $t_{1/2} = 1.1 \times 10^{14}$ y

s) radioactive, $t_{1/2} = 3.6 \times 10^{10}$ y

t) slightly radioactive, $t_{1/2} = 2.0 \times 10^{15}$ y

u) radioactive, $t_{1/2} = 4 \times 10^{10}$ y

v) slightly radioactive, $t_{1/2} = 2 \times 10^{15}$ y

w) radioactive, $t_{1/2} = 6 \times 10^{11}$ y

x) radioactive, $t_{1/2} = 1.41 \times 10^{10}$ y

y) radioactive, $t_{1/2} = 7.038 \times 10^{8}$ y

z) radioactive, $t_{1/2} = 4.468 \times 10^{9}$ y

aa) Po (polonium), At (astatine), Rn (radon), Fr (francium), Ra (radium), Ac (actinium).

Table 2

Precise Titanium Isotope Ratios

For Various Samples[(a)]

Material	$^{46}Ti/^{49}Ti$	$^{48}Ti/^{49}Ti$	$^{50}Ti/^{49}Ti$
99.9% Ti metal, batch Ti/002, Roc-ric Co.	1.4618(14)	13.442(4)	0.9723(8)
NBS TiO_2 SRM 154	1.4614(8)	13.441(8)	0.9730(2)
Potassium titanyl oxalate, BDH Analar grade	1.4616(8)	13.442(5)	0.9728(5)
Rutile, Beachsand concentrate, South Queensland	1.4614(9)	13.443(9)	0.9723(6)
Allende meteorite, "inclusions with oxygen anomalies"	1.4619(2)	13.440(13)	0.9738(3)

---

a) The results are weighted averages of many determinations, normalized to an assumed $^{47}Ti/^{49}Ti$ ratio of 1.3360. Numbers in parentheses are uncertainties (3σ) in the last place(s). The authors (7) conclude that there is definite evidence for an anomalous $^{50}Ti/^{49}Ti$ ratios in samples from some portions of the meteorite.

Table 3

Isotopic Abundance of Natural Lead Samples[a]

Sample	Abundance, atom percent			
	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
Common Lead (NBS SRM 981)	1.4245(12)	24.1447(57)	22.0827(27)	52.3481(86)
Radiogenic Lead (NBS SRM 983)	0.0342(20)	92.1497(41)	6.5611(25)	1.2550(22)

(a) From ref. (12). From calibrated mass spectrometric measurements. The numbers in parentheses are uncertainties in the last places (95% confidence limits).

Table 4

Types of Processes Used or Proposed for Isotope Separation

1. Processes used for small-scale commercial production of many isotopes:

    Electromagnetic*
    Thermal diffusion
    Distillation (C, N, O)
    Chemical exchange (Li, B)
    Photochemical, photophysical (laser)*[b]

2. Processes used for large-scale commercial production:

    Chemical exchange (H)
    Distillation (H)
    Electrolysis (H)
    Gaseous diffusion (U)
    Gravitational (gas centrifuge) (U)[a]
    Aerodynamic (separation nozzle) (U)[a]
    Photochemical, photophysical (laser)(U,H)*[b]

3. Other processes

    Chromatographic (Ion-exchange)
    Mass and sweep diffusion
    Adsorption
    Electromigration
    Biological

---

* Large (>>1) separation factors

a) Commercial-size plants are planned

b) Pilot-scale plants planned or under construction

Table 5

Elements Separated Electromagnetically at Oak Ridge, 1966-1979[a]

Element	Total weight separated,g	Element	Total weight separated,g	Element	Total weight separated,g
H		Kr		Lu	376
He		Rb	1,586	Hf	1,084
Li	2,985	Sr	13,710	Ta	1,427
Be	0.003 (b,c)	Y	c	W	9,576
B	65	Zr	3,134	Re	370
C	150	Nb	c	Os	334
N	41	Mo	12,385	Ir	195
O	0.022	Tc	d	Pt	294
F	c	Ru	114	Au	c
Ne		Rh	c	Hg	852
Na	c	Pd	385	Tl	6,974
Mg	2,889	Ag	801	Pb	5,280
Al	c	Cd	4,312	Bi	51 (b,c)
Si	5,757	In	531	Po	d
P	c	Sn	6,123	At	d
S	3,447	Sb	384	Rn	d
Cl	752	Te	7,410	Fr	d
Ar		I	c	Ra	d
K	2,200	Xe		Ac	d
Ca	52,460	Cs	c	Th	35 (b)
Sc	c	Ba	1,963	Pa	d
Ti	2,561	La	294	U	6,653 (b)
V	186	Ce	2,123	Np	d
Cr	4,959	Pr	c	Pu	1,506 (b,d)
Mn	c	Nd	2,571	Am	2 (b,d)
Fe	32,657	Pm	d	Cm	0.5 (b,d)
Co	c	Sm	2,666		
Ni	15,401	Eu	627		
Cu	3,517	Gd	1,911		
Zn	4,552	Tb	2.1 (b,c)		
Ga	713	Dy	1,178		
Ge	1,984	Ho	c		
As	c	Er	1,664		
Se	1,191	Tm	c		
Br	572	Yb	3,584		

a) From ref. 23 and E. Newman, private communication, July, 1980. The weight separated excludes a few "waste" isotopes that were collected together and discarded.
b) Includes artificially produced isotopes
c) Monoisotopic element
d) No stable isotopes

Table 6

Stable Isotope Sales by the Mound Facility in FY1978[(a)]

Isotope	Enrichment, Atom %	Total Sales[b], g	Average Price[c], $/g
^{3}He	99.9-99.9995	963	804
^{12}C	99.9,99.95	327	8.24
^{13}C	20-99	2,861	69
^{14}N	99.99	689,818	0.156
^{15}N	40,99	1,353	95
^{16}O	99.98	9,093	1.41
^{17}O	20-55	73.7	281
^{18}O	20-99	867	90
^{20}Ne	99.95	113	92
^{21}Ne	90	0.20	16,732
^{22}Ne	70-99.9	40	225
^{34}S	90	17.7	313
^{35}Cl	90	12.0	278
^{37}Cl	90	16.6	480
^{36}Ar	99.5	2.98	2,506
^{38}Ar	25,95	0.80	2,654
^{40}Ar	99.95	253	8.33
^{78}Kr	8-99	17.2	688
^{80}Kr	70,90	0.46	7,400
^{82}Kr	70,90	38.4	2,048
^{83}Kr	70	2.89	2,293
^{84}Kr	90	24.3	240
^{86}Kr	99	47.0	168

Isotope	Enrichment, Atom %	Total Sales, g	Average Price, $/g
^{124}Xe	1-40	3.18	15,924
^{126}Xe	2	--	
^{129}Xe	60	1.15	760
^{131}Xe	60	0.12	2,096
^{134}Xe	50	--	
^{136}Xe	80-99	61.2	1,282

---

a) From ref. (32). Nitrogen, oxygen, and (in part) carbon isotopes were enriched at Los Alamos Scientific Laboratory by distillation; all other isotopes were enriched at Mound by thermal diffusion.

b) Quantities stated in liters (32) were converted to grams, assuming STP (273^{o}K, 1 atm.).

c) Rounded to the nearest dollar for values over $50.

Table 7

Separation Factors for Distillation(a)

Compounds	Triple point T, °C	Triple point α	Normal Boiling point T, °C	Normal Boiling point α
ortho H_2-HD	-259.4	3.61	-252.9	1.81
NH_3-ND_3	- 77.7	1.080	- 33.6	1.036
H_2O-D_2O	0.0	1.120	100	1.026
^{12}CO-^{13}CO	-205.7	1.0113	-191.3	1.0068
^{14}NO-^{15}NO	-163.6	1.033	-151.8	1.027
$N^{16}O$-$N^{18}O$	-163.6	1.046	-151.8	1.037
$H_2{}^{16}O$-$H_2{}^{18}O$	0	1.010	100	1.0046
^{20}Ne-^{22}Ne	-248.6	1.046	-245.9	1.038
^{36}Ar-^{40}Ar	-189.4	1.006	-185.7	--
^{128}Xe-^{136}Xe	-111.8	1.000	-109.1	--

---

a) Estimated (equation 1.21) from vapor pressure ratios, ref. (14). References to the measurements are given in the original table, from which these data were abstracted.

Table 8

Separation Factors for Some Isotopic Exchange Reactions(a)

	Reaction	$\alpha(25^oC)$
	Hydrogen	
1.	$H_2O(\ell) + HD \rightleftarrows HDO(\ell) + H_2$	3.81
2.	$H_2O(\ell) + HDS \rightleftarrows HDO(\ell) + H_2S$	2.37
3.	$NH_3(\ell) + HD \rightleftarrows NH_2D(\ell) + H_2$	3.62
4.	$CH_3NH_2(\ell) + HD \rightleftarrows CH_3NHD(\ell) + H_2$	4.0
5.	$H_2O(\ell) + NH_2D \rightleftarrows HDO(\ell) + NH_3$	1.00
6.	$H_2O(\ell) + PH_2D \rightleftarrows HDO(\ell) + PH_3$	2.44
7.	$H_2O(\ell) + DCl \rightleftarrows HDO(\ell) + HCl$	2.51
	Lithium	
8.	$^6LiX(in\ (CH_3)_2NOCH) + {}^7Li(Hg) \rightleftarrows {}^7LiX(in\ (CH_3)_2NOCH)) + {}^6LiX(Hg)$ [X = Cl, Br]	1.05
9.	$^6LiOH(aq.) + {}^7Li(Hg) \rightleftarrows {}^7LiOH(aq.) + {}^6Li(Hg)$	1.07
	Boron	
10.	$^{10}BF_3 + (CH_3)_2O\cdot{}^{11}BF_3(\ell) \rightleftarrows {}^{11}BF_3 + (CH_3)_2O\cdot{}^{10}BF_3(\ell)$	1.027 b
11.	$^{10}BF_3 + (CH_3)_2S\cdot{}^{11}BF_3(\ell) \rightleftarrows {}^{11}BF_3 + (CH_3)_2S\cdot{}^{10}BF_3(\ell)$	1.037 b
	Carbon	
12.	$^{13}CO_2 + H^{12}CO_3^- \rightleftarrows {}^{12}CO_2 + H^{13}CO_3^-$	1.012
13.	$H^{12}CN + {}^{13}CN^- \rightleftarrows H^{13}CN + {}^{12}CN^-$	1.013
	Nitrogen	
14.	$^{15}NO + H^{14}NO_3(aq.) \rightleftarrows {}^{14}NO = H^{15}NO_3(aq.)$	1.055
15.	$^{14}NH_3 + {}^{15}NH_4^+ \rightleftarrows {}^{15}NH_3 + {}^{14}NH_4^+$	1.034

	Reaction	$\alpha(25^{o}C)$
	Sulfur	
16.	$^{34}SO_2 + H^{32}SO_3^- \rightleftarrows {}^{32}SO_2 + {}^{34}SO_3^-$	1.019
	Calcium	
17.	$^{40}Ca^{2+}(aq.) + {}^{44}Ca^{2+}(C_{20}H_{36}O_6) \rightleftarrows {}^{44}Ca^{2+}(aq.) + {}^{40}Ca^{2+}(C_{20}H_{36}O_6)$	1.004[c]
	Uranium	
18.	$^{235}UF_6 + {}^{238}UF_5NOF \rightleftarrows {}^{238}UF_6 + {}^{235}UF_5NOF$	1.0016
19.	$^{235}U(IV, Dowex\ 50) + {}^{238}UO_2^{2+} \rightleftarrows {}^{238}U(IV, Dowex\ 50) + {}^{235}UO_2^{2+}$	1.0005[d]

(a) Data from ref. 14 and references contained therein, unless otherwise noted.
(b) From ref. 39.
(c) From ref. 33. The ligand is a crown polyether, dissolved in an organic solvent.
(d) From ref. 40

Table 9: Comparison of some methods for production of heavy water. Methods below the line are uneconomic (ref.35).

Process	Effective separation factor[a]	Energy input[b] GJ/kg D_2O	Deuterium recovery[c] (%)	Operating conditions[c]			Reflux ratio[c,d] (10^3 moles per mole of D_2O)	
				T or T_c (°C)	T_h (°C)	Pressure (MPa)	Gas	Liquid
GS	1.29	30	14	32	138	2.0	73	37
Monothermal NH_3-H_2	5.2	20	85	-25		35	16	4
Bithermal NH_3-H_2	1.7	7	85	-25	60	35	37	4.3
Bithermal CH_3NH_2-H_2	2.2	11	80	-50	40	5	14	2.2
Bithermal H_2O-H_2	1.6	19	30	50	170	7	59	22
H_2Distillation	1.5	21	90	-249		0.25	20	
CECE	≃4	500 (2)[e]	66	60[f]		7	10	10
Electrolysis	5-10	700	24	20		0.10	28	28
H_2O Distillation	1.04	70	2	82		0.05	200	

---

a) The listed separation factor for a bithermal process is α_c/α_h
b) Thermal energy plus electrical energy ÷ 0.4.
c) Typical values for actual plants or estimates for proposed processes.
d) Average value. Actual flows may vary in different parts of the system (e.g., hot or cold towers).
e) The lower energy, for "parasitic" CECE, represents the additional energy needed to produce D_2O as a byproduct of hydrogen.
f) Temperature of the H_2O-H_2 reactor.

Table 10

Light Elements for which Radioactive Tracers are Difficult to Use.

Element	Stable tracer	Radioactive tracers[a]
H	^{2}H	^{3}H ($t_{1/2}$=12.33 y, low-energy β^{-} difficult to detect)
Li	^{6}Li, ^{7}Li	^{8}Li ($t_{1/2}$=0.84 s)
B	^{10}B, ^{11}B	^{8}B ($t_{1/2}$=0.769 s)
C	^{13}C	^{11}C ($t_{1/2}$=20.38 m) ^{14}C ($t_{1/2}$=5730 y)
N	^{15}N	^{13}N ($t_{1/2}$=9.96 m)
O	^{17}O, ^{18}O	^{15}O ($t_{1/2}$=122 s)
Cl	^{35}Cl, ^{37}Cl	^{39}Cl ($t_{1/2}$=56 m) ^{36}Cl ($t_{1/2}$=3.00x10^{5} y)

---

a) The isotope with the longest half-life below 10 y is given; for elements with a very long-lived isotope, its half-life is given also. Data from ref. (3).

Table 11

Stable or Long-lived Isotopes with Spin 1/2

Isotope	Magnetic moment, nm[a]	Natural abundance, atom %	Isotope	Magnetic moment, nm	Natural abundance, atom %
^{1}H	+2.7928456(11)	99.985	^{115}Sn	-0.91883(7)	0.38
^{3}He	-2.127624(1)	1.38x10^{-4}	^{117}Sn	-1.00104(7)	7.75
^{13}C	+0.702411(1)	1.11	^{119}Sn	-1.04728(7)	8.6
^{15}N	-0.2831892(3)	0.366	^{123}Te	-0.73679(2)	0.89
^{19}F	+2.628866(8)	100	^{125}Te	-0.88828(3)	7.0
^{29}Si	-0.55529(3)	4.67	^{129}Xe	-0.777976(9)	26.4
^{31}P	+1.13160(3)	100	^{169}Tm	-0.2316(15)	100
^{57}Fe	+0.09044(7)	2.15	^{171}Yb	+0.49367(1)	14.4
^{77}Se	+0.53506(1)	7.6	^{183}W	+0.1177847(1)	14.3
^{89}Y	-0.1374153(3)	100	^{187}Os	-0.06465184(6)	1.6
^{103}Rh	-0.08840(2)	100	^{195}Pt	+0.60949(6)	33.8
^{107}Ag	-0.113570(20)	51.83	^{199}Hg	+0.5058851(9)	16.8
^{109}Ag	-0.130562(23)	48.17	^{203}Tl	+1.622257(1)	29.5
^{111}Cd	-0.5948856(9)	12.8	^{205}Tl	+1.6382134(7)	70.5
^{113}Cd	-0.6223005(9)	12.2	^{207}Pb	+0.58219(2)	22.1

---

a) Data taken from *Table of Nuclear Moments*, App. VII in ref. 3. Moments are given in units of nuclear magnetons, with the uncertainty in the last place or places. Diamagnetic corrections are included. For further details, consult the original reference.

Table 12

$^3He/^4He$ Ratios for Various Sources(a)

Source	$^3He/^4He$
Some uranium minerals	10^{-10}
Crust (radiogenic) helium	$10^{-7} - 10^{-8}$
Modern atmospheric helium	1.38×10^{-6}
Modern mantle helium	$10^{-4} - 10^{-5}$
Primordial helium	$10^{-3} - 10^{-4}$
Some meteorites	10^{-2}

---

a) From ref. 128.

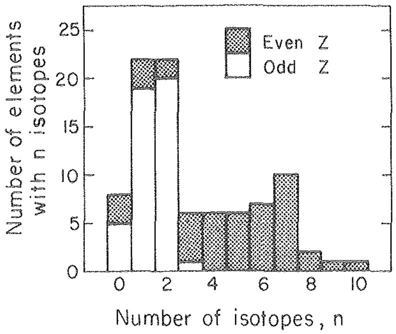
Figure Captions

1. Distribution of the number of stable or long-lived, naturally occurring isotopes per element ($Z = 1$ to 92).
2. Schematic representation of an isotope separation process. The six variables characterizing the three external flows are defined in the text.
3. Schematic representation of the simple cascade.
4. Schematic representation of the standard ideal cascade. Stage numbers are shown on the separation units representing the stages. The size of the actual stages varies, with the largest stage at the feed point. n_s and n_e are the number of stripping and enriching sections, respectively. The cut of each stage is approximately 1/2 ($M_i \approx N_i \approx Z_i/2$).
5. Shape of the ideal cascade. The relative flow rates and the number of stages are for the enrichment of uranium from its natural composition (0.720 atom % ^{235}U) to a product with 90% and tails with 0.3% ^{235}U with a separation factor $\alpha = 1.00429$. Separation units drawn in are not to scale. (After refs. 14, 66).
6. Diagram of a beta (24-inch) calutron. The magnetic field is perpendicular to the plane of the page. From ref. 23.
7. Diagram of a thermal diffusion column of the type used at Mound Laboratory. The inset shows the velocity profile of the countercurrent flow. The hot center tube replaces a wire in earlier designs. (After refs. 33, 28).
8. Cascade arrangement of thermal diffusion columns used at Mound Laboratory to separate krypton isotopes (33).
9. H_2S-H_2O exchange: a hypothetical monothermal system.
10. Temperature dependence of the separation factor for some chemical exchange reactions. Data from refs. 14, 39.
11. Simplified flow diagram for the GS process. Flow rates for the liquid and gas are relative to 1 for the water feed. The product feeds next stage for further enrichment. Based on ref. 14.
12. (a) Cumulative world production of heavy water to May, 1977. From data given in ref. 35. (b) World heavy water capacity around 1979, including all plants of capacity greater than 1 metric ton per year. Data from ref. 14. (c) Estimated world heavy water capacity in 1892. Data from refs. 14, 35.
13. Variation in the total pressure and local separation factor $\left(\frac{^{235}U}{^{238}U}\right) \Big/ \left(\frac{^{235}U}{^{238}U}\right)_{feed}$ with radius in a gas centrifuge with $v_a = 400$ m/s. P_0 and $\left(\frac{^{235}U}{^{238}U}\right)_{feed}$ are the pressure and isotopic ratio of the original, non-rotating gas. The vertical scale is logarithmic for P, linear for the separation factor.

14. Calculated performance (68,14) of a gas centrifuge with radius = 0.09145 m, length = 3.353 m, v_a = 400 m/s, T = 300°K. The upper curve shows the stage separation factor $\frac{y_P - z_F}{z_F - x_W}$, the lower curve the separative capacity. The internal feed rate has been optimized with respect to the external flows.

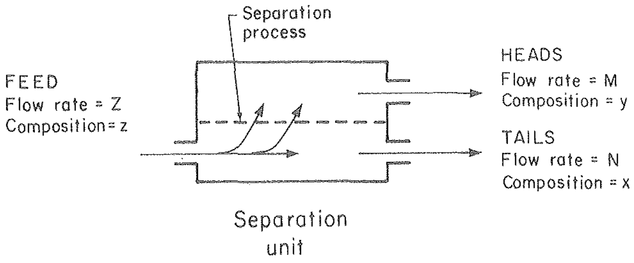
15. Projected nuclear electric generating capacity. The high and low CONAES projections (72,90) represent the extreme scenarios considered in that study. The WAES projections (91) are "minimum likely" and "maximum likely" estimates for the U.S. and for the world outside communist areas (WOCA). The band labelled 79 DOE is a projection for the U.S. (ref. 92); previous projections by the Department of Energy have been higher. Shaded regions below the WAES-WOCA min. curve depict the portion of the estimate that is due to systems other than light-water reactors (LWR): HWR = heavy-water reactor, FBR = fast breeder reactor. The band below the CONAES high estimate, for "advanced" reactors, includes heavy-water reactors, fast breeders, and "converters." Little or no deployment of advanced reactors before year 2010 is necessary in the CONAES low scenario.

16. Comparison of the uranium separative capacity required with that planned. Curves labelled CONAES low, high, and WAES-WOCA min. are the requirements corresponding to the electric generating capacities estimated in Figure 15. (The WAES-US curve is similar to the CONAES high projection; the WAES-WOCA max. curve, not shown, is thought by the author to be unreasonably high.). Except for the CONAES low curves, the projections assume some use of advanced reactors with much lower separation requirements. Curves of separative capacity in existence, under construction, or planned are labelled US and WOCA. They are based on data in refs. 14 and 34.



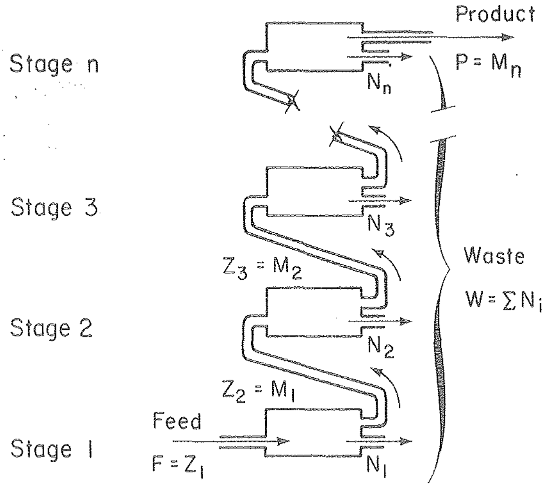
XBL 7912-13331

Figure 1



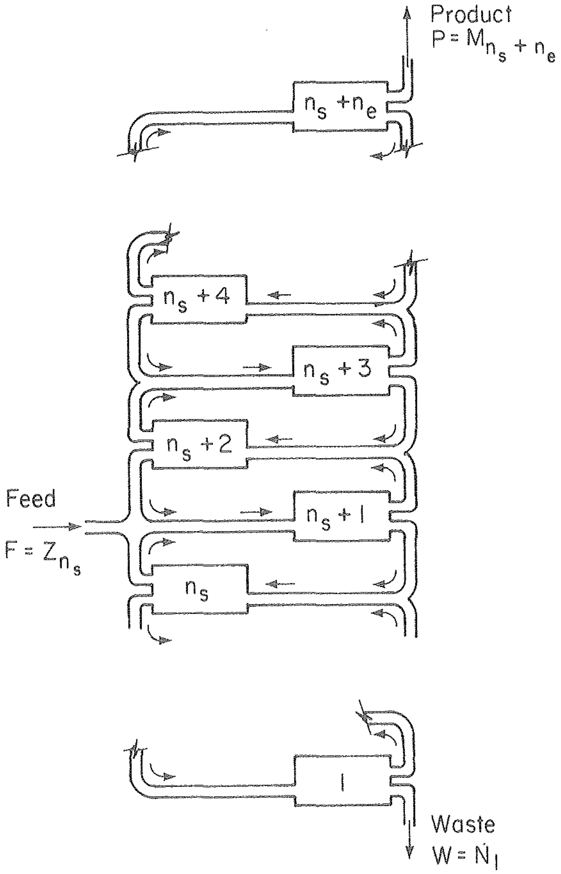
XBL 7912-13332

Figure 2



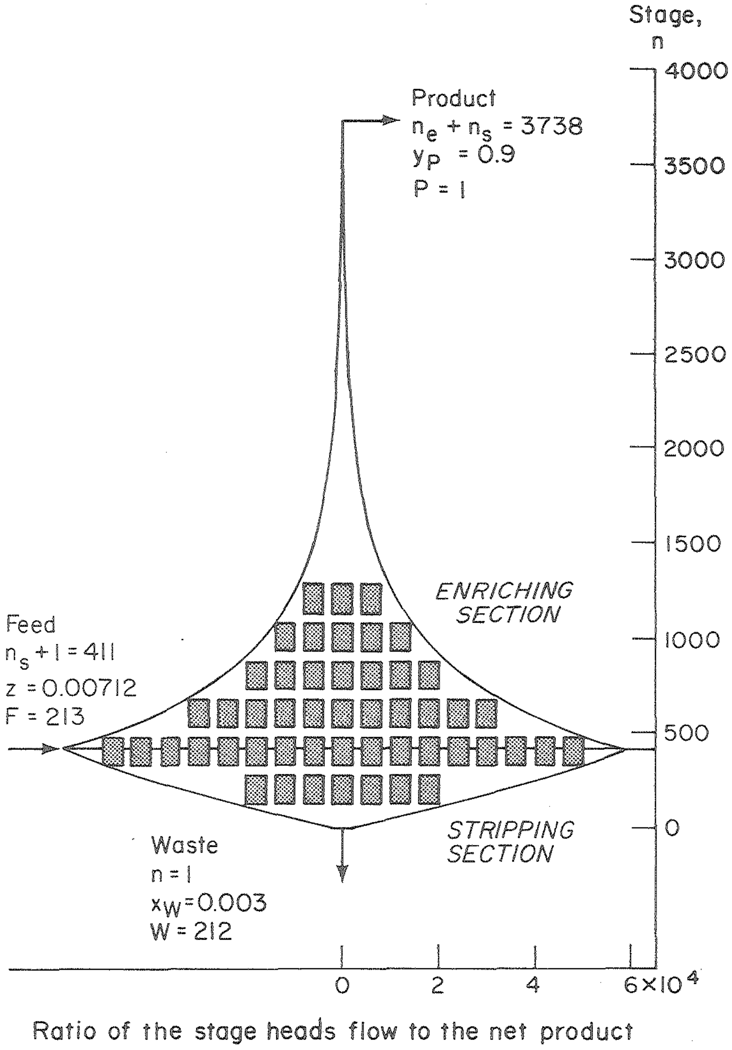
XBL 7912-13333

Figure 3



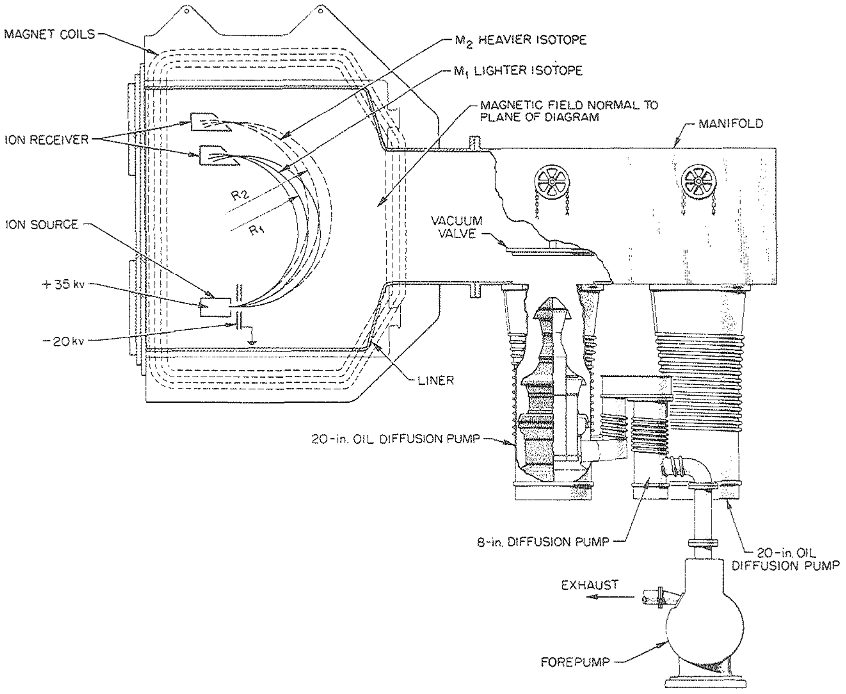
XBL 7912-13334

Figure 4



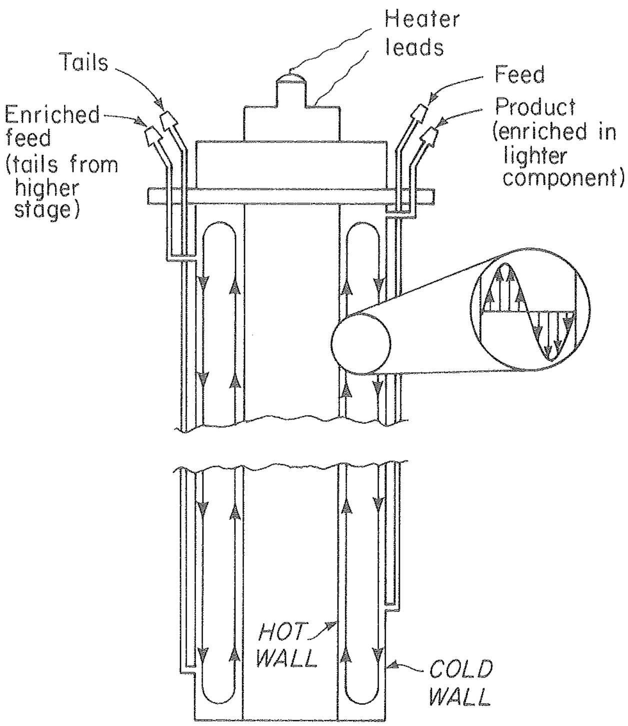
XBL 7912-13335

Figure 5



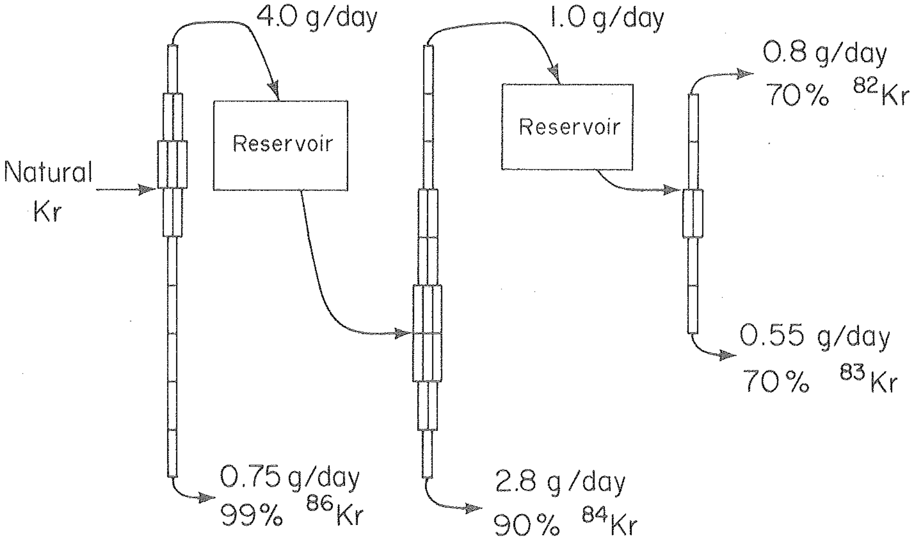
XBL 804-9045

Figure 6



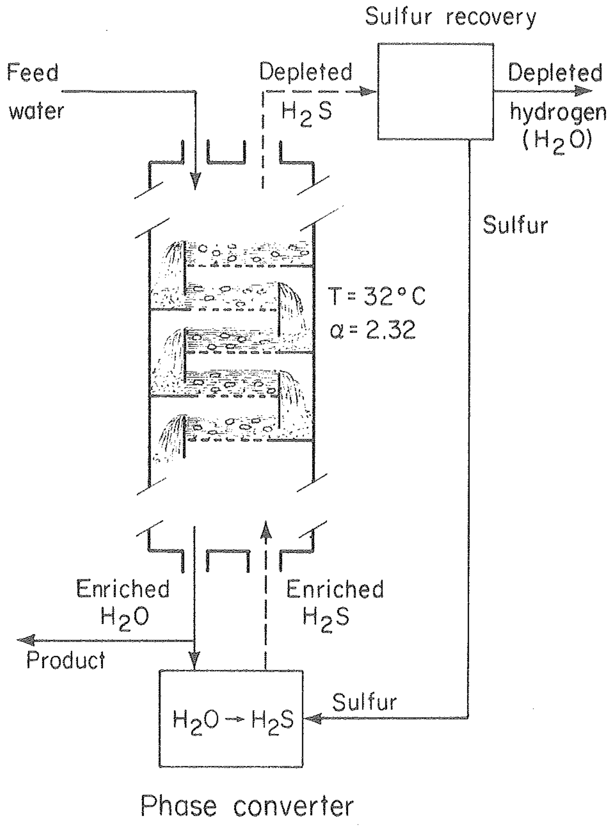
XBL7912-13336

Figure 7



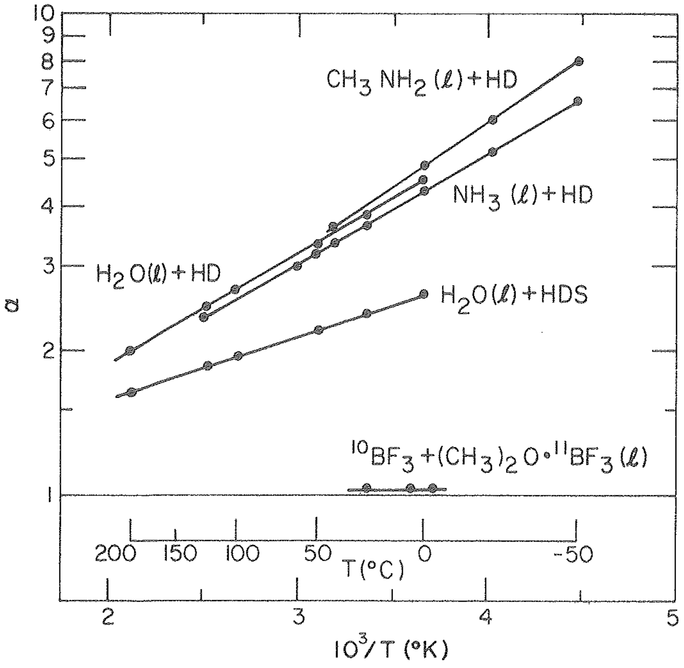
XBL7912-13337

Figure 8



XBL 7912-13338

Figure 9



XBL 7912-13344

Figure 10

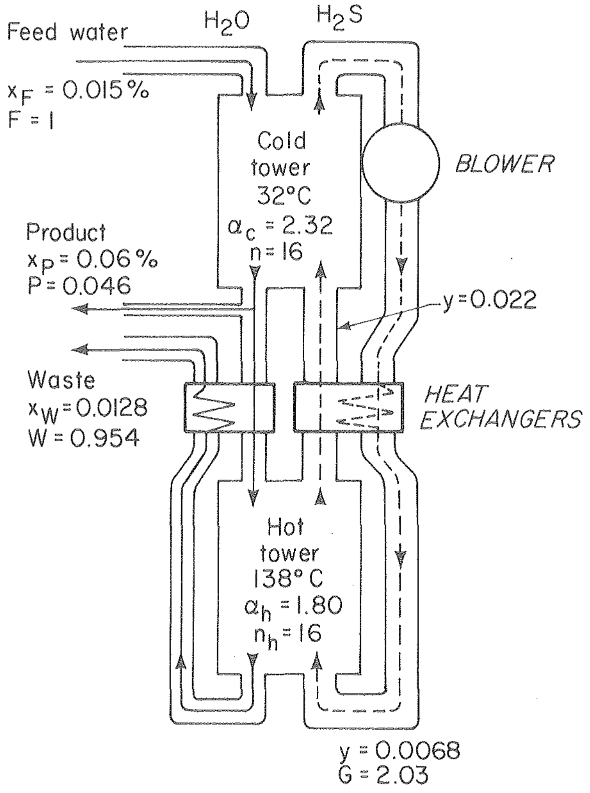


Figure 11

XBL 7912-13343

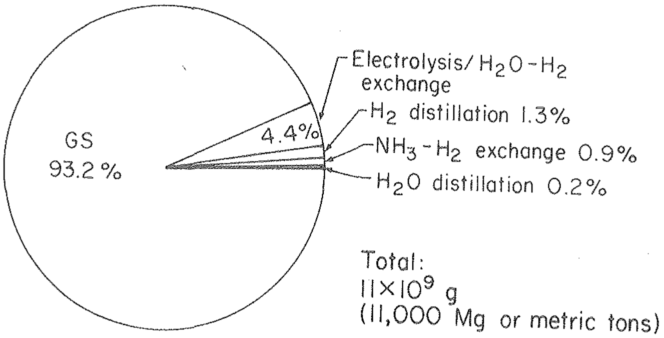
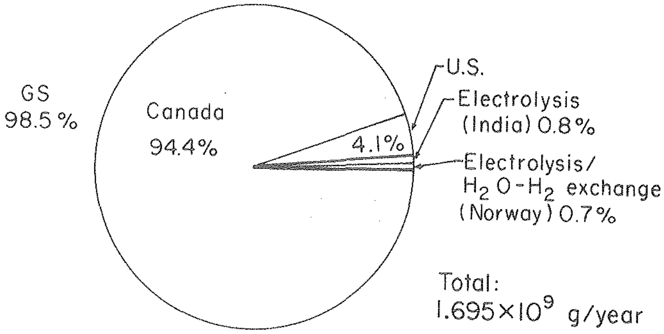


Figure 12a



XBL 7912-13342

Figure 12b

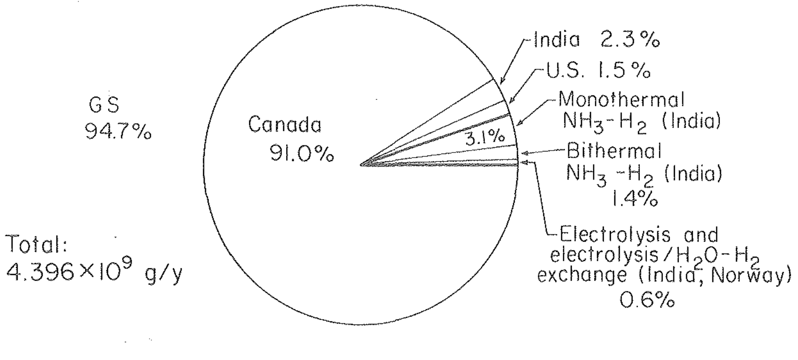


Figure 12c

XBL 7912-13341

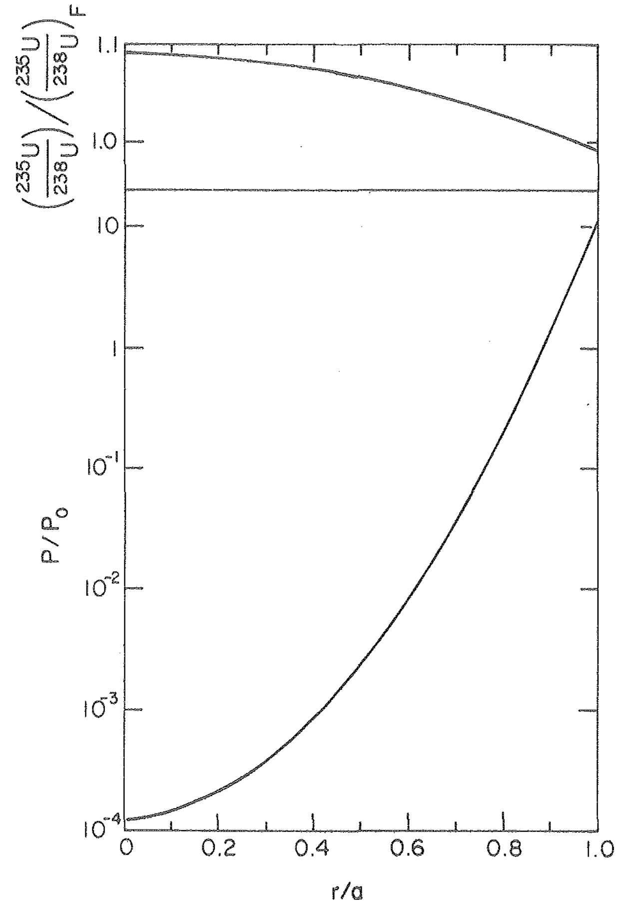
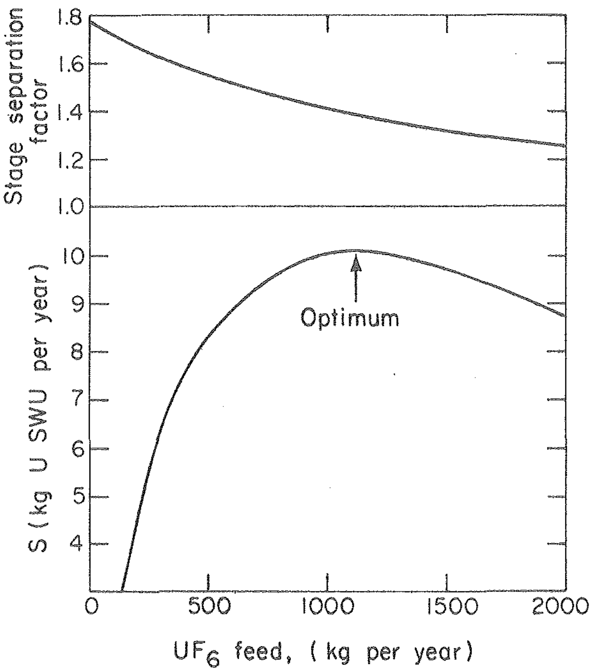


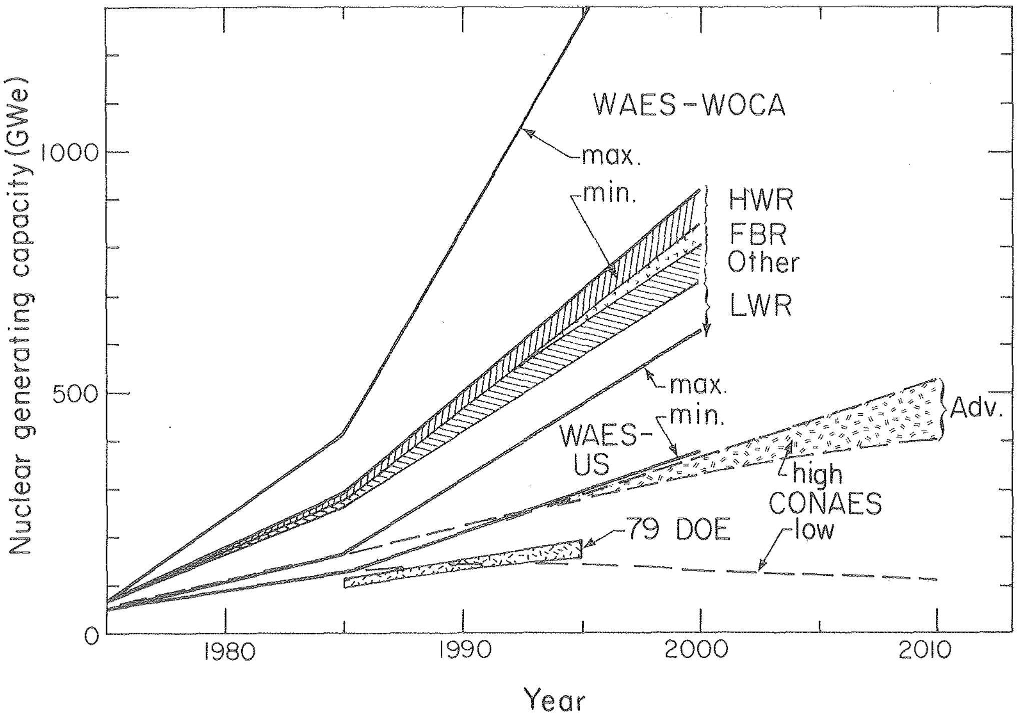
Figure 13

XBL 7912-13340

Figure 14

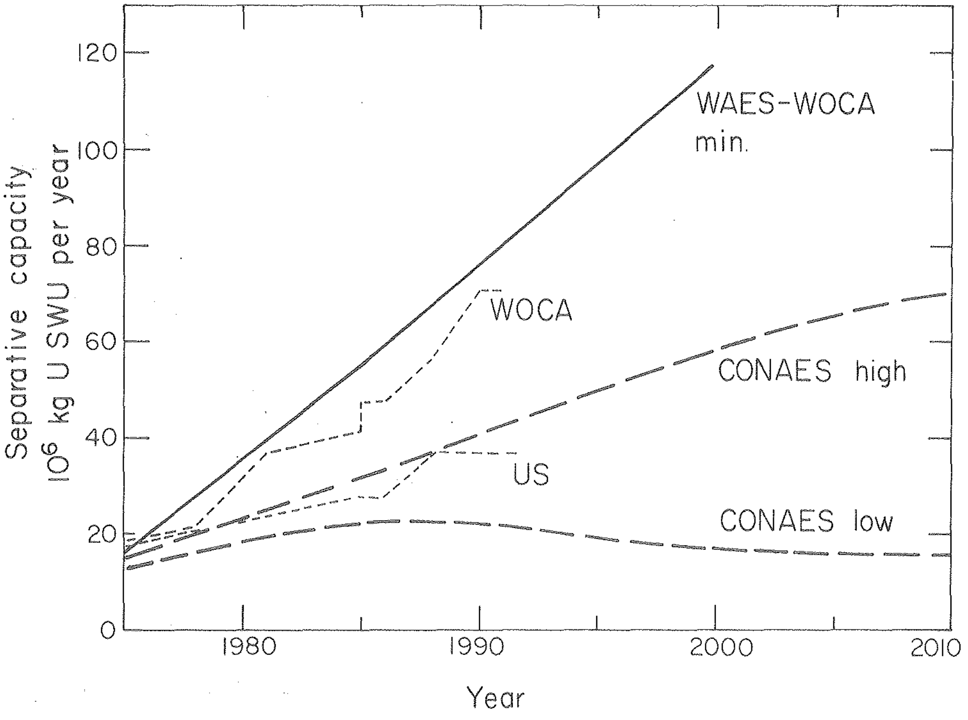


XBL 7912-13339



XBL 7912-13345

Figure 15



XBL 7912-13346

Figure 16