Kirk-Othmer Encyclopedia of Chemical Technology.

ISOTOPE SEPARATION

The high cost of isotope separation has limited the use of separated isotopes in nuclear reactors to specific cases where substitutes that do not involve separated isotopes are not available. The most important example is that of uranium-235 [15117-96-1], ^{235}U, the most abundant naturally occurring fissionable material (see Uranium and uranium compounds). Other isotopes that are separated for nuclear use are deuterium, ^{2}H or D, which as deuterium oxide [7789-20-1], D_2O, is used as a neutron moderator in water-cooled reactors; tritium, ^{3}H or T, which is produced in nuclear reactors and is a probable fuel in future thermonuclear or fusion reactors (see Deuterium and tritium; Fusion energy; Radioisotopes); boron-10 [14798-12-0], ^{10}B, which has a high neutron cross section and is used in control rods and safety devices for nuclear reactors; and lithium-7 [13982-05-3], ^{7}Li, which is used in reactor cooling-water systems because of its low thermal neutron cross section.

1. Uranium-235

The separation of the isotope ^{235}U, which occurs in natural uranium to the extent of 0.72 atomic %, is discussed in detail elsewhere (see Diffusion separation methods). Uranium-235 is concentrated mostly by means of the gaseous diffusion process using uranium hexafluoride [7783-81-5], UF_6, as the process gas. The separation effect in this process arises from relatively more of the lighter gas molecules passing through a porous membrane, called a diffusion barrier, per unit time than of the heavier gas molecules. The effective single-stage separation factor is proportional to the ratio of mean thermal velocities of the molecules or inversely proportional to the ratio of the square root of their molecular weights. That factor is quite small, ie, somewhat less than the theoretical value of 1.0043. A cascade containing more than a thousand separation stages is therefore required to enrich uranium to reactor grade (3–4 atomic %) and several thousand stages are required to produce highly enriched material. The first large gaseous diffusion cascade was built in the early 1940s at Oak Ridge, Tennessee (1). Additional plants were built in the 1950s at Oak Ridge, Tennessee; Paducah, Kentucky; and Portsmouth, Ohio. Gaseous diffusion cascades for uranium enrichment have also been built in the United Kingdom, France, the former USSR, China, and, more recently, in Argentina.

The gaseous diffusion process is energy-intensive. As a consequence of this and other economic considerations, as of this writing (ca 1995) most facilities for uranium enrichment utilize the gas centrifuge process. Gas centrifuge cascades for the enrichment of uranium, using UF_6 as the process gas, have been built and operated in the former USSR, the United Kingdom, the Netherlands, Germany, Japan, Pakistan, India, Brazil, and China. A small aerodynamic uranium enrichment facility, based on vortex tube technology and using a mixture of UF_6 and hydrogen as the process gas, has been built and operated by South Africa, but it too is energy-intensive. A chemical exchange process for uranium enrichment, based on the isotopic distribution between uranium compounds in the +3 and +4 valence states, has been developed and tested in France (2), and an ion-exchange (qv) process for uranium enrichment based on the isotopic distribution between uranium compounds in the +4 and +6 valence states has been developed and tested by Asahi Chemical Co. in Japan (3). Several laser photochemical processes (4) have also been developed (see Lasers; Photochemical technology).

The atomic vapor laser isotope separation method (AVLIS) developed in the United States is also ready for deployment. However, as of the mid-1990s the supply of enriched uranium exceeds demand. New facilities are not expected until the demand for enriched uranium increases. General discussions of uranium enrichment are available (4–6).

2. Deuterium

The use of deuterium in nuclear reactors is discussed in detail elsewhere (see Deuterium and tritium). Fast neutrons, obtained by the fission of ^{235}U, must be slowed to propagate the chain reaction or to react with ^{238}U to produce plutonium (see Plutonium and plutonium compounds). Heavy water, D_2O, is one of the most efficient of those substances that are able to accomplish this purpose. Methods of isotope separation include catalytic exchange between H_2 and H_2O, electrolysis, water distillation, hydrogen distillation, and various chemical-exchange systems (7, 8). Quantities of D_2O have been produced by catalytic exchange electrolysis and by vacuum distillation of water. The hydrogen sulfide–water, dual-temperature exchange process is used to produce multiton quantities of heavy water (9–13). Canada has built a number of large plants to furnish heavy water as a coolant and moderator of their CANDU (Canada–Deuterium–Uranium) power reactors. Other smaller plants in various countries employ water electrolysis, H_2–NH_3 exchange, water distillation, and liquid-hydrogen distillation (14) for deuterium concentration. Many plants use combinations of the above methods. Deuterium separation has been reviewed (15–17).

3. Tritium

Tritium is radioactive and decays with a half-life of 12.26 yr.

$$\mathrm{H}_1^3 \longrightarrow \mathrm{H}_2^3\mathrm{e}+\beta^-$$

However, it is produced in the upper atmosphere by cosmic rays (18, 19).

Tritium is produced in heavy-water-moderated reactors and sometimes must be separated isotopically from hydrogen and deuterium for disposal. Ultimately, the tritium could be used as fuel in thermonuclear reactors (see Fusion energy). Nuclear fusion reactions that involve tritium occur at the lowest known temperatures for such reactions. One possible reaction using deuterium produces neutrons that can be used to react with a lithium blanket to breed more tritium.

$$\mathrm{H}_1^3 + \mathrm{H}_1^2 \longrightarrow \mathrm{H}_2^4\mathrm{e} + n_0^1 + 17.6\ \mathrm{MeV}$$

Tritium can be produced in a manner requiring very little isotopic separation by the reaction of neutrons with ^{6}Li.

$$\mathrm{L}_3^6\mathrm{i} + n_0^1 \longrightarrow \mathrm{H}_1^3 + \mathrm{H}_2^4\mathrm{e}$$

This method is used in nuclear reactors at the plant at Savannah River, Georgia, to produce quantities of tritium. Final purification from hydrogen and deuterium can be accomplished by any of the methods used for deuterium separation. Separation factors for tritium from hydrogen are larger than for deuterium from hydrogen, and those for separation of tritium from deuterium are smaller than the deuterium–hydrogen factors. Complex mixtures of all three isotopes of hydrogen are problematic because of the numerous mixed species present, eg, HD, HT, and DT. A plant has been built and is in operation for the simultaneous extraction of hydrogen and tritium from heavy water (20). In this plant, low temperature rectification of liquid hydrogen at 150 kPa (1125 torr) is used to accomplish isotopic fractionation.

4. Boron-10

Boron-10 has a natural abundance of 19.61 atomic % and a thermal neutron cross section of 3.837×10^{-25} m^2 (3837 barns) as compared to the cross section of ^{11}B, 5×10^{-31} m^2 (0.005 barns). Boron-10 is used at 40–95 atomic % in safety devices and control rods of nuclear reactors. Its use is also intended for breeder-reactor control rods.

Examination of possible systems for boron isotope separation resulted in the selection of the multistage exchange-distillation of boron trifluoride–dimethyl ether complex, $BF_3{\cdot}O(CH_3)_2$, as a method for ^{10}B production (21, 22). Isotope fractionation in this process is achieved by the distillation of the complex at reduced pressure, ie, 20 kPa (150 torr), in a tapered cascade of multiplate columns. Although the process involves reflux by evaporation and condensation, the isotope separation is a result of exchange between the liquid and gaseous phases.

$$B^{11}F_3{\cdot}O(CH_3)_2\ (l) + B^{10}F_3\ (g) \rightleftharpoons B^{10}F_3{\cdot}O(CH_3)_2\ (l) + B^{11}F_3\ (g)$$

The equilibrium constant for this reaction is ca 1.022 at 100°C. The ^{10}B concentrates in the liquid phase (23). However, the vapor phase contains ca 40% undissociated complex, which lowers the effective single-stage separation factor to ca 1.014.

A plant built by Amoco (Standard Oil of Indiana) and operated from 1944–1946 produced ca 50 kg of enriched ^{10}B (24). A larger plant, constructed in 1953 by the Hooker Electrochemical Company (Model City, New York) produced ca 3400 kg of ^{10}B enriched to >90 atomic % (25, 26). In 1977, the Eagle-Picher Company reconstructed and operated the Model City boron isotope separation plant at Quapaw, Oklahoma. In addition, a separation cascade involving the boron trifluoride–dimethyl ether exchange-distillation process was designed and built for Eagle-Picher by Sulzer Brothers. This plant has a capacity of >2 metric tons ^{10}B as metal per year enriched to 95 atomic %. Tails concentration is ca 5 atomic % ^{10}B. There are two identical separation cascades. Each cascade consists of two distillation columns, which operate in series. The first column is 50.8 cm ID and has a packed height of 42 m; the second column is 30.5 cm ID and has a packed height of 27.4 m. Equilibrium time to achieve product level is ca 14 d. Either ^{10}B or ^{11}B can be supplied at >99 atomic % isotopic enrichment. The operating pressure is 27 kPa (200 torr), and the distillation boilup temperature is 96°C.

The search for a system with less decomposition and a higher separation factor has been summarized (27–29). The most promising system is the BF_3–anisole system, in which BF_3 (g) exchanges with the anisole [100-66-3] (methyl phenyl ether) $\cdot BF_3$ complex (l) (30):

$$C_6H_5OCH_3{\cdot}^{11}BF_3\ (l) +^{10} BF_3\ (g) \rightleftharpoons C_6H_5OCH_3{\cdot}^{10}BF_3\ (l) +^{10} BF_3\ (g)$$

The equilibrium constant for this reaction is 1.029 at 25°C and reflux may be accomplished by decomposing the complex with heat and by absorbing BF_3 in anisole. This system, in contrast to the dimethyl ether–BF_3 system, is a true gas–liquid exchange system and contains no associated complex in the gas phase (30).

5. Lithium-7

The normal abundance of lithium-7 is 92.44 atomic %. Because of its low thermal neutron absorption cross section, ie, 3.7×10^{-30} m^2, highly enriched ^7Li as lithium hydroxide, LiOH, is used to control the pH in pressurized water reactors. Many possible systems have been investigated for the separation of lithium isotopes (31). Lithium-7 has been produced in the United States by chemical exchange between lithium hydroxide and lithium amalgam.

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