DEUTERIUM AND TRITIUM

1. Deuterium

1.1. Introduction. Deuterium [16873-17-9] (symbol ^{2}H or D) occurs in nature in all hydrogen-containing compounds to the extent of about 0.0145 atom%. Small but real differences in the deuterium content of water from various sources (rain, snow, glaciers, freshwater, seawater from different oceans) can readily be detected, and variations in the natural abundance of deuterium resulting from evaporation, precipitation, and molecular exchange make it possible to draw far-reaching conclusions about the genesis and geological history of natural waters.

Molecular deuterium [7782-39-0], D_2, was first isolated in relatively pure form by Urey and co-workers at Columbia University in 1931 (1), and nearly pure D_2O was prepared by G. N. Lewis shortly thereafter by electrolysis (2). Subsequently applications of deuterium as a tracer for the path of hydrogen in biological systems were developed and became widely used. In physical organic chemistry, the differences in rates of reaction between corresponding ^{1}H and D compounds became an important tool for the elucidation of organic reaction mechanisms. The significance of deuterium isotope effects in a biological context attracted attention very early (3,4). The discovery in 1959 that it was possible to grow fully deuterated organisms (5,7) opened new areas of isotope chemistry and biology for exploration.

The recognition in 1940 that deuterium as heavy water [7789-20-0] has nuclear properties that make it a highly desirable moderator and coolant for nuclear reactors (qv) (8,9) fueled by uranium (qv) of natural isotopic composition stimulated the development of industrial processes for the manufacture of heavy water. Between 1940 and 1945 four heavy water production plants were operated by the United States Government, one in Canada at Trail, British Columbia, and three at the U.S. Army Ordinance Works operated by the DuPont Company at Morgantown, West Virginia; Childersburg, Alabama; and Dana, Indiana. The plant at Trail used chemical exchange between hydrogen gas and steam for the initial isotope separation followed by electrolysis for final concentration. The three plants in the United States used vacuum distillation of water for the initial separation followed by electrolysis. Details of these plants and their operations may be found in the literature (10).

In 1950 construction of a large-scale heavy water facility was initiated at the Savannah River site near Aiken, South Carolina, for the nuclear reactors operated there. The dual temperature exchange of deuterium between hydrogen sulfide and water (the GS process) was selected (11,12) for isotopic enrichment of deuterium. This plant was designed to produce 450 metric tons of heavy water per year, and a plant of similar capacity was constructed at Dana, Indiana. In the 1990s, the plant at Savannah River was the only heavy water plant in operation in the United States and produced about 160 t of heavy water annually. Canadian D_2O capacity was about 1450 t/yr (13). France, Norway, Switzerland, and India also have small production plants. The continued production of heavy water is closely coupled to the use of heavy water in nuclear reactor technology. The general decline in the construction of new nuclear reactors has dimmed the prospects for the large-scale production of deuterium.

1.2. Physical Properties. Although the chemical and physical properties of all isotopes of an element are qualitatively the same, there are quantitative differences among them. The physical and chemical differences between the hydrogen isotopes are relatively much greater than those among the isotopes of all other elements because of the large relative differences in mass, ie, $H : D : T = 1 : 2 : 3$.

As in the case of hydrogen and tritium, deuterium exhibits nuclear spin isomerism (see MAGNETIC SPIN RESONANCE) (14). However, the spin of the deuteron [12597-73-8] is 1 instead of ½ as in the case of hydrogen and tritium. As a consequence, and in contrast to hydrogen, the ortho form of deuterium is more stable than the para form at low temperatures, and at normal temperatures the ratio of ortho- to para-deuterium is 2 : 1 in contrast to the 3 : 1 ratio for hydrogen.

The physical and thermodynamic properties of elemental hydrogen and deuterium and of their respective oxides illustrate the effect of isotopic mass differences.

Properties of Light and Heavy Hydrogen. Vapor pressures from the triple point to the critical point for hydrogen, deuterium, tritium, and the various diatomic combinations are listed in Table 1 (15). Data are presented for the equilibrium and normal states. The equilibrium state for these substances is the low temperature ortho–para composition existing at 20.39 K, the normal boiling point of normal hydrogen. The normal state is the high (above 200 K) temperature ortho–para composition, which remains essentially constant.

Thermodynamic data on H_2, the mixed hydrogen–deuterium molecule [13983-20-5], HD, and D_2, including values for entropy, enthalpy, free energy, and specific heat have been tabulated (16). Extensive PVT data are also presented in Reference 16 as are data on the equilibrium–temperature behavior of the ortho and para forms of H_2 and D_2. Some physical properties of liquid H_2 and D_2 at 20.4 K are presented in Table 2.

Properties of Light and Heavy Water. Selected physical properties of light and heavy water are listed in Table 3 (17). Thermodynamic properties are given in Table 4. The liquid plus vapor critical-temperature curve for (xD_2O–$(1-x)H_2O$) mixtures over the entire concentration range has been reported (28).

Structure. At room temperature both light and heavy water appear to be highly structured, ie, extensively hydrogen bonded (17). Heavy water is the more structured. This is reflected in a higher temperature of maximum density, a

Table 1. **Vapor Pressures and Triple and Critical Points of Hydrogen Isotopes**[a,b]

Factor	*e*-H_2	*n*-H_2	HD	HT	*e*-D_2	*n*-D_2	DT	*n*-T_2
triple point, T_{tr}, K	13.81	13.96	16.60	17.62	18.69	18.73	21.71	20.62
vapor pressure, kPa[c]								
T_{tr}	7.04	7.20	12.37	14.59	17.13	17.14	19.43	21.60
20.0 K	93.22	90.31	51.02	38.50	29.66	29.41	21.98	
22.5 K	185.1	179.1	112.3	89.49	71.82	71.17	56.46	44.80
25.0 K	327.65	316.63	214.42	177.66	147.19	145.79	120.82	100.03
27.5 K	534.07	515.13	369.98	315.36	288.02	265.28	227.11	194.10
30.0 K	819.56	788.49	592.74	515.65	447.55	442.56	388.42	339.88
32.5 K	1203.4	1153.8	898.50	792.91	700.58	691.91	619.04	548.47
35.0 K			1307.4	1164.0	1044.7	1030.0	935.27	843.06
T_{cr}	1293.9	1298.0	1484.41	1570.53	1649.59	1664.79	1773.18	1850.24
critical point, T_{cr}, K	32.99	33.24	35.91	37.13	38.26	38.35	39.42	40.44

[a] Adapted from Ref. 15.

[b] The prefixes *e*- and *n*- refer to equilibrium and normal states. For T, data are available only for the normal state. The equilibrium state for these substances is the low temperature ortho-para composition existing at 20.39 K, the normal boiling point of normal hydrogen. The normal state is the ortho-para composition above 200 K. See text.

[c] To convert kPa to mm Hg, multiply by 7.5.

higher boiling point, and a generally lower solubility of inorganic salts in the D_2O (29). At room temperature, the viscosity of D_2O is also about 25% higher than that of H_2O (30). Nonpolar solutes elicit greater structure-making properties from D_2O than for H_2O and structure-breaking salts disrupt more structure in D_2O because there is more structure to break. Structure breaks down faster in D_2O than H_2O with increase in temperature. Thus D_2O may be more structured or less structured than H_2O, depending on the temperature.

Table 2. **Properties of Liquid H_2 and D_2 at 20.4 K**

Property	H_2[a]	D_2[b]
Equilibrium states		
density, g/L	70	169
viscosity, mPa · s(= cP)	1.4×10^{-2}	4.0×10^{-2}
surface tension, mN/m(= dyn/cm)	2.17	3.72
thermal conductivity, W/(cm · K)	11.6	12.64
dielectric constant	1.226	1.275
Normal states		
molar volume at 20 K, mL	28.3	23.5
heat of vaporization, J/mol[c]	904	1226
heat of fusion, J/mol[c]	117	197

[a] The equilibrium state of hydrogen has 0.21% *o*-H_2O; the normal state has 75% *o*-H_2O.

[b] The equilibrium state of deuterium has 97.8% *o*-D_2; the normal state has 67% *o*-D_2.

[c] To convert J to cal, divide by 4.184.

Table 3. **Physical Properties of Light and Heavy Water**

Property	H_2O	Ref.[a]	D_2O	Ref.[b]
molecular weight	18.015		20.028	
melting point, T_m, °C	0.00		3.81	
triple point, T_{tr}, °C	0.01		3.82	
temp of max density, °C	3.98		11.23	
normal boiling point, T_b, °C	100.00		101.42	
critical constants		19		20
temperature, °C	374.1		371.1	
pressure, MPa[c]	22.12		21.88	
volume, cm^3/mol	55.3		55.0	
density at 25°C, g/cm^3	0.99701		1.1044	
vapor pressure, liquid at 25°C, kPa[d]	3.166		2.734	
molar volumes, cm^3/mol				
solid at T_m	19.65		18.679	
liquid at T_m	18.018		18.118	
liquid at T_{max} density	18.016		18.110	
liquid at 25°C	18.069		18.134	
coefficients of thermal expansion, $°C^{-1}$				
solid at T_m	1.39×10^{-4}		1.39×10^{-4}	
liquid at T_m	-5.9×10^{-5}		-3.2×10^{-5}	
liquid at 25°C	26.2×10^{-5}		21.8×10^{-5}	
compressibility at 20°C, Pa^{-1}[d]	4.45	19	4.59	19
crystallographic parameters at 0°C, nm		21		21
a	0.45228		0.45258	
c	0.73673		0.73689	
c/a	0.1629		0.1628	
length of the hydrogen bond, nm	0.2765		0.2760	
dipole moment, C · m[e]				
benzene soln at 25°C	5.87×10^{-30}		5.94×10^{-30}	
vapor at 100–200°C	6.14×10^{-30}		6.14×10^{-30}	
dielectric constant at 25°C	78.304		77.937	
refractive index, $n^{20}{}_D$	1.3330		1.3283	
polarizability of vapor near 100°C, cm^3/mol	58.5		61.7	
viscosity at 25°C, mPa · s(= cP)	0.8903	22	1.107	
surface tension at 25°C, mN/m (= dyn/cm)	71.97		71.93	
moments of inertia, 10^{40}g · cm^2				
I_e^A	1.0224		1.833	
I_e^B	1.9180		3.841	
I_e^C	2.9404		5.674	
vibrational fundamentals, cm^{-1}		23		23
v_1	3657.05		2671.69	
v_2	1594.59		1178.33	
v_3	3755.79		2788.03	
ion product constant at 25°C	1.01×10^{-14}	24	1.11×10^{-15}	24
heat of ion product at 25°C, kJ/mol[f]	56.27	24	60.33	24

[a] Unless otherwise indicated, data are from Ref. 17.

[b] Unless otherwise indicated, data are from Ref. 18.

[c] To convert MPa to atm, multiply by 10.1.

[d] To convert kPa to mm Hg, multiply by 7.5.

[e] To convert C · m to debye, multiply by 3.00×10^{29}.

[f] To convert Joules to calories, divide by 4.184.

Table 4. **Thermodynamic Properties of Light and Heavy Water**

Parameter[a]	H_2O	Ref.[b]	D_2O	Ref.[c]
ΔH_{fus} at T_{m}, kJ/mol	−6.008		6.339	16
ΔS_{fus} at T_{m}, J/K	22.0		22.67	
ΔH_{vap} at 3.82°C, kJ/mol	44.77		46.8	
ΔE_{vap} at 3.82°C, kJ/mol	42.47	[d]	44.18	[d]
ΔS_{vap} at 3.82°C, J/K	161.62		167.8	
ΔH_{subl} at T_{tr}, kJ/mol	50.91		52.84	
ΔE_{subl} at T_{tr}, jJ/mol	48.66	[d]	50.54	
ΔS_{subl} at T_{tr}, J/K	186.4		190.7	
$\Delta H^{*}_{\mathrm{vap}}$ at 25°C, kJ/mol	44.02	25	45.39	
$\Delta G^{*}_{\mathrm{vap}}$ at 25°C, kJ/mol	8.62	25	8.95	19
$\Delta S^{*}_{\mathrm{vap}}$ at 25°C, J/K	118.8	[d]	122.25	[d]
$\Delta E^{*}_{\mathrm{vap}}$ at 25°C, kJ/mol	41.55	[d]	42.93	[d]
$(\Delta H^{\circ}_{\mathrm{f}})_{298}$, liquid, kJ/mol	−285.9	26	−294.6	25
$(\Delta G^{\circ})_{298}$, liquid, kJ/mol	−237.2	26	−243.5	25
S°_{298}, liquid, J/K	70.08	26	76.11	25
$(\Delta H^{\circ}_{\mathrm{f}})_{298}$, gas, kJ/mol	−241.8	26	−249.2	25
$(\Delta G^{\circ}_{\mathrm{f}})_{298}$, gas, kJ/mol	−228.6	26	−234.6	25
S°_{298}, gas, J/K	188.8	26	198.3	27
H°_{298}-H°_{0} gas, kJ/mol	9.908	26	9.954	25
C_p, liquid at 25°C, J/(mol · K)	75.27		84.35	
C_v, liquid at 25°C, J/(mol · K)	74.48		83.7	

[a] To convert J to cal, divide by 4.184.

[b] Unless otherwise indicated, data are from Ref. 17.

[c] Unless otherwise indicated, data are from Ref. 18.

[d] Calculated from data given in Table 3.

Ionic Equilibria. The ion product constant of D_2O (see Table 3) is an order of magnitude less than the value for H_2O (24,31,32). The relationship $\mathrm{pD} = \mathrm{pH} + 0.41$ (molar scale; 0.45 molal scale) for pD in the range 2–9 as measured by a glass electrode standardized in H_2O has been established (33). For many phenomena strongly dependent on hydrogen ion activity, as is the case in many biological contexts, the difference between pH and pD may have a large effect on the interpretation of experiments.

Deuterium as Neutron Moderator. Deuterium has very desirable properties as a moderator for neutrons. A good moderator is a material in which there is, on the average, a considerable decrease in neutron energy per collision (the logarithmic energy decrement ξ is large), one in which the probability of a scattering interaction with neutrons (the macroscopic scattering cross section Σ_s) is large, and finally a material where the absorption cross section for neutrons Σ_a is low. These factors all combine in a term called the moderating ratio, the ratio of the slowing-down power of the material to its neutron-absorption characteristics. As illustrated in Table 5 heavy water has a much greater moderating ratio than any of the other materials commonly used as moderators (34).

Kinetic Isotope Effects. The principal difference in chemical behavior between H and D derives from the generally greater stability of chemical

Table 5. **Properties of Neutron Moderators**

Moderator	Slowing-down power $\xi \times \Sigma_s$, cm^{-1}	Macroscopic absorption cross section Σ_a, cm^{-1}	Moderating ratio, $\xi \times \Sigma_a/\Sigma_a$
water	1.28	2.2×10^{-2}	58
heavy water	0.18	8.5×10^{-6}	21,000
helium	10^{-5}	2.2×10^{-7}	45
beryllium	0.16	1.2×10^{-3}	130
graphite	0.065	3.3×10^{-4}	200

bonds formed by D. Thus a C—D bond is less reactive than a comparable C—H bond, a greater amount of energy is required to activate a C—D bond for reaction, and general reactions involving the rupture of a C—D bond proceed considerably more slowly than for a comparable C—H bond. The most important factor contributing to the difference in bond energy and the kinetic isotope effect is the lower (5.021–5.275 kJ/mol (1.2–1.5 kcal/mol)) zero-point vibrational energy for D bonds. A comprehensive quantum and statistical mechanical theory of kinetic isotope effects has been developed (35). Kinetic isotope effects are particularly important in the elucidation of organic reaction mechanisms, and are the subject of a large literature (36).

Biological Effects of Deuterium. Replacement of more than one third of the hydrogen by deuterium in the body fluids of mammals or two thirds of the hydrogen in higher green plants has catastrophic consequences for the organisms. At lower deuterium levels in higher plants, growth is markedly slowed. In mice and rats low levels of deuterium result in sterility, and at higher concentrations neuromuscular disturbances, fine muscle tremors, and a tendency to convulsions can be noted (37,38). Impairment of kidney function, anemia, disturbed carbohydrate metabolism, central nervous system disturbances, and altered adrenal function have been found in deuterated mice (39,40). Hemoglobin and red blood cell count, serum glucose, and cholesterol all decrease in deuterated dogs (38).

Extensive replacement of H by D in living organisms is, however, not invariably fatal to the organisms. Numerous green and blue-green algae have been grown in which >99.5% of the hydrogen has been replaced by D. These fully deuterated organisms can be used to start a food chain to provide fully deuterated nutrients for organisms that have more demanding nutritional requirements. Numerous varieties of bacteria, molds, fungi, and even a protozoan have been successfully grown in fully deuterated form. These organisms of unnatural isotopic composition and the deuterated compounds that can be extracted from them have found uses in many areas of biological research (41).

Kinetic isotope effects are an important factor in the biology of deuterium. Isotopic fractionation of hydrogen and deuterium in plants occurs in photosynthesis. The lighter isotope ^{1}H is preferentially incorporated from water into carbohydrates and lipids formed by photosynthesis. Hydrogen isotopic fractionation has thus become a valuable tool in the elucidation of plant biosynthetic pathways (42,43).

Deuterium isotope effects provide information about the mechanisms of enzyme action (44–46). A bacterial alkaline phosphatase and a plant alkaline phosphatase have been prepared from fully deuterated organisms grown in 99.6% D_2 (47). The enzymatic behavior of the H and D enzymes were quite similar. Fully deuterated griseofulvin (48) (see ANTIBIOTICS, PEPTIDES) and benzylpenicillin (49) (see ANTIBIOTICS, β LACTAMS–PENICILLIN AND OTHERS) have antifungal and antibiotic potencies at least as great as their ordinary hydrogen analogues, and are probably metabolized *in vivo* more slowly because of the enhanced stability of C—D relative to C—H bonds. Synthetic deuterated drugs have also been considered as therapeutic agents (50). Administration of D_2O has been reported to prevent hypertension in hypertensive rats (51), and this has even been the subject of patent applications. Considering the well-documented toxic effects of deuterium in mammals, long-term administration of D_2O to humans is not likely to become a routine procedure. However, D_2O confers significant protection to yeast against hydrostatic pressure damage (52), and pretreatment with D_2O has been claimed to protect cultured cells against x-ray damage (53). Protein structure is affected by dissolution in D_2O. One manifestation is increased resistance to thermal denaturation. Few systematic studies of fully deuterated proteins or the effects of D_2O on the structures of proteins of natural isotopic composition are available.

Isotope Effects on Superconductivity. Substitution of hydrogen by deuterium affects the superconducting transition temperature of palladium hydride [26929-60-2], PdH_2 (54,55), palladium silver hydride, $Pd_{1-y}Ag_yH_zD_x$ (56), and vanadium–zirconium–hydride, $V_2ZrH_x(D_x,T_x)$ (57).

1.3. Production of Heavy Water. Because of the low natural abundance of deuterium, very large amounts of starting material, which is water, must be processed to produce relatively small amounts of highly enriched deuterium. No water or other hydrogen compound has been found either in nature or as a by-product of an industrial operation that is significantly enriched in deuterium. The cost of subsequent enrichment to 99% is negligible compared to the costs incurred in the initial enrichment from natural abundance to 1%. For small-scale preparations, a highly efficient but very expensive process such as electrolysis can be used. For large-scale use, however, a high enrichment factor per stage is of only secondary importance to the overall costs of operation both in power and in capital investment. The isotope separation methods that have attracted the greatest interest include chemical exchange between water and hydrogen sulfide, hydrogen and water, and hydrogen and ammonia; distillation of water or hydrogen; and electrolysis of water in combination with other procedures (58).

Chemical Exchange Processes. Isotope exchange reactions (20) between hydrogen gas and water or ammonia, and between water and hydrogen sulfide provide the basis for the most efficient large-scale methods known for the concentration of deuterium. Equilibrium constants for these reactions are shown in Table 6. These equilibria are temperature dependent. The efficiency of chemical exchange processes can be increased by taking advantage of the difference in the equilibrium constants as a function of temperature in the form of a dual-temperature exchange process.

In the dual-temperature H_2O/H_2S process (61,62), exchange of deuterium between $H_2O(l)$ and $H_2S(g)$ is carried out at pressures of ca 2 MPa (20 atm). At elevated temperatures deuterium tends to displace hydrogen in the hydrogen

Table 6. **Chemical Exchange Reactions**

Reaction	Equilibrium constant[a]	Reference
$H_2O(1) + HDS(g) \rightleftharpoons HDO(1) + H_2S(g)$	$K_{30} = 2.18$	59
	$K_{130} = 1.83$	
	$K^*_{-50} = 6.60$	60
	$K^*_0 = 4.42$	
$NH_3(1) + HD(g) \xrightleftharpoons{\text{catalyst}} NH_2D(1) + H_2(g)$	$K_{25} = 3.62$	59
$H_2O(g) + HD(g) \xrightleftharpoons{\text{catalyst}} HDO(g) + H_2(g)$	$K_{125} = 2.43$	

[a] Subscripts indicate temperature in °C.

sulfide and thus concentrates in the gas. At lower temperatures the driving force is reversed and the deuterium concentrates in H_2S in contact with water on the liquid phase.

The deuterium exchange reactions in the H_2S/H_2O process (the GS process) occur in the liquid phase without the necessity for a catalyst. The dual-temperature feature of the process is illustrated in Figure 1**a.** Dual-temperature operation avoids the necessity for an expensive chemical reflux operation that is essential in a single-temperature process (11,163) (Fig. 1**b**).

As shown in Figure 1**a,** the basic element of the H_2S/H_2O process is a pair of gas–liquid contacting towers each containing a number of sieve or bubble-cap plates (see DISTILLATION). The cold tower operates at a temperature of 30°C and the hot tower at 120–140°C. Water entering this system flows downward through the cold tower and then through the hot tower countercurrent to a

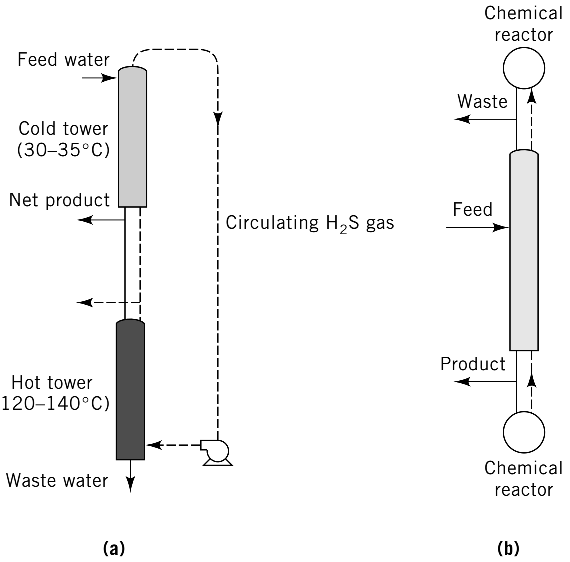

Fig. 1. Simplified flow diagrams for H_2S/H_2O heavy water processes. (**a**) Dual-temperature system where the pressure is 1.90 MPa; (**b**) single-temperature system. To convert MPa to atm, divide by 0.100.Courtesy of George Newnes, Ltd., London.

stream of hydrogen sulfide gas at 1896 kPa (275 psig). The water is progressively enriched in deuterium as it passes through the cold tower, and progressively depleted as it passes through the hot tower, eventually leaving the hot tower at a concentration below that at which it entered the system. The HDO and HDS that build up within the process are withdrawn from the base of the cold tower and top of the hot tower, respectively, by withdrawing a fraction of the water and gas flow. These enriched fractions are fed to a succeeding stage for further concentration. The hydrogen sulfide gas, which acts as a transport medium for the deuterium, circulates in a closed loop within the several stages of the process. About 20% of the deuterium in natural water can be economically extracted in this manner.

In producing tonnage quantities of heavy water, large equipment must be used to perform the initial separation because of the low feed concentration and the high throughput. To produce one metric ton of D_2O the plant must process 41,000 t of water, and must cycle 135,000 t of hydrogen sulfide. By appropriate process staging, the amount of materials handled and the size of equipment can be reduced almost in proportion to the increase in concentration of heavy water through the plant. This staging may be done using any of the possible heavy-water processes, or the process may be changed from stage to stage. In a properly staged plant most of the capital investment is incurred in the first hundredfold concentration gain, ie, from about 0.015 to 1.5 mol% D_2O.

In the heavy-water plants constructed at Savannah River and at Dana, these considerations led to designs in which the relatively economical GS process was used to concentrate the deuterium content of natural water to about 15 mol%. Vacuum distillation of water was selected (because there is little likelihood of product loss) for the additional concentration of the GS product from 15 to 90% D_2O, and an electrolytic process was used to produce the final reactor-grade concentrate of 99.75% D_2O.

In addition to the large contacting towers, a large amount of heat-recovery equipment was required to improve thermal efficiency. There were three principal heat-recovery circuits at the Savannah River production units: (*1*) the humidifier, comprising the bottom ten plates of the hot tower and the primary gas coolers; (*2*) the liquid heaters; and (*3*) the waste-stripper feed preheaters. The most important is the humidifier circuit, in which about half of the heat contained in the gas stream leaving the top of the hot tower is exchanged with a recirculating water stream that in turn heats and humidifies the gas entering the base of the hot tower. To make up for heat losses, steam is added to the hot tower after first being used in the stripper to remove the dissolved H_2S from the waste.

A dual-temperature system requires twice the number of separating stages (hot and cold columns) required for a single temperature system having the same effective separation factor. However, the requirement for a refluxing step is eliminated. The heat energy needed to maintain the temperature difference between the hot and cold columns can be minimized by heat exchange at appropriate points to preheat the gas and liquid streams entering the hot column and to precool the gas entering the cold column (64). All of the installations producing highly enriched deuterium in quantities greater than 20 metric tons D_2O annually use the H_2S/H_2O dual-temperature exchange system.

The fundamental parameters for the ammonia–hydrogen exchange (Table 6) are much more favorable than the corresponding factors in the H_2S/H_2O system, but the exchange reaction must be catalyzed to achieve a useful rate of exchange. The discovery (65) that the amide ion, NH_2^-, produced by addition of alkali metal to liquid ammonia, is an efficient catalyst for the NH_3/H_2 exchange stimulated intensive interest in this system (66,67). A dual-temperature system operating with a hot column at 70°C (single stage separation factor of 2.9) and a cold column at −40°C (single stage separation factor of 5.9) would have an effective separation factor of 2.0, which would permit extraction of 50% of the deuterium from the ammonia feed. Catalysis of the exchange by potassium amide is sufficiently effective even at−40°C to attain equilibrium in reasonably sized exchange columns. A single-temperature plant had been operated in France to produce about 20 t/yr D_2O (68). The primary limitation on the use of this process has been the availability of sufficient quantities of ammonia for plant feed. Even an ammonia plant producing 1000 t/d would provide sufficient feed only to permit production of 60–70 t/yr D_2O. A concept using an enrichment stripping system with a regeneration column has been developed (59,60) in which water is the deuterium feed via a hydrogen–water exchange step. This would, in principle, allow H_2/NH_3 chemical exchange plants of unlimited production capacity.

A variant of the H_2/NH_3 chemical exchange process uses alkyl amines in place of ammonia. Hydrogen exchange catalyzed by NH_2^- is generally faster using alkyl amines than ammonia, and a dual-temperature flow sheet for a H_2/CH_3NH_2 process has been developed (69).

Chemical exchange between hydrogen and steam (catalyzed by nickel–chromia, platinum, or supported nickel catalysts) has served as a pre-enrichment step in an electrolytic separation plant (10,70). If the $H_2(g)$/$H_2O(l)$ exchange could be operated as a dual-temperature process, it very likely would displace the H_2S/H_2O process. However, suitable catalysts for liquid-phase use have not been reported.

Distillation. Vacuum distillation (qv) of water, which contains the three molecular species H_2O, HDO, and D_2O, was the first method used for the large-scale extraction of deuterium (10,58) (Fig. 2). From the equilibrium constant in the liquid phase it is evident that the distribution of ^1H and D is not statistical. The differences in vapor pressure between H_2O and D_2O are significant, and a fractionation factor (see Table 7) of 1.05 can be obtained at about 50°C. As the fractionation factor decreases with increasing temperature, vacuum distillation is used that can be carried out at low temperatures. However, low pressure distillation requires larger towers to handle a given mass flow rate of vapor at lower pressure. In practice, tower top pressures between 6.7–16.7 kPa (50–125 mm Hg) were used, corresponding to temperatures between 30–50°C and separation factors between 1.06–1.05. Maximum deuterium recovery in a water distillation plant was considerably less than 5%, and the deuterium was concentrated from an initial value of 0.0143 atom% to 87–91 atom%. Further concentration to 99.8% was achieved by electrolysis. Operating parameters for a water distillation plant for deuterium recovery are given in Table 7. Distillation of water is now only used for final enrichment of D_2O (71).

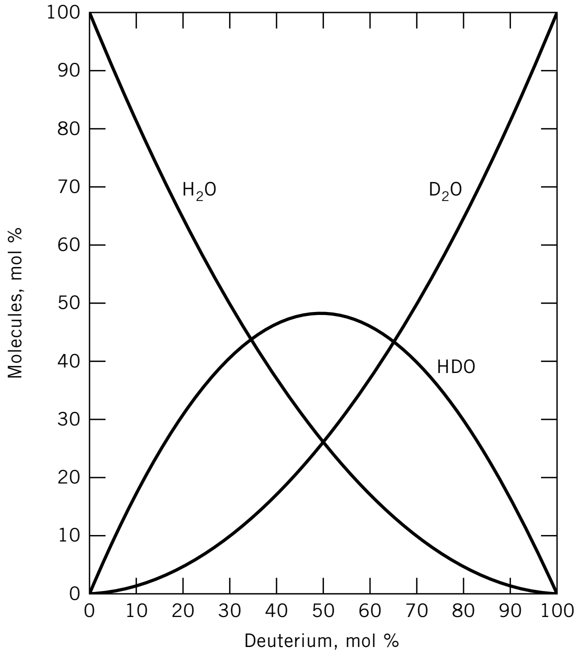

Fig. 2. Equilibrium concentrations of H_2O, HDO, and D_2O vs overall concentration of deuterium in water. $K_{25^\circ C} = 3.80$ for $H_2O + D_2O \rightleftharpoons 2\,HDO$.

Distillation of liquid hydrogen as a method for separating deuterium received early consideration (10,58) because of the excellent fractionation factor that can be attained and the relatively modest power requirements. The cryogenic temperatures, and the requirement that the necessarily large hydrogen feed be extremely pure (traces of air, carbon monoxide, etc, are solids at liquid hydrogen temperature) have been deterrents to the use of this process (see CRYOGENICS).

Table 7. **Distillation Process Requirements for the Production of Deuterium**[a]

Requirement	Water distillation	Hydrogen distillation
deuterium content of feed, %	0.0149	0.0149
separation factor, α	1.05[b]	1.52[c]
temperature, K	323	23
pressure, kPa[d]	ca 13.3 kPa	ca 160 kPa
min no. stages	308	41
min reflux ratio	141,000	19,600
recovery, %	ca 5	90
mol feed per mol product	133,940	7,442
ratio of operating costs	11	1

[a] Ref. 61.
[b] $\alpha = (p_{H_2O}/p_{D_2O})^{1/2}$.
[c] $\alpha = (p_{H_2}/p_{D_2})^{1/2}$.
[d] To convert kPa to psi, multiply by a 0.145.

In the separation of deuterium by distillation of liquid hydrogen, the presence of nuclear spin isomers must be taken into account. Ordinary hydrogen gas consists of three parts of ortho-H_2 (nuclear spins parallel) and one part para-H_2 (nuclear spins antiparallel)(see HYDROGEN). The antiparallel orientation is the lowest energy state ($J = 0$). It is the usual practice in the production of liquid hydrogen to include chromium oxide, Cr_2O_3, a paramagnetic species that catalyzes the conversion of the parallel to the antiparallel para spin orientation. A comparison of the operating characteristics of a water distillation plant with those of a liquid hydrogen distillation plant are given in Table 7. Hydrogen distillation may become important to deuterium production (see also HYDROGEN ENERGY).

Electrolysis. For reasons not fully understood (76), the isotope separation factor commonly observed in the electrolysis of water is between 7 and 8. Because of the high separation factor and the ease with which it can be operated on the small scale, electrolysis has been the method of choice for the further enrichment of moderately enriched H_2O–D_2O mixtures. Its usefulness for the production of heavy water from natural water is limited by the large amounts of water that must be handled, the relatively high unit costs of electrolysis, and the low recovery.

1.4. Economic Aspects.

The principal market for deuterium has been as a moderator for nuclear fission reactors fueled by unenriched uranium. The decline in nuclear reactor construction has sharply reduced the demand for heavy water. The United States has stopped large-scale production of D_2O, and Canada is the only supplier of heavy water at this time. Heavy water is priced as a fine chemical, and its price is not subject to market forces.

1.5. Analytical Methods.

The principal methods for determination of the deuterium content of hydrogen and water are based upon measurements of density, mass, or infrared spectra. Other methods are based on proton magnetic resonance techniques (77,78), ^{19}F nuclear magnetic resonance (79), interferometry (80), osmometry (81), nuclear reaction (82), combustion (83), and falling drop methods (84).

Density. Measurement of the density of water by pycnometry is the classical method (30) for establishing deuterium concentrations in heavy water. Very precise measurements can be made by this method, provided the sample is prepared free of suspended or dissolved impurities and the concentration of oxygen-18 in water is about 0.2 mol%. However, in nearly all heavy water manufactured since 1950 in the United States, the concentration of oxygen-18 is about 0.4 mol % as the result of its concentration in the water-distillation portion of the production facilities. Using a correction for oxygen-18, the sensitivity of the densimetric method is ±0.2% D_2O, but the accuracy is not better than 0.03% D_2O because of an uncertainty of 30 ppm in the density of pure heavy water.

Mass Spectrometry. Mass spectrometric methods (85) are used for both hydrogen gas and water (see MASS SPECTROMETRY). These are capable of determining directly the concentration of different isotopic species in samples of H_2O, HDO, and D_2O, eg, by measuring the relative abundance of ions of mass 18 and 19 or mass 19 and 20. The principal limitation of the method is the contamination of the sample-introduction system with water vapor. This contamination causes significant memory effects on succeeding samples. To obtain accurate analyses it is necessary to use a comparative standard having an isotopic concentration within 7% of that of the unknown. The precision of this method is 0.005–0.1 mol% over the range 0.05–15% and is 0.2 mol% in the range 99–100% D_2O.

Infrared Spectrophotometry. The isotope effect on the vibrational spectrum of D_2O makes infrared spectrophotometry the method of choice for deuterium analysis. It is as rapid as mass spectrometry, does not suffer from memory effects, and requires less expensive laboratory equipment. Measurement at either the O–H fundamental vibration at 2.94 μm (O–H) or 3.82 μm (O–D) can be used. This method is equally applicable to low concentrations of D_2O in H_2O, or the reverse (86,87). Absorption in the near infrared can also be used (88,89) and this procedure is particularly useful (see INFRARED AND RAMAN SPECTROSCOPY; SPECTROSCOPY). The D/H ratio in the nonexchangeable positions in organic compounds can be determined by a combination of exchange and spectrophotometric methods (90).

Raman Spectroscopy. Raman spectroscopy is an excellent method for the analysis of deuterium containing mixtures, particularly for any of the diatomic H–D–T molecules. For these, it is possible to predict absolute light scattering intensities for the rotational Raman lines. Hence, absolute analyses are possible, at least in principle. The scattering intensities for the diatomic hydrogen isotope species is comparable to that of dinitrogen, N_2, and thus easily observed.

Gas Chromatography. Gas chromatography is a well recognized method for the analysis of H–D–T mixtures. The substrate is alumina, Al_2O_3, coated with ferric oxide, Fe_2O_3. Neon is used as the carrier gas. Detectors are usually both thermal conductivity (caratherometer) and ion chamber detectors when tritium is involved (see CHROMATOGRAPHY).

1.6. Uses. The only large-scale use of deuterium in industry is as a moderator, in the form of D_2O, for nuclear reactors. Because of its favorable slowing-down properties and its small capture cross section for neutrons, deuterium moderation permits the use of uranium containing the natural abundance of uranium-235, thus avoiding an isotope enrichment step in the preparation of reactor fuel. Heavy water-moderated thermal neutron reactors fueled with uranium-233 and surrounded with a natural thorium blanket offer the prospect of successful fuel breeding, ie, production of greater amounts of ^{233}U (by neutron capture in thorium) than are consumed by nuclear fission in the operation of the reactor. The advantages of heavy water-moderated reactors are difficult to assess.

Deuterium Fusion. At sufficiently high temperatures, deuterium undergoes nuclear fusion with the production of large amounts of energy:

$$^2H + ^2H \longrightarrow ^3H + ^1H + 4.0\ \text{MeV}$$

$$^2H + ^2H \longrightarrow ^3He + n + 3.3\ \text{MeV}$$

The temperature required to surmount the barrier to fusion is considerably reduced for the $^2H(^3H,n)^4He$ reaction, and the efforts to develop a nuclear fusion reactor are all based on the D–T fusion reaction. Many different pathways have been explored to reach the temperature at which a self-sustaining D–T fusion reaction occurs. These include magnetic confinement of a D–T plasma, laser implosion, and particle acceleration. The prospect of an energy source that meets global energy demand and mitigates environmental concerns about global warming, coupled with the depletion of fossil fuel energy sources, provide powerful incentives to pursue nuclear fusion (see FUSION ENERGY).

It has been claimed that the D–D fusion reaction occurs when D_2O is electrolyzed with a metal cathode, preferably palladium, at ambient temperatures. This claim for a cold nuclear fusion reaction that evolves heat has created great interest, and has engendered a voluminous literature filled with claims for and against. The proponents of cold fusion report the formation of tritium and neutrons by electrolysis of D_2O, the expected stigmata of a nuclear reaction. Some workers have even claimed to observe cold fusion by electrolysis of ordinary water (see, for example, Ref. 91). The claim has also been made for the formation of tritium by electrolysis of water (92). On the other hand, there are many experimental results that cast serious doubts on the reality of cold fusion (93–96). Theoretical calculations indicate that cold fusions of D may indeed occur, but at the vanishingly small rate of 10^{-23} events per second (97).

Other Uses. Other uses mentioned in recent patents include an optical fiber deposition tube fused in a deuterium atmosphere for attenuation improvement (98); treatment of bipolar disorders using deuterium-substituted carbonate (99); a deuterium heat generator that contains a nuclear fusion reaction (100); a deuterium lamp box and portable light source apparatus that provides three kinds of light (101); deuterium treatment of semiconductor devices for improved performance (102); and commercial power production by catalytic fusion of deuterium gas (103).

2. Tritium

2.1. Introduction. Tritium [15086-10-9], the name given to the hydrogen isotope of mass 3, has symbol ^3H or more commonly T. Its isotopic mass is 3.0160497 (104). Moletecular tritium [10028-17-8], T_2, is analogous to the other hydrogen isotopes. The tritium nucleus is energetically unstable and decays radioactively by the emission of a low-energy β particle. The half-life is relatively short (~12 yr), and therefore tritium occurs in nature only in equilibrium with amounts produced by cosmic rays or man-made nuclear devices.

Tritium was first prepared in the Cavendish Laboratory by Rutherford, Oliphant, and Harteck in 1934 (105,106) by the bombardment of deuterophosphoric acid using fast deuterons. The D–D nuclear reaction produced tritium ($^2D + ^2D \longrightarrow ^3T + ^1H$ + energy), but also produced some ^3He by a second reaction ($^2D + ^2D \longrightarrow ^3He + n^1$ + energy). It was not immediately known which of the two mass-3 isotopes was radioactive. In 1939 it was established (107) that ^3He occurred in nature and was stable. Tritium was later proved to be radioactive. A vivid history of the unravelling of the complex relationships between tritium, deuterium, and helium-3 is available (108).

2.2. Physical Properties. Tritium is the subject of various reviews (109–111), and a book (112) provides a comprehensive survey of the preparation,

Table 8. **Physical Properties of Molecular Tritium**[a]

Property	Value
melting point, at 21.6 kPa[b], K	20.62
boiling point, K	25.04
critical temperature, K	40.44[c]
critical pressure, MPa[d]	1.850
critical volume, cm^3/mol	57.1[e]
heat of sublimation, J/mol[f]	1640
heat of vaporization, J/mol[a]	1390
entropy of vaporization, J/(mol · K)[f]	54.0
molar density of liquid, mol/L	
20.62 K[b]	45.35
25 K	42.65
29 K	39.66

[a] Values are from Ref. 114, unless otherwise indicated.
[b] Value represents the triple point (162 mm Hg).
[c] From Ref. 113.
[d] To convert MPa to psi, multiply by 145.
[e] Value is calculated.
[f] To convert J to cal, divide by 4.184.

properties, and uses of tritium compounds. Selected physical properties for molecular tritium, T_2, are given in Table 8.

Calculated vapor pressure relationships of T_2, HT, and DT have been reported (113). An equation for the vapor pressure of solid tritium in units of kPa, T in Kelvin, has been given (114):

$$\log p = 5.6023 - 88.002/T$$

The three-phase region of D_2–DT–T_2 has been studied (115). Relative volatilities for the isotopic system deuterium–deuterium tritide–tritium have been found (116) to be 5–6% below the values predicted for ideal mixtures.

All components appear miscible in both liquid and solid phases from 17 to 22 K. For a 50–50 mol% mixture of liquid D–T at ca 19.7 K, the gas phase contains ca 42% T and the solid phase 52%.

The T–T bond energy has been estimated at 4.5881 *e*V (117).

The entropy of T_2 at 298.15 K is 164.8562 kJ/mol (39.4016 kcal/mol), the specific heat is 29.1997 J/(mol·°C) (6.9789 cal/(mol·°C)), and the Gibbs free energy is 135.9083 kJ/mol (32.4829 kcal/mol). These values were derived from extensive *ab initio* calculations for T_2 at spin equilibrium, ortho and para T_2, and the isotopomers HT and DT (118).

Ortho-Para Tritium. As in the case of molecular hydrogen, molecular tritium exhibits nuclear spin isomerism. The spin of the tritium nucleus is ½, the same as that for the hydrogen nucleus, and therefore H_2 and T_2 obey the same nuclear isomeric statistics (119). Below 5 K, molecular tritium is 100% para at equilibrium. At high (100°C) temperatures the equilibrium concentration is 25% para and 75% ortho. The kinetic parameters of conversion for T_2 at low

Table 9. **Physical Properties of T_2O**

Property	Value	Reference
mol wt	22.032	
triple point, °C	4.49	121
temperature of maximum density, °C	13.4	
boiling point, °C	101.51	121
density at 25°C, g/mL	1.2138	122
$\Delta H^\circ_{\mathrm{vap}}$ at 25°C, kJ/mol[a]	ca 45.81	121
liquid vapor pressure at 25°C, kPa[b]	2.64	
vibrational fundamentals, cm^{-1}	1017, 2438	123
ionization constant at 25°C	ca 6×10^{-16}	124

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to mm Hg, multiply by 7.5.

temperatures are faster than rates at corresponding temperatures for H_2. In the solid phase the conversion of molecular tritium to a state of ortho-para equilibrium is 210 times as fast as that for molecular hydrogen.

The experimental and theoretical aspects of the radiation and self-induced conversion kinetics and equilibria between the ortho and para forms of hydrogen, deuterium, and tritium have been correlated (120). In general, the radiation-induced transitions are faster than the self-induced transitions.

Properties of T_2O. Some important physical properties of T_2O are listed in Table 9. Tritium oxide [14940-65-9] can be prepared by catalytic oxidation of T_2 or by reduction of copper oxide using tritium gas. T_2O, even of low (2–19% T) isotopic abundance, undergoes radiation decomposition to form HT and O_2. Decomposition continues, even at 77 K, when the water is frozen. Pure tritiated water irradiates itself at the rate of 10 MGy/d (10^9 rad/d). A stationary concentration of tritium peroxide, T_2O_2, is always present (112). All of these factors must be taken into account in evaluating the physical constants of a particular sample of T_2O.

2.3. Nuclear Properties. *Radioactivity.* Tritium decays by β emission, $^3T \longrightarrow {}^3He + \beta^-$. A summary of the radioactive properties of T, adapted from Ref. 125, is given in Table 10.

Table 10. **Radioactive Properties of Tritium**

Property	Value
half-life, yr	12.43[a]
decay constant, s^{-1}	1.7824×10^{-9}
mean β energy, keV	5.7
molar activity, TBq/mol[b]	2128

[a] Courtesy of the National Institute of Standards and Technology.

[b] To convert Bq to Ci, divide by 3.7×10^{10}.

Nuclear Fusion Reactions. Tritium reacts with deuterium or protons (at sufficiently high temperatures) to undergo nuclear fusion:

$$^{3}\mathrm{T} + {}^{2}\mathrm{D} \longrightarrow {}^{4}\mathrm{He} + n^{1} + 17.6\ \mathrm{MeV}$$

$$^{3}\mathrm{T} + {}^{1}\mathrm{H} \longrightarrow {}^{4}\mathrm{He} + 19.6\ \mathrm{MeV}$$

The first of these nuclear fusion reactions produces a neutron that can be used to form a new atom of tritium as well as evolving a very large amount of energy in the form of extremely hot helium. Nuclear fusion using tritium can be initiated and sustained at the lowest temperature (at least in principle) of any nuclear fusion reaction known. Tritium thus becomes the key element both for controlled thermonuclear energy sources and in the uncontrolled release of thermonuclear energy in the hydrogen bomb (see FUSION ENERGY).

Nuclear Magnetic Resonance. All three hydrogen isotopes have nuclear spins, $I \neq 0$, and consequently can all be used in nmr spectroscopy (Table 11) (see MAGNETIC SPIN RESONANCE). Tritium is an even more favorable nucleus for nmr than is ^{1}H, which is by far the most widely used nucleus in nmr spectroscopy. The radioactivity of T and the ensuing handling problems are a deterrent to widespread use for nmr. Considerable progress has been made in the applications of tritium nmr (126,127).

2.4. Chemical Properties. Most of the chemical properties of tritium are common to those of the other hydrogen isotopes. However, notable deviations in chemical behavior result from isotope effects and from enhanced reaction kinetics induced by the β-emission in tritium systems. Isotope exchange between tritium and other hydrogen isotopes is an interesting manifestation of the special chemical properties of tritium.

Isotope Effects. Any difference in the chemical or physical properties of two substances that differ only in isotopic composition constitutes an isotope effect. Isotope effects are usually largest when the isotope is directly involved in the rate-determining step of a reaction. The greater the mass of an atom, the lower its zero-point bond energy, and the greater the activation energy required to cleave a chemical bond. In general, therefore, reactions involving rupture of a $-C-T$ bond may proceed at a markedly slower rate than those involving cleavage of a corresponding $-C-H$ bond. Kinetic isotope effects arising from bond cleavage are termed primary isotope effects. Secondary isotope effects occur as a result of the presence of the isotope in nearby molecular

Table 11. **Nuclear Magnetic Resonance Properties of Hydrogen Isotopes**

Isotope	Nuclear spin	Resonance frequency,[a] MHz	Relative sensitivity[b]	Magnetic moment, 10^{-4} J/T[c]
H	1/2	100.56	1.000	25.8995
D	1	15.360	9.64×10^{-3}	7.9513
T	1/2	104.68	1.21	27.625

[a] At a field of 2.35 T (23.5 kilogauss).

[b] At constant field.

[c] To convert J/T to μ_B (nuclear Bohr magnetons), divide by 9.274×10^{-24}.

sites. Bonds involving the isotope are neither broken nor formed in the reaction. Secondary isotope effects are generally smaller than primary effects. The latter may easily be 10 to 100 times greater. Solvent isotope effects include many important primary effects, eg, solvolyses and acid-base reactions, as well as secondary effects such as solvation. Although primary and secondary kinetic isotope effects are the most extensively studied, numerous other isotope effects have been observed with tritium. Thus, an H/T separation factor of about 14 occurs in the electrolysis of HOT (128,129). Other tritium isotope effects of significant magnitude have been observed in ion exchange (qv) (130) and gas chromatography (qv) (131,132). Many other examples have been described (112).

Enhanced Reaction Kinetics. For reactions involving tritium, the reaction rates are frequently larger than expected because of the ionizing effects of the tritium β-decay. For example, the uncatalyzed reaction $2\ T_2 + O_2 \longrightarrow 2\ T_2O$ can be observed under conditions (25°C) for which the analogous reaction of H_2 or D_2 would be too slow for detection (133).

Isotopic Exchange Reactions. Exchange reactions between the isotopes of hydrogen are well known and well substantiated. The equilibrium constants for exchange between the various hydrogen molecular species have been documented (121). Kinetics of the radiation-induced exchange reactions of hydrogen, deuterium, and tritium have been critically and authoritatively reviewed (134). The reaction $T_2 + H_2 \longrightarrow 2HT$ equilibrates at room temperature even without a catalyst (133).

In 1957, it was demonstrated (135) that tritium could be introduced into organic compounds by merely exposing them to tritium gas. Since that time hundreds of compounds, of types as simple as methane and as complex as insulin, have been labeled with tritium by this basic method of isotope exchange. Much work has been done to optimize conditions for the exchange technique through control of operating variables such as temperature, pressure, and addition of noble gases to facilitate energy transfer (136). Exchange of the hydrogen of organic compounds with tritium gas has been facilitated by activating the gas by ultraviolet light, γ- and x-ray irradiation, and microwave discharge. Although high chemical yields are obtained by the original, ie, Wilzbach, technique, highly tritiated impurities of structures similar to but not identical with that of the starting material are formed by direct irradiation damage of the target material and by decomposition of the tritiated products by self-irradiation. Separation of radioactive impurities produced in Wilzbach labeling may prove difficult, as is the task of proving that the radioactive T introduced into the substrate compound is actually in the compound of interest.

Catalytic exchange in solution between an organic compound and tritium gas or T_2O is a general procedure for introducing tritium with high specificity. Much higher molar specific activities (greater than 1.85 GBq/mmol (50 mCi/mmol)) can be attained than with the Wilzbach method. Both homogeneous and heterogeneous catalysts, as well as acid-base catalysis, can be used.

Hot atom reactions have also been used to label organic compounds with T. Irradiation of helium-3 with neutrons according to the nuclear reaction $^3He(n,p)^3H$ produces very energetic tritium atoms that can displace ordinary hydrogen in organic compounds. This procedure is not very selective, and the labeling pattern must be determined to enable the tritiated product to be used effectively as a tracer (137).

2.5. Natural Production and Occurrence. Tritium arises in nature by the action of primary cosmic rays (high-energy protons) or cosmic-ray neutrons on a number of elements. Natural tritium was first detected in the atmosphere (138) and was later shown to be present in rainwater (139). Because of its relatively short radioactive half-life, naturally produced tritium does not accumulate indefinitely and the amount of tritium found in nature is very small. The unit for measurement of natural tritium, the tritium unit (TU) signifies a ratio of 1 atom of tritium per 10^{18} atoms of hydrogen. A very excellent worldwide survey of tritium levels in natural waters has been compiled (140). Values range from less than one TU for water in certain deep wells and at extreme sea depths to several hundred TU in samples of rainwater taken during periods of active thermonuclear weapons testing. The level of tritium in atmospheric hydrogen increased from 3800 TU in 1948–1949 to 490,000 TU in 1959 (141).

The principal source of natural tritium is the nuclear reactions induced by cosmic radiation in the upper atmosphere, where fast neutrons, protons, and deuterons collide with components of the stratosphere to produce tritium:

$$^{14}\mathrm{N} + n^{1} \longrightarrow {}^{3}\mathrm{T} + {}^{12}\mathrm{C}$$

$$^{14}\mathrm{N} + {}^{1}\mathrm{H} \longrightarrow {}^{3}\mathrm{T} + \text{fragments}$$

$$^{2}\mathrm{D} + {}^{2}\mathrm{D} \longrightarrow {}^{3}\mathrm{T} + {}^{1}\mathrm{H}$$

The most important of these reactions by far is the $^{14}\mathrm{N}(n,\ {}^{12}\mathrm{C})^{3}\mathrm{T}$ reaction (142). The energetic tritons so produced are incorporated into water molecules by exchange or oxidation, and the tritium reaches the earth's surface as rainwater.

Large-scale detonation of hydrogen bombs in the atmosphere during the 1950s and 1960s, and inadvertent tritium losses have had a permanent impact on the tritium content of the atmosphere. For example, some 20,000 TBq (500,000 Ci) of tritium was released by accident into the atmosphere at Aiken, South Carolina in September, 1984 (143). The deposition of tritium in rainfall (mainly as HTO) is not uniform, and water in different localities can have very different tritium contents. The total deposition of tritium on the continental United States for the period 1953–1983 is estimated (144) at 12 ± 2 kg. In the United States, tritium in ground water is smallest in the Southwest, and highest in the Midwest. These differences may be associated with annual rainfall, the introduction of water from the Pacific Ocean, weather patterns, and the like. The transport, dispersion, cycling, and analysis of tritium in the environment receives considerable attention (145) because of the possible large-scale use of tritium in nuclear fusion.

Tritium has also been observed in meteorites and material recovered from satellites (see also EXTRA TERRESTRIAL MATERIALS). The tritium activity in meteorites can be reasonably well explained by the interaction of cosmic-ray particles and meteoritic material. The tritium contents of recovered satellite materials have not in general agreed with predictions based on cosmic-ray exposure. For observations higher than those predicted (Discoverer XVII and satellites), a theory of exposure to incident tritium flux in solar flares has been proposed. For observations lower than predicted (Sputnik 4), the suggested explanation is a diffusive loss of tritium during heating up on reentry.

2.6. Production. *Nuclear Reactions.* The primary reaction for the production of tritium is

$$^{6}\mathrm{Li} + n^{1} \longrightarrow {}^{3}\mathrm{T} + {}^{4}\mathrm{He} + 4.78\ \mathrm{MeV}$$

The capture cross section of ^{6}Li for this reaction using thermal neutrons is 930×10^{-28} m^2 (930 b) (146). All of the experimental data available to the end of 1986 on the cross sections for the nuclear reaction $^{7}\mathrm{Li} + n \longrightarrow {}^{4}\mathrm{He} + n + \mathrm{T} - 2.47$ MeV, which utilizes the much more abundant isotope ^{7}Li, are collected in a review (147).

A second, more favorable reaction is

$$^{3}\mathrm{He} + n^{1} \longrightarrow {}^{3}\mathrm{T} + {}^{1}\mathrm{H}$$

for which the capture cross section of ^{3}He to thermal neutrons is 5200×10^{-28} m^2 (5200 b). The limited availability of ^{3}He (0.00013–0.00017% natural abundance) (148) restricts the practical importance of this mode of production (see also HELIUM-GROUP GASES). Tritium is also produced by the action of high energy protons (such as primary cosmic rays) on a number of elements, and by the reaction of cosmic ray neutrons and ^{14}N. Reaction cross sections are small, generally a few to a few hundred m^2 $\times 10^{-31}$ (millibarns).

Production in Target Elements. Tritium is produced on a large scale by neutron irradiation of ^{6}Li. The principal U.S. site of production is the Savannah River plant near Aiken, South Carolina where tritium is produced in large heavy-water moderated, uranium-fueled reactors. The tritium may be produced either as a primary product by placing target elements of Li–Al alloy in the reactor, or as a secondary product by using Li–Al elements as an absorber for control of the neutron flux.

The confinement region in which nuclear fusion proceeds is surrounded by a blanket in which the neutrons produced by the fusion reaction are captured to produce tritium. Because of its favorable cross section for neutron capture, lithium is the favored blanket material. Various lithium blanket materials have been considered, ranging from liquid lithium metal, lithium-lead alloys, or lithium dioxide to aqueous solutions of lithium salts. Lithium ceramics such as lithium aluminate, $\mathrm{LiAlO_2}$, and lithium zirconates, $\mathrm{Li_2ZrO_3}$, $\mathrm{Li_6Zr_2O_7}$, and $\mathrm{Li_8ZrO_6}$, continue to show promise as candidate breeder materials (149). Extraction of tritium from the breeder blanket also poses many problems.

Production in Heavy Water Moderator. A small quantity of tritium is produced through neutron capture by deuterium in the heavy water used as moderator in the reactors. The thermal neutron capture cross section for deuterium is extremely small (about 6×10^{-32} m^2), and consequently the tritium produced in heavy water moderated reactors is generally significant only as a potential health hazard. However, in a high-flux reactor such as that at the Institute Max von Laue-Paul Langevin (Grenoble, France), the heavy water moderator is a useful source of tritium (142).

Production in Fission of Heavy Elements. Tritium is produced as a minor product of nuclear fission (150). The yield of tritium is one to two atoms in 10,000 fissions of natural uranium, enriched uranium, or a mixture of transuranium nuclides (see ACTINIDES AND TRANSACTINIDES; URANIUM).

Production-Scale Processing. The tritium produced by neutron irradiation of ^{6}Li must be recovered and purified after target elements are discharged from nuclear reactors. The targets contain tritium and ^{4}He as direct products of the nuclear reaction, a small amount of ^{3}He from decay of the tritium and a small amount of other hydrogen isotopes present as surface or metal contaminants.

In the recovery process the gaseous constituents of the target are evolved, and the hydrogen isotopes separated from other components of the gas mixture. A number of methods that can be applied to a process mixture or to naturally occurring sources are available for separating the tritium from the hydrogen and deuterium. Because of the military importance of tritium, details of the large-scale production of this isotope have not been published. A report, however, is available that describes the large-scale production of tritium and its uses in France (151).

Isotopic Concentration. A number of techniques have been reported for concentrating tritium from naturally occurring sources. For example, separation factors (H/T) of 6.6 to 29 were observed (152) for the concentration of tritium by electrolysis of tritiated water. Tritium is concentrated in the undecomposed water.

Low (20–25 K) temperature distillation has been widely used to separate hydrogen and deuterium and has also been successfully applied to the separation of tritium from the other hydrogen isotopes (153,154). At Los Alamos National Laboratory, a system of four interlinked cryogenic fractionation columns has been designed for the separation of an approximately equal mixture of deuterium and tritium containing a small amount of ordinary hydrogen into a tritium-free stream of HD for waste disposal, and streams of high-purity D_2, DT, and T_2 (155) (see CRYOGENICS). Mathematical models that are in good agreement with experimental results on the separation of deuterium–tritium by cryogenic distillation have been developed (156).

Concentration by gas chromatography has also been demonstrated. Elution chromatography has been used on an activated alumina column to resolve the molecular species H_2, HT, and T_2, thereby indicating a technique for separation or concentration of tritium (157). This method was extended (158) to include deuterium components. The technique was first demonstrated in 1964 using macro quantities of all six hydrogen molecular species (159).

Successful separations of tritium from hydrogen and deuterium have been achieved by a cryogenic thermal diffusion column (160), by diffusion through a palladium–silver–nickel membrane (161), and by chromatography on coated molecular sieves (162). Laser separation of tritium also appears to be competitive with more conventional isotope separation methods (163) (see LASERS). Large separation coefficients have been reported for zirconium chromium hydride ($ZrCr_2H_x$)–hydrogen isotope systems (164). A number of processing options thus are available for processing fuel and product streams containing H, D, and T in nuclear fusion reactors.

2.7. Analytical Methods. Tritium is readily detectable because of its radioactivity. Under certain conditions concentrations as low as 370 μBq/mL (10^{-8} μCi/mL) can be detected. Most detection devices and many analytical techniques exploit the ionizing effect of the tritium β-decay as a principle of operation (165,166).

Ionization Chamber. The ionization chamber is a simple, sensitive, and sturdy device filled with gas and containing two electrodes between which a potential difference is maintained. When gas containing tritium is admitted to the chamber, the radiation ionizes the gas, the ions are drawn to the electrodes, and a flow of current results that is proportional to the tritium concentration. Because of the ability to detect very small currents, this technique is very sensitive and can be adapted to either static or flow systems. Ionization chambers are used as process-stream monitors, leak detectors, stack monitors, breathing-air monitors, detectors for surface contamination, and detectors instrumented with vibrating-reed electrometers. For the last instrument, concentrations of tritiated water vapor in air of 370 μBq/mL (10^{-8} μCi/mL) (STP) can be measured. Developments in very low background proportional counters and chambers to be used for low-level internal gas counting of β-particles emitted by tritium are the subject of a comprehensive review (167). The combination of a proportional counter and a computer significantly enhances the measurement of very low levels of tritium in air.

Mass Spectrometer. The mass spectrometer is the principal analytical tool of direct process control for the estimation of tritium. Gas samples are taken from several process points and analyzed rapidly and continually to ensure proper operation of the system. Mass spectrometry is particularly useful in the detection of diatomic hydrogen species such as HD, HT, and DT. Mass spectrometric detection of helium-3 formed by radioactive decay of tritium is still another way to detect low levels of tritium (168). Accelerator mass spectroscopy (ams) has also been used for the detection of tritium and carbon-14 at extremely low levels. The principal application of ams as of this writing has been in archeology and the geosciences, but this technique is expected to facilitate the use of tritium in biomedical research, various clinical applications, and in environmental investigations (169).

Thermal-Conductivity Analyzer. The thermal-conductivity analyzer operates on the principle that the loss of heat from a hot wire by gaseous conduction to a surface at a lower temperature varies with the thermal conductivity of the gas, and is virtually independent of pressure between 1.3 kPa (10 mm Hg) and 101 kPa (1 atm). This technique is frequently used in continuous monitors for tritium in binary gas mixtures for immediate detection of process change.

Calorimeter. The β-decay energy of tritium is very precisely known (112). The thermal energy generated by the decay can thus be used with a specially designed calorimeter to measure the quantity of tritium in a system of known heat capacity.

Liquid Scintillation Counter. The rapid and sensitive technique of liquid scintillation counting is applied for the determination of tritium in liquid systems. The tritiated sample is dissolved in a solvent that contains an organic scintillator. Because many samples, particularly those of a biological nature, are not soluble in water or organic solvents, emulsions are usually used in scintillation counting (170,171). The accurate determination of tritium in biosystems is a particularly difficult problem because of the sizeable isotope effect encountered in the removal of tissue water. Methods for minimizing tritium fractionation during water removal have been described (172).

The emitted β particles excite the organic molecules which, in returning to normal energy levels, emit light pulses that are detected by a photomultiplier tube, amplified, and electronically counted. Liquid scintillation counting is by far the most widely used technique in tritium tracer studies and has superseded most other analytical techniques for general use (173).

Analysis of H–D–T Mixtures. Raman spectroscopy is a very useful and practical method for the analysis of diatomic molecules containing tritium and deuterium or hydrogen. Absolute light scattering intensities for the rotational Raman lines can be predicted, thus making absolute analyses possible. Gas chromatography is another excellent method for the analysis of H–D–T mixtures. The stationary phase consists of alumina, Al_2O_3, coated with ferric oxide, Fe_2O_3; neon is used as the carrier gas. Detectors are usually both thermal conductivity (caratherometer) and ion chamber detectors.

2.8. Health and Safety Factors. *Hazards.* Because tritium decays with emission of low-energy radiation ($E_{\text{av}} = 5.7$ keV), it does not constitute an external radiation hazard. However, tritium presents a serious hazard through ingestion and subsequent exposure of vital body tissue to internal radiation. The body assimilates tritiated water and distributes it throughout body fluids with remarkable speed and efficiency. When exposed to tritiated water vapor via inhalation, people absorb 98–99% of the activity inspired through the respiratory system (174). Uniform distribution throughout body fluids occurs within 90 minutes. Also, when exposed to such an atmosphere, tritium entering the body through the total skin area approximately equals that entering the lungs. Molecular or elemental tritium (T_2) or HT is much less readily assimilated. Approximately 0.004% of such activity inspired is absorbed, apparently after preliminary oxidation in the lungs. Negligible amounts of elemental tritium are absorbed through the skin.

It is generally assumed that ingested tritiated water is rapidly absorbed and uniformly distributed in the body fluids, with the result that the entire organism is uniformly irradiated. This may not necessarily be the case. In experiments using mice, the ingestion of low-level tritiated water causes liver damage (175). The ingestion of tritium used as a tracer in organic molecules that are metabolized in specific pathways can concentrate tritium, resulting in the possibility of localized radiation damage. For example, tritiated thymidine concentrates selectively in the DNA of cells, resulting in selective damage to cell nuclei (176). Environmental assessments of tritium must take these factors into consideration (177).

The body excretes tritium with a biological half-life of 8–14 d (10.5 d average) (178), which can be reduced significantly with forced fluid intake. For humans, the estimated maximum permissible total body burden is 37 MBq (1 mCi). The median lethal dose (LD_{50}) of tritium assimilated by the body is estimated to be 370 GBq (10 Ci). Higher doses can be tolerated with forced fluid intake to reduce the biological half-life.

Monitoring and Control. Detailed descriptions of methods used for handling and monitoring tritium at Savannah River (179,180) and the European Tritium Handling Program (181) have been published.

A widely used instrument for air monitoring is a type of ionization chamber called a Kanné chamber. Surface contamination is normally detected by means of smears, which are simply disks of filter paper wiped over the suspected surface and counted in a windowless proportional-flow counter. Uptake of tritium by personnel is most effectively monitored by urinalyses normally made by liquid scintillation counting on a routine or special basis. Environmental monitoring includes surveillance for tritium content of samples of air, rainwater, river water, and milk.

The radiological hazard of tritium to operating personnel and the general population is controlled by limiting the rates of exposure and release of material. Maximum permissible concentrations (MPC) of radionuclides were specified in 1959 by the International Commission on Radiological Protection (182). For purposes of control all tritium is assumed to be tritiated water, the most readily assimilated form. The MPC of tritium in breathing air (continuous exposure for 40 h/wk) is specified as 185 kBq/mL (5 μCi/mL) and the MPC for tritium in drinking water is set at 3.7 GBq/mL (0.1 Ci/mL) (182). The maximum permitted body burden is 37 MBq (one millicurie). Whenever bioassay indicates this value has been exceeded, the individual is withdrawn from further work with tritium until the level of tritium is reduced.

Personnel are protected in working with tritium primarily by containment of all active material. Containment devices such as process lines and storage media are normally placed in well-ventilated secondary enclosures (hoods or process rooms). The ventilating air is monitored and released through tall stacks; environmental tritium is limited to safe levels by atmospheric dilution of the stack effluent. Tritium can be efficiently removed from air streams by catalytic oxidation followed by water adsorption on a microporous solid absorbent (183) (see ABSORPTION).

Several new technologies are in the process of development at the Savannah River plant that would considerably enhance safety in handling large amounts of tritium. Metal hydride technology has been developed to store, purify, pump, and compress hydrogen isotopes. Conversion to or extraction from metal triteride would offer flexibility and size advantages compared to conventional processing methods that use gas tanks and mechanical compressors, and should considerably reduce the risk of tritium gas leaks (see HYDRIDES).

Personnel who must work in areas in which tritium contamination exceeds permitted levels are safeguarded by protective clothing, such as ventilated plastic suits. Detailed descriptions of laboratories suitable for manipulation of tritium can be found in Reference 112.

2.9. Uses. Nuclear fusion is an approach to the ever increasing global demands for energy. All nuclear fusion reactions require very high temperatures for initiation. The thermal threshold is lowest for light ions, and the nuclear reaction $D(T,n)^4He$, involving the fusion of deuterium and tritium nuclei is considered to be the most practical approach to the realization of nuclear fusion energy (qv). Whereas the technology for large-scale production of deuterium exists, the production and handling of tritium is one of the key problems in the achievement of practical nuclear fusion.

The development of a tritium fuel cycle for fusion reactors is likely to be the focus of tritium chemical research.

Tritium is widely used as a tracer in molecular biology (see RADIOACTIVE TRACERS).

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