DUAL-TEMPERATURE METHODS FOR PREPARING HEAVY WATER

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INTRODUCTION

In the 30 years since the discovery of the heavy isotope of hydrogen, deuterium, in 1931, the production of its compound with oxygen, heavy water, has grown from the preparative scale to several hundred tons per year, as a result of the development of atomic energy programmes.

Heavy water is the best neutron moderator, and its use makes it possible to work with uranium of natural isotopic composition and to decrease considerably the size of the reactor. In a number of cases the heavy water can be used simultaneously as a heat-exchange medium[1] 100–200 tons of heavy water are required for a large-scale reactor.

When estimating the demand for heavy water, it is necessary to consider not only the present demand, which arises from the use of heavy water as moderator and heat--exchange medium in nuclear reactors employing uranium as fuel, but also future requirements resulting from progress in the field of controlled thermonuclear reactions employing deuterium as fuel.

The demand for heavy water for atomic reactors in different countries depends to a great extent on the general trend of the development of the atomic energy programmes. Thus in England, with a high level of atomic energy development, heavy-water reactors are built chiefly for research purposes, so that the demand for D_2O is estimated at 100 tons per year[2,3]. Extensive plans for the construction of heavy-water reactors in Sweden have resulted in an estimated demand of 80 tons per year by 1964 increasing to 400 tons per year by 1974.[4] The demand in Western Germany has been estimated at 100 tons of D_2O per year[5]. The total demand in the Western European countries in the Organisation for European Economic Cooperation will amount to 400–500 tons of D_2O per year by 1965 and 2000–4000 tons per year by 1970.[6-8] The demand in the USA has been estimated at 1000 tons of heavy water per year[9].

The growth of the demand for heavy water for reactors depends to a great extent on the cost of D_2O. According to Harteck's calculations, the use of heavy water becomes economic at a price of 88 dollars per kg of D_2O, and at a price of 22 dollars per kg the cost of the heavy water is insignificant compared with the total cost of the reactor[9]. In the case of a recently-constructed Canadian heavy-water reactor the total cost of 55.8 million dollars included 11 million dollars for heavy water, that is, 20% of the total[10].

Progress in the field of controlled thermonuclear synthesis gives grounds for the expectation that in the near future deuterium will be used as a fuel for thermonuclear reactors. The production of heavy water will then be determined entirely by the energy requirements of a particular country, and the division of countries into rich and poor with reference to sources of energy will disappear, since the raw material, water, is almost equally available in all countries. The cost of the heavy water will not then be important, since the cost per unit of energy will be much smaller than that for coal or oil. According to Kurchatov's calculations, the calorific value of 1000 million tons of coal or oil (the estimated level of production in the USSR by 1975) is equivalent to that of 2000 tons of heavy water used in thermonuclear reactors[11]. The earth's hydrosphere contains 2×10^{14} tons of heavy water, that is the reserves are almost inexhaustible. The development of thermonuclear energy programmes will make heavy water one of the basic materials of atomic technology, instead of an auxiliary material, as it is at present.

We can thus expect, in the near future, a further growth in the production of heavy water, both to satisfy existing demands for it as a moderator in heavy-water energy reactors, and also to meet future demands for heavy water as a fuel for thermonuclear synthesis.

METHODS FOR THE PREPARATION OF HEAVY WATER

Methods of preparing heavy water have been described in a number of review articles[12-32] and in a monograph edited by Murphy[33]. The chief difficulty in the isolation of heavy water is the necessity to deal with vast quantities of raw material, exceeding the quantity of final product by a factor of several tens of thousands, because the concentration of deuterium in natural water is only 0.016 mole %. Since the difference between the properties of deuterium and protium are small, the separation factors of the various methods are small, and the production of heavy water requires a multi-stage counter current process of concentration, carried out in a cascade of multi-stage assemblies.

In principle, all the existing methods of separating isotopes can be used for concentrating heavy water. A number of these are of no industrial importance, however, because of low efficiency (diffusion, thermal diffusion, and adsorption), low separation factors (absorption and extraction), or difficulty in setting up counter current conditions (fractional crystallisation and zone melting), and only the following methods are used industrially: electrolysis of water, electrolysis of water combined with isotopic exchange between water and hydrogen, fractional distillation of water, low-temperature fractional distillation of hydrogen, and dual-temperature exchange between water and hydrogen sulphide. The first three methods were the first to be used to prepare heavy water, but in the last 10 years the last two have become more important[34].

These principal methods for preparing heavy water are normally used in combination, depending on the specific conditions employed. This makes it possible to choose the most convenient combination to give a pure product. The economics of the process are essentially determined by the initial stage of the concentration, which requires the handling of vast quantities of raw material. Calculations show that concentration to 1–2% D_2O accounts for 90% of the total cost of the complete process. The chief factors to be taken into account when selecting the most convenient method of separation are the cost per unit of the product and the possibility of organising its production on a large scale. The processes for preparing D_2O can be classified as independent or dependent on other production processes. The first group includes methods involving distillation of water and the dual-temperature exchange between water and hydrogen sulphide, since the source of deuterium is ordinary water. The second group includes all other methods, whose output is limited by the level of production of hydrogen for the synthesis of ammonia. Some data on the specific capital investment, operating cost, quantities of energy and material used, and separation factors for different methods of preparing heavy water are given in Table 1, which shows that the only methods worthy of serious consideration as far as the cost of the product is concerned are those involving dual-temperature exchange or the low-temperature fractional distillation of hydrogen. This last method, however, is limited by the supply of hydrogen, and cannot satisfy the expected demand for heavy water. According to Weiss, the world production of hydrogen (excluding the USSR) is equivalent to 2800 tons of heavy water per year, assuming 100% extraction[35]. Since all sources of hydrogen cannot be used for the economic production of deuterium and the extraction will always be less than 100%, this figure can be at least halved. Thus distillation of hydrogen can in principle yield considerable quantities of heavy water, but the applicability of the method is limited. The distillation of water has been found to be uneconomic, even under the most favourable conditions, at Wairaki (New Zealand)[37]. Fractional distillation of water and electrolysis are now widely used for the final concentration of heavy water.

The two most economic methods for the production of heavy water on the industrial scale – dual-temperature exchange and low-temperature fractional distillation – were first carried out in the USSR[11,43]. Slightly later, dual-temperature exchange was used in the USA[40], and low-temperature fractional distillation was used in France[44,45] and Western Germany[46,47]. Plants in operation and the chief projects for heavy-water production are listed in another review by the present authors[30]; the volume of heavy-water production in various countries has been reported in a number of publications[34,48,49].

MAIN FEATURES OF THE DUAL-TEMPERATURE METHOD

In a multi-stage counter current process for concentrating isotopes, it is necessary at each stage to transfer the material to be concentrated from one stream to another, that is, to transfer the isotope in which we are interested to another phase which can set up a counter current to the main current of raw material or intermediate product containing the isotope. A large proportion of the total energy necessary for the separation is used up in the "stream transfer". In some cases, the transfer is achieved by evaporation (fractional distillation), and in others by electrochemical or chemical decomposition (electrolysis or chemical methods of isotopic exchange). Harteck and Suess[50] have proposed a method for stream transfer which is based on the use of the temperature dependence of the equilibrium constant for isotopic exchange and involves the addition to the assembly of a supplementary column working at a temperature different from that of the main one. This method has been called the dual-temperature method. All other methods of carrying out isotopic exchange may be termed single-temperature methods. The dual-temperature method was first used for the extraction of deuterium, and it may be carried out in two ways.

1. A cascade of separate pairs of one-stage assemblies is set up, one of which operates at low temperatures and the other at high temperatures (Fig.1). This was the method first suggested by Harteck and Suess[12,50]. Although the dimensions of the stages in the cascade are inversely proportional to the concentrations, this version of the dual-temperature process involves the repeated heating and cooling of the streams and requires large amounts of energy.

2. Two multi-stage columns are connected, one working at low temperature (cold column) and the other at high temperature (hot column). This version of the dual-temperature method was proposed by Geib[12], and Spevack[51], and

TABLE 1. Comparison of different methods of preparing heavy water.

Method	Calculated data				Technical data				Reference
	separation factor	% extraction of deuterium	moles of water treated per mole of product	power required per kg	location of plant	capital expenditure, dollars per kg per year	operating costs, dollars per kg	cost or selling price, dollars per kg	
Electrolysis of water, combined with chemical exchange	7;2.8	60	20 000	70 000 kWh	Trail (Canada) Rjukan (Norway)	500	60	132* 182*	15,24,36 37
Distillation of water	1.04	4	200 000	180 tons of steam at 1,5 atm	Morgantown, Childersburg, Newport (USA) Wairaki (New Zealand)	1100**		390 110—120	15,24,36 37
Distillation of hydrogen	1.4	90	35 000	5000 kWh	Etter (USA), Frankfurt-am-Main project (Western Germany)	375 400	35	73* 80	15,24 38,39
Dual-temperature exchange water–hydrogen water–hydrogen sulphide	1.22 1.12	30 18	40 000 20 000	5000 kWh 8 tons of steam	Savannah River project (USA)	362	30	62	40–42

* Including profit.

** According to Benedict's calculations this figure can be halved [24].

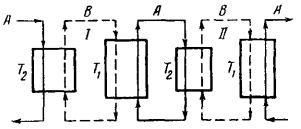


Fig. 1. Dual-temperature process in a cascade of one-stage assemblies. I) First pair of single-stage high-and low-temperature assemblies; II) second pair of single-stage high-and low-temperature assemblies.

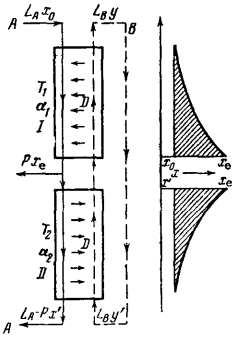


Fig. 2. Dual-temperature process in a cascade of multi-stage columns. I) Cold column; II) hot column.

is illustrated in Fig.2. Column I is the cold column with temperature T_1, at which the separation coefficient is α_1, and column II is the hot column with temperature T_2, at which the separation coefficient is α_2. L_A mole h^{-1} of substance A (for example, water), with deuterium concentration x_0, enters column I. L_B mole h^{-1} of substance B (for example, hydrogen sulphide) circulates through the closed cycle. Isotopic exchange takes place between A and B leading to an increase in the concentration of deuterium in A, the cold column operating as a normal counter current enrichment column in which the deuterium is concentrated in the lower section, in the stream of substance A. This enrichment can in principle be increased to any desired value by increasing the height of column I, if the deuterium concentration of the current B entering the lower part of column I is equal to the deuterium concentration in current A in this part of the column. These concentrations are made equal in the dual-temperature method by means of the counter current stripping column II, through which currents A and B pass in opposite directions at as high a temperature as possible. Deuterium moves from current B to current A in the cold column I, and it moves from current A to current B in the hot column II. Current B extracts deuterium completely from current A in column II only if the separation coefficient is equal to 1 or if the stripping column is infinitely high: in this case the enrichment column I gives complete transfer. Since this extreme case is not attained in practice, the dual-temperature method gives a lower degree of enrichment than a column giving complete transfer between the phases, but the high consumption of energy required for complete transfer is no longer necessary. A much smaller quantity of energy is required to heat currents A and B to the temperature of the hot column and cool them to the temperature of the cold column. This energy can be reduced to a minimum by recovering the heat from the counter currents, and the only energy which has to be supplied is that equivalent to the non-recoverable fraction of the heat stream and the heat lost through the insulation.

By definition, the separation coefficient is

$$\alpha = \frac{x_e}{1-x_e}\frac{1-y_e}{y_e}, \tag{1}$$

where x_e and y_e are the equilibrium concentrations of deuterium in A and B respectively. At low concentrations

$$\alpha = x_e/y_e. \tag{2}$$

If the number of stages in the two columns is high, the maximum transfer occurs at the start of the process and it can be assumed that at the ends of the columns we have equilibrium between A and B at concentrations x_0 and y', and x' and y'. Thus $y' = x_0/\alpha_1$ (cold column) and $y' = x'/\alpha_2$ (hot column), from which

$$x' = x_0\alpha_2/\alpha_1. \tag{3}$$

Since $\alpha_1 > \alpha_2$, $x' < x_0$ and deuterium accumulates in the system. The greatest concentration will evidently be reached in the lower part of the cold column I and in the upper part of the hot column II, and P mole h^{-1} of substance A with deuterium concentration x_e are removed from these points. Eqn.(3) shows that the concentration is more readily achieved the greater the difference between the separation coefficients.

It is possible to extract $(x_0 - x')$ moles of deuterium from each mole of the stream of substance A passing through the system of columns. If we take the value of x' from Eqn.(3), it is possible to extract $x_0(1 - \alpha_2/\alpha_1)$ moles of deuterium. The factor $(1 - \alpha_2/\alpha_1)$ is the maximum possible degree of extration:

$$\varphi_{max} = \frac{\alpha_1-\alpha_2}{\alpha_1}. \tag{4}$$

The actual degree of extraction φ is a fraction of the maximum φ_{max}. The degree of extraction of deuterium can be increased by increasing the temperature difference between the hot and cold columns. All the extracted deuterium is taken from the stream of substance A.

The process taking place in the dual-temperature system may be represented by plotting x vs. y: the equation for the equilibrium line of the cold column is

$$x = \alpha_1 y, \tag{5}$$

and that for the hot column is

$$x = \alpha_2 y. \tag{6}$$

The equations for the actual concentrations may be derived from the material balance. For the cold column we have

$$L_A(x - x_0) = L_B(y - y'). \tag{7}$$

Dividing by L_A and denoting L_B/L_A by λ, we obtain

$$x = \lambda y - \lambda y' + x_0. \tag{8}$$

For the hot column we have

$$L_B/(L_A - P) = \lambda',$$

and

$$x = \lambda' y - \lambda' y' + x'. \qquad (9)$$

In the dual-temperature process, we have two equilibrium-concentration lines and two operating-concentration lines (Fig.3). Since the deuterium concentrations x_e (A) and y_e (B) in the currents are the same for both columns, the operating lines should intersect at S. If no product is removed, the two operating lines merge into a single line.

The possibility of changing the position of the operating lines is restricted by the space between the two equilibrium lines. Since the position of the operating lines is determined by the stream ratios λ and λ', the actual change in the stream ratio is also restricted. We have

$$\alpha_1 > \lambda \geqslant \lambda' > \alpha_2, \qquad (10)^*$$

that is in the dual-temperature process it is necessary to maintain a definite molar stream ratio.

The physical significance of this restriction is that the dual-temperature counter current process of concentration requires that a sufficiently high fraction of the deuterium which enters stream A from the stream B in the cold column *I* is transferred back to stream B in the hot column *II*. Since the separation factor at temperature T_2 is much greater than unity, and since the deuterium concentration in stream A when equilibrium has been reached exceeds that in stream B, the transfer of deuterium to stream B is greatly facilitated by a decrease in stream A, that is by an increase in the stream ratio λ to values of λ greater than α_2. The stream ratio λ must not be made greater than α_1, however, since this leads to breakdown of the process of concentration in the cold column *I*. At a stream ratio less than α_2 or greater than α_1, it is possible to obtain only a very slight enrichment, which cannot be increased significantly by increasing the height of the column[52]. The influence of the stream ratio on the degree of enrichment is shown in Fig.4.

The product may be removed in two ways: in the first method (Fig.2) the product is removed and is not returned to the system; in the second method an equal quantity, P mole h^{-1}, of stream A, with concentration x'_e less than x_e, is supplied to column II. The dual-temperature cascade process of concentration (Fig.5) consists essentially, of removal by the second method in the first two stages and removal by the first method in the third stage. It is important in this process to remove the product by the second method from both streams simultaneously (Fig.6). This avoids changing the stream ratio as a result of removal from only one stream, decreases slightly the time taken for the steady state to be reached in the cascade of dual-temperature columns, and reduces the heat-exchange apparatus in the subsequent stages. A number of possible methods of carrying out the dual-temperature process have been described by Roth[45] and in some French patents[53,54].

The principle of the dual-temperature method for preparing heavy water has been described in a number of papers[12,19-25,30,31,35,55-57]. The details of the dual-temperature separation have been examined by Bier[52,58], Rozen[59,60], and others[57,61,62]. Approximate calculations[59-61] for the dual-temperature process suggest that the separation coefficient can be taken as $\sim\sqrt{\alpha_1/\alpha_2}$. The remaining calculations can then be carried out as for the usual cascade-concentration schemes.

* The restriction in the stream ratio [Eqn.(10)] does not apply to operation according to the scheme illustrated in Fig.1.

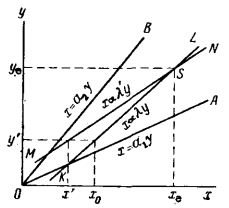


Fig. 3. Plot of x vs. y for the dual-temperature process. *OA* is the equilibrium line of the cold column, *OB* the equilibrium line of the hot column, *KL* the operating line of the cold column, and *MN* the operating line of the hot column.

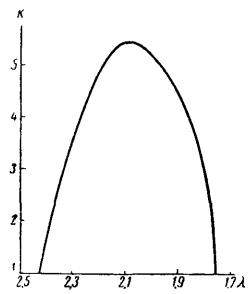


Fig. 4. Dependence of the enrichment (K) on the stream ratio (λ), from Savannah River data.

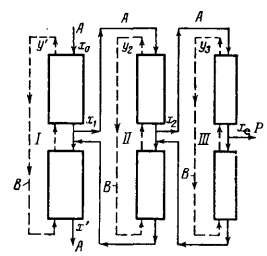


Fig. 5. Dual-temperature columns connected in a cascade with removal of product from stream A. I) First stage; II) second stage; III) third stage; P) removal of product.

When choosing operating temperatures, allowance must be made for the fact that although increase in temperature accelerates the isotopic exchange, the temperature coefficient of the equilibrium constant (or of the separation factor) decreases with increase in temperature, so that to obtain the same degree of extraction of deuterium it is necessary to extend the interval between the operating temperatures of the hot and cold columns. Low temperatures, on the other hand, reduce the activity of the catalysts which

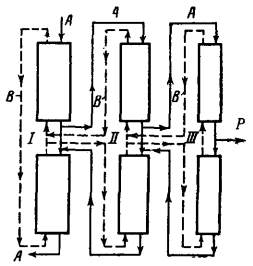


Fig. 6. Dual-temperature columns connected in a cascade with removal of product from both streams. I) First stage; II) second stage; III) third stage; P) removal of product.

are often used to accelerate the isotopic exchange. For water-cooling to be possible, the lower temperature should not be less than 25–30°. The temperature of the hot column should not be too high, since this increases the consumption of high-pressure steam. In the choice of operating temperatures allowance should be made for all the characteristics of the substances in the separation system. The pressure should be as high as possible for a given system of substances, used for deuterium exchange, in order to decrease the volume of gas to be pumped over, to increase the efficiency, and to reduce the total volume of the apparatus. The use of very high pressure, however, introduces technical difficulties and leads to high capital expenditure.

The plot of x vs. y for the dual-temperature process (Fig.3) shows that by changing the stream ratio we can vary the number of theoretical separation stages of the hot and cold columns to obtain the same degree of deuterium enrichment. In the choice of the number of stages of hot and cold columns n_h and n_c account should be taken of the height of the equivalent theoretical stage of hot and cold columns h_h and h_c, so that the total height (and volume) of the columns shall be a minimum, i.e. $(n_h h_h + n_c h_c)$ shall have a minimum value.

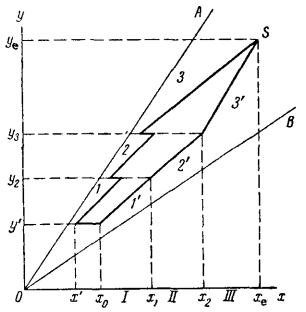


Fig. 7. Plot of x vs. y for the cascade of dual-temperature columns illustrated in Fig. 5. [60] OA is the equilibrium line of the cold column, OB the equilibrium line of the hot column, 1 and 1' are the operating lines of the first stage, 2 and 2' the operating lines of the second stage, and 3 and 3' the operating lines of the third stage.

The division of the total enrichment throughout the stages of the cascade must be made in such a way that the number of stages of the cascade does not exceed 2–4, since a higher number gives no advantage in reducing the total volume of the apparatus. The plot of x vs. y for the cascade in Fig.5 is given in Fig.7. [60]

DEUTERIUM-EXCHANGE SYSTEMS

The choice of substances A and B is influenced by the following considerations. The separation factor should be as high as possible, and should change significantly with change in temperature. The substances should be readily separable from one another, should be chemically stable, and should not be decomposed by repeated circulation under changing temperature conditions. They should contain the smallest possible "ballast" of non-exchanging atoms and should have the smallest possible corrosive action on the material of the apparatus. It is desirable that the isotopic exchange between the substances should take place sufficiently rapidly to make the use of a catalyst unnecessary.

An approximate calculation of unknown separation factors for many pairs of substances can be carried out by a method developed by Varshavskii and Vaisberg [63–65]. Data for the separation factors, their temperature dependence, and the degrees of extraction for the most promising systems in the range 20°–100° are given in Table 2.

TABLE 2. Comparison of different systems of deuterium-exchange substances.

System	α_{20}/α_{100}	$\sqrt{\alpha_{20}/\alpha_{100}}$	φ_{max}	System	α_{20}/α_{100}	$\sqrt{\alpha_{20}/\alpha_{100}}$	φ_{max}
H_2–NH_3	1.51	1.23	0.34	H_2O–AsH_3	1.20	1.09	0.13
H_2–H_2O	1.48	1.22	0.32	H_2O–H_2Se	1.27	1.12	0.21
H_2O–PH_3	1.14	1.07	0.12	H_2O–HBr	1.33	1.15	0.25
H_2O–H_2S	1.26	1.12	0.18	H_2O–HI	1.41	1.19	0.29
H_2O–HCl	1.27	1.13	0.21				

It is usually convenient to choose water as one of the substances, since it provides an almost inexhaustible source of deuterium and it is readily available.

The highest extraction of deuterium is obtained with the water–hydrogen, water–hydrogen halide, and ammonia–hydrogen systems. For practical reasons, however, it is most convenient to use the water–hydrogen sulphide system, which is widely employed. The principal systems which have been proposed for use in the dual-temperature process are examined below.

Water–Hydrogen

This system was the first to be used for the dual-temperature process. The temperature dependence of the equilibrium constant (which in this case is equal to the separation factor) for the reaction

$$H_2O_{vap} + HD \rightleftarrows HDO_{vap} + H_2 \qquad (I)$$

is given in Table 3.[19]

TABLE 3. Temperature dependence of the separation factor for exchange reaction (I).

Temp., °C	50	60	70	100	200	300	600	700
$\alpha(K)$	3.05	2.92	2.83	2.56	1.98	1.69	1.30	1.24

It is possible to obtain a maximum degree of extraction, $\varphi_{max} = 0.49$, by using operating temperatures of 100° and 600°. The scheme proposed initially by Harteck and Suess is illustrated in Fig.1. An experimental assembly was built at Leuna in 1943-1944 for the initial enrichment of water to 1% D_2O. The system consisted of 10 pairs of cold and hot contact assemblies, packed with a catalyst, and was intended to operate at 100° and 600°, [12,19,36] but it was destroyed during an air raid. The production of heavy water by this scheme requires the expenditure of large quantities of heat and energy, since repeated evaporation and condensation are necessary; in each apparatus there is a single flow of hydrogen and steam, and the cold and hot stages work at different pressures.

Cerrai and coworkers [19,24,66] developed an improved version of the dual-temperature process with water and hydrogen (Fig.8). The water enters the enrichment column *I*, consisting of alternating layers of catalyst and bubble-cap trays, analogous to the Trail column [15] and then passes to a stripping column *II* consisting of bubble-cap trays only, after which it is rejected. The temperature of columns *I* and *II* is fairly low (80°). A mixture of water vapour and hydrogen flows in the opposite direction to that of the water and passes from the upper part of column *I* to column *III*, which is filled with catalyst and operates at a high temperature (600°). The deuterium concentration in the water increases in column *I* as a result of the catalysed isotopic exchange between water vapour and hydrogen at low temperatures and the phase exchange between water and water vapour. The product can be removed from the lower part of column *I*. In column *II*, the phase exchange between water and water vapour leads to a decrease in the deuterium concentration in the water, since the water vapour entering the lower part of column *II* is poorer in deuterium as a result of the catalytic isotopic exchange with hydrogen at high temperature in column *III*. This arrangement reduces slightly the quantity of heat used, but this is still fairly high. Each stage cannot give an enrichment greater than α_1/α_2.

The scheme illustrated in Fig.2 is advantageous from considerations of capital and operating costs. Reaction (I) takes place in the gaseous phase, however, so that it is impossible to set up continuous counter current conditions. To carry out the exchange reaction in a column apparatus it is necessary to make use of the exchange between hydrogen and liquid water,

$$H_2O_{liq} + HD_{gas} \rightleftarrows HDO_{liq} + H_{2gas}, \qquad (II)$$

for which the equilibrium constants are given in Table 4.[19]

The difficulty in carrying out reaction (II) lies in the lack of a suitable catalyst, since liquid water rapidly decreases the activity of ordinary catalysts. It is convenient to use as catalysts compounds which are soluble in water or which can be dispersed in water, as in the scheme developed by Becker (Fig.9)[19]: here the water circulates in a closed circuit and the hydrogen is the source of deuterium, so that the efficiency of the method is limited by the quantity of available hydrogen. This restriction can be eliminated by introducing another supplementary column *III* for exchange between water and hydrogen at 250°, but this technique is not economic.

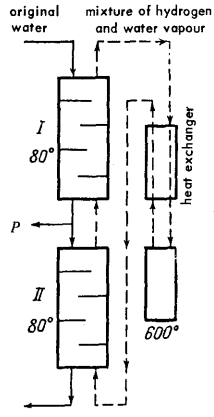


Fig. 8. Cerrai's scheme for dual-temperature exchange between water and hydrogen. I) Cold column for phase and catalytic isotopic exchange; II) cold column for phase exchange; III) hot column for catalytic isotopic exchange; *P*) removal of product.

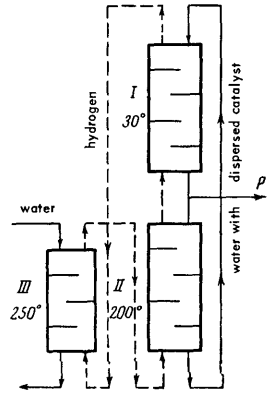


Fig. 9. Dual-temperature isotopic exchange between water and hydrogen with a dispersed catalyst. I) Cold column; II) hot column; III) regenerative hot column; *P*) removal of product.

TABLE 4. Temperature dependence of the separation factor of exchange reaction (II).

Temp., °C	0	25	50	75	100	125
$\alpha(K)$	4.69	3.87	3.37	2.99	2.69	2.47

To increase the degree of extraction of deuterium, Becker suggested reducing the temperature of the cold column from 80° to 30°–40°, while leaving the temperature of the hot column at 200°:[57] in this case $\varphi_{max} = 0.44$. To reduce the volume of gas to be pumped over and increase the efficiency, an operating pressure of 200 atm was chosen. The use of hydrogen as raw material (without the supplementary column *III*) gives material streams per unit of product approximately α times smaller, since the hydrogen leaving column *III* after exchange with water has a lower deuterium content than natural hydrogen (the equilibrium constant favours increase in the deuterium concentration in the water, not in the hydrogen). It should be borne in mind, however, that ordinary technical hydrogen has a slightly lower deuterium content (by 10–20%) than natural hydrogen.

TABLE 5. Temperature dependence of the separation factor for exchange between ammonia and hydrogen.

Temp., °C	−50	0	25	100
α	6	4.56	3.88	2.73

Becker made a detailed study of the catalyst (consisting of platinum on a support of wood charcoal dispersed in water) which he proposed for the liquid-phase exchange [19,57,67]. The platinum content varies over wide limits but is normally 7 g per litre of water, dispersed on a tenfold excess of wood charcoal. The experiments were carried out with sieve plates under conditions similar to those used in industrial production. According to Becker's calculations, the specific volume of the sieve column should be 23 m^3 ton^{-1} D_2O and the platinum consumption 16 kg ton^{-1} D_2O per year. The energy required for heating was estimated as 0.94×10^6 kcal kg^{-1} D_2O for a heat-exchanger efficiency of 75%, and the energy required for mixing was estimated as 200 kWh kg^{-1} D_2O. A number of French workers have also studied the catalyst for liquid-phase exchange [45,68].

The firm of Degussa (Western Germany) recently decided to construct an experimental apparatus to prepare ~ 1 ton of heavy water per year by dual-temperature exchange between water and hydrogen with dispersed platinum as catalyst [69-76].

Ammonia–Hydrogen

The possibility of using the isotopic exchange between ammonia and hydrogen for preparing heavy water by the dual-temperature method was examined in the USA in 1942 [33a]. The separation coefficients of this system have a marked temperature dependence (Table 5).[77] When the operating temperatures are 25° and 100°, $\varphi_{max} = 0.30$, that is, the system has a high degree of extraction at a comparatively small difference between the temperature of the two columns. The scheme is illustrated in Fig.10. The supplementary column *III* is not essential, since the process is then complicated by the need to extract the ammonia from the drainage water, but it eliminates the dependence on a large-scale source of hydrogen. The study of this system was discontinued in 1943 because of the absence of a suitable catalyst for the isotopic exchange.

In 1950 it was found that potassamide is a convenient catalyst for the isotopic exchange between ammonia and hydrogen. This exchange was studied in detail by Bigeleisen et al.[78,79]. At a potassamide concentration approximately 10^{-3} M, the rate of exchange is controlled by chemical factors and depends on the concentration of the amide ion. At higher concentrations, approximately 10^{-1} M, the rate of exchange is independent of the concentration and is determined by diffusion. The slowest diffusion process is apparently the transfer of hydrogen across the layer of liquid at the liquid–gas interface. When the gas was bubbled through the liquid in an apparatus with bubble-cap trays (plates), the Murphree plate efficiency amounted to 0.5–9%. French workers [45] who studied the kinetics of exchange in packed columns and on sieve plates obtained higher efficiency values; they also showed that potassamide is highly sensitive to the presence of moisture and oxygen.

Using data on the exchange equilibrium between ammonia and hydrogen, the marked temperature dependence of the separation factor, and the catalytic properties of potassamide, the English firm constructors John Brown Ltd. developed a project for preparing 27 tons of heavy water per year. The initial process of concentration to 0.4% D_2O was carried out by a combination of single-temperature and dual-temperature exchange between hydrogen and ammonia [80-84]. The initial enrichment is illustrated in Fig.11. In column *I* single-temperature exchange takes place between the hydrogen of a nitrogen–hydrogen mixture and ammonia containing potassamide catalyst, and the deuterium content of the ammonia is increased by a factor of 5. In columns *II* and *III*, working at -40° and 100°, dual-temperature exchange takes place between the ammonia and hydrogen, and the deuterium content of the ammonia leaving the cold column *II* is increased by a factor of 23. The impoverished ammonia passes from the hot column *III* to column *I* and then to cold column *II*. The operating pressure in the system is 250 atm. The enriched ammonia is removed and passed to a distillation cascade of 7 columns. The distillation of the ammonia increases the deuterium concentration to 75%. The final process of concentration to 99.8% is carried out in a Kuhn column irrigated with water which is enriched in deuterium by exchange with the ammonia from the distillation cascade. Naturally, this assembly can only be set up in a nitrogen fetiliser plant. This would reduce capital expenditure, since standard equipment is used. An advantage of the method is that it is possible to use the nitrogen–hydrogen mixture without the expensive purification which is necessary when low-temperature distillation is used. A significant disadvantage is the large volume of apparatus working under high pressure. According to the project data, the method can produce heavy water at a cost of 47.6 dollars per kg [81-84].

A study has been made in the USA of the possibility of

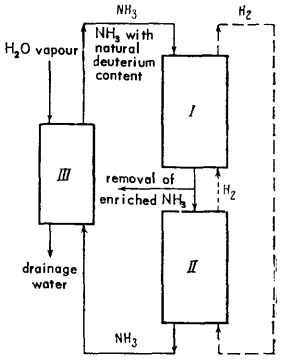


Fig. 10. Dual-temperature exchange in the ammonia – hydrogen system. I) Cold column; II) hot column; III) regenerative colomn.

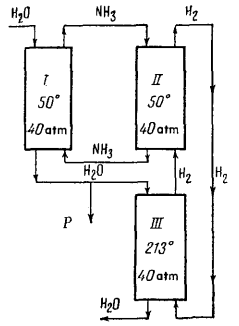


Fig. 12. Dual-temperature process for the water – – ammonia – hydrogen system. I) Cold column for exchange between water and ammonia; II) cold column for exchange between hydrogen and ammonia; III) hot column for exchange between water and hydrogen; P) removal of product.

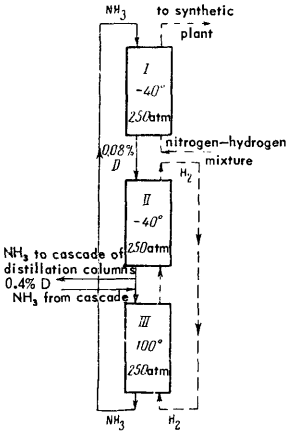


Fig. 11. Preparation of heavy water by a combination of single-and dual-temperature exchange between hydrogen and ammonia. I) Cold colum for single-temperature exchange; II) cold column for dual-temperature exchange; III) hot column for dual-temperature exchange.

using a three-component water–ammonia–hydrogen system, which eliminates the dependence on a large-scale source of hydrogen [33b]. The process is illustrated in Fig.12. In column *I* the water is enriched in deuterium by exchange with deuterium-rich ammonia; the product is removed along the line *P*, and the greater part of the water stream enters column *III*, in which hydrogen extracts deuterium from the water at high temperature. The hydrogen leaving column *III* undergoes exchange with ammonia in the cold column *II*. This is thus a modification of the water–-hydrogen exchange process, rather than a modification of the ammonia-hydrogen exchange process. All the extracted deuterium comes from the water. The presence of the ammonia does not alter the degree of extraction of deuterium, but makes it possible to replace the difficult counter current exchange between water and hydrogen at low temperatures by the easier exchange between ammonia and hydrogen. The capital expenditure required by this scheme, however, makes it uneconomic.

Water–Hydrogen Sulphide

The chief advantage of the water–hydrogen sulphide system is the high rate of exchange, which makes it possible to use ordinary columns without a catalyst. The high rate of exchange is due to the ionic mechanism of the exchange, a consequence of the ionic dissociation of hydrogen sulphide in water. By increasing the pressure in the system, it is possible to reduce the concentration of water vapour in the hot gas, to decrease the volume of the columns, and to lower the energy required for transporting the gas. The upper pressure limit is 18–20 atm, however, since higher pressure greatly increases the solubility of hydrogen sulphide in water and its condensation in the cold column can occur at 23 atm. Harteck has suggested using exchange between water and liquid hydrogen sulphide [35], but this is inconvenient since the specific gravity of liquid hydrogen sulphide is close to unity, so that it is difficult to set up counter current conditions in the liquid–liquid system. It is possible, moreover, that the rate of exchange between water and liquid hydrogen sulphide is much smaller than that between water and gaseous hydrogen sulphide.

The separation factor for the hydrogen isotopes in the exchange reaction

$$H_2O_{liq} + HDS_{gas} \rightleftarrows HDO_{liq} + H_2S_{gas} \qquad (III)$$

has been determined by a number of workers [19,45, 51,85–88]. The value is usually found by a static method: when equilibrium has been reached, the water and hydrogen sulphides are separated from one another at the equilibrium temperature and analysed for deuterium.

When exchange is carried out under ordinary conditions, the main reaction (III) is complicated by other exchange processes, due to the solubility of hydrogen sulphide in water and the presence of water vapour in the hydrogen sulphide:

$$H_2O_{gas} + HDS_{gas} \rightleftarrows HDO_{gas} + H_2S_{gas}, \quad (IV)$$

$$H_2S_{soln} + HDS_{gas} \rightleftarrows HDS_{soln} + H_2S_{gas}, \quad (V)$$

$$H_2O_{liq} + HDO_{gas} \rightleftarrows HDO_{liq} + H_2O_{gas}. \quad (VI)$$

The separation factor for reaction (IV) can be calculated from the formula proposed by Bigeleisen[86].

$$\alpha = 1.051 e^{\frac{218 \pm 2}{T}}. \quad (11)$$

The applicability of the Bigeleisen formula was confirmed by Gemmell, MacClair and Carrick[79]. To calculate α_3 we will use the following relationship between α_3 and α_4:

$$\alpha_{(3)} = \alpha_{(4)}/f. \quad (12)$$

The relative volatility f is

$$f = \frac{HDO_{gas} H_2O_{liq}}{H_2O_{gas} HDO_{liq}} \quad (13)$$

Eqn.(12) can be used to calculate the separation factors for the hydrogen isotopes in the exchange between gaseous hydrogen sulphide and liquid water at different temperatures.

The separation factor values obtained by various workers are given in Table 6. The temperature dependence of the separation factor for the exchange between water and hydrogen sulphide is much less marked than that between water and hydrogen, so that for operating temperatures of 20° and 100°, $\varphi_{max} = 0.18$, which is approximately half the value for exchange between water and hydrogen.

Spevack[51] and Weiss[35] suggested using the effective separation factors β for technological calculations because of the solubility of gaseous hydrogen sulphide in water and the presence of water in the hydrogen sulphide. Spevack[51] suggested determining β from the formula

$$\beta = \frac{(1+H)(S+\alpha_{(4)})}{f(1+S)(1+\alpha_{(4)})}, \quad (14)$$

where H is the moisture content of the gas phase in moles of H_2O per mole of H_2S, S the solubility of hydrogen sulphide in water in moles of H_2S per mole of H_2O, and f the relative volatility given by Eqn.(13).

Values of the effective separation factors at 18 atm are given in Table 7.[35] In the calculation of the dual-temperature process from a plot of x vs. y it is convenient to use the values of β_1 and β_2.

The kinetics of the isotopic exchange between water and hydrogen sulphide have been studied by French workers[45], who showed that the rate is independent of the concentration of dissolved hydrogen sulphide when 50% of the equilibrium concentration has been reached. Their study of the corrosion of the materials used in the apparatus by hydrogen sulphide is of particular interest[45].

Weiss has given a detailed discussion of the optimum conditions for the dual-temperature process with the water–hydrogen sulphide system[35]. He suggests keeping the temperature of the cold column at 30° in order to prevent precipitation of solid hydrogen sulphide hydrate, $H_2S.5H_2O$, and allow for the fact that the temperature of the coolant water in the summer months is 20°. He suggests that the temperature of the hot column should be 120°, which is a compromise between reduction of the heat consumption and increase in the degree of extraction of deuterium. Weiss also discusses the choice of optimum gas and liquid streams, number of stages, and division of the total enrichment among the stages of the cascade. An electronic computer has been used in England to find the optimum conditions for the exchange between water and hydrogen sulphide, and analogous results were obtained: optimum temperatures are 30° and 120°–130° and optimum pressure 20 atm.[89]

The chief disadvantage of the water–hydrogen sulphide system is the extensive corrosion of constructional materials by hydrogen sulphide, necessitating expensive stainless-steel apparatus. The dual-temperature exchange between water and hydrogen sulphide was first studied by Geib in Leuna during the second world war[12,19,90]. About the same time, a study of this system was begun in the USA[15,51], but the method was not then established on an industrial scale because of the expected extensive corrosion of the constructional materials.

The dual-temperature exchange between water and hydrogen sulphide was first carried out on an industrial scale in the Soviet Union. A large-scale industrial plant was constructed in the USSR in 1946–49, and this is still operating successfully. Somewhat later the dual-temperature exchange between water and hydrogen sulphide was also used in the USA. During 1951–1953 the firm of Dupont, under contract to the AEC, constructed two large-scale plants for the production of heavy water, in Dana (Indiana) and on the Savannah River (South Carolina). The total productive capacity of the two plants is ~ 800 tons of heavy water per year[57,91]. The construction of the Dana

TABLE 6. Temperature dependence of the separation factor for exchange between water and hydrogen sulphide.

Temperature, °C	0	5	10	25	50	100	150	Reference
Separation factor				2.37				85
		2.52	2.48	2.34		1.92		19,24,50
	2.55			2.35	2.17	1.95	1.80	51
				2.35				35,88
	2.52		**2.39**	2.26	2.09	1.86	1.71	45

TABLE 7. Effective separation factors for exchange between water and hydrogen sulphide at 18 atm.

t°C	$\alpha_{(4)}$	$\alpha_{(3)}$	$\frac{P_{H_2O}}{P_{HDO}}$	H	S	β	t°C	$\alpha_{(4)}$	$\alpha_{(3)}$	$\frac{P_{H_2O}}{P_{HDO}}$	H	S	β
10	2.27	2.47	0.92	0.001	0.045	2.40	75	1.97	2.05	0.96	0.027	0.014	1.98
20	2.21	2.38	0.93	0.002	0.036	2.33	100	1.88	1.94	0.97	0.074	0.010	1.81
30	2.16	2.31	0.93	0.003	0.030	2.27	120	1.83	1.86	0.98	0.144	0.008	1.68
50	2.06	2.18	0.95	0.009	0.020	2.13	140	1.78	1.80	0.99	0.280	0.007	1.53

plant cost 100 million dollars, and that of the Savannah River plant 164 million dollars[40,57,92,93]. These two plants produced such a large quantity of heavy water that at the beginning of 1957 the AEC decided to close temporarily the Dana plant[94-98]. The Dana plant was chosen since the equipment in it was made of less corrosion-resistant material and the cost of the heavy water produced there was higher than that in the Savannah River plant. Later, the Dana plant was transferred to the Chemical Corps of the US Army for the production of a new chemical product[99,100] The Savannah River plant is still operating and its maximum productive capacity is 450 tons of D_2O per year[40].

Dual-temperature exchange between water and hydrogen sulphide is used in the Savannah River plant for the initial process of concentration from the natural level to 15% D_2O. According to recent reports, the initial process of concentration in this plant is carried out by a two-stage cascade of dual-temperature columns. The operating temperatures

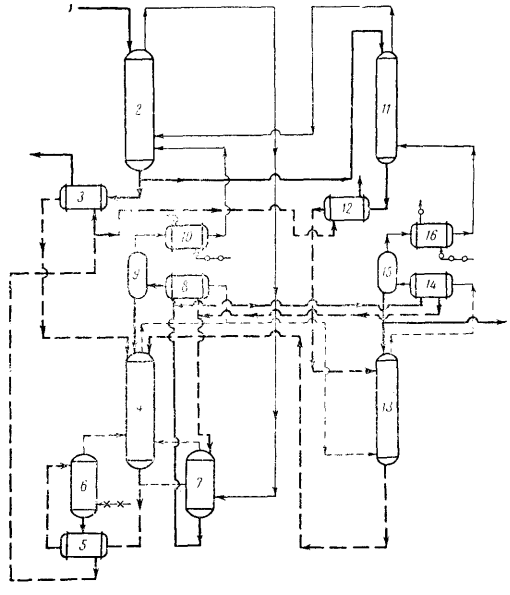


Fig. 13. Preparation of heavy water by dual-temperature exchange between water and hydrogen sulphide in the Savannah River plant (USA). 1) Feed water after purification; 2) cold column of first stage; 3) shell-and-tube liquid – liquid heat exchanger; 4) hot column of first stage 5) shell-and-tube liquid – liquid heat exchanger; 6) 2 m packed column for the reduction of hydrogen sulphide content to one millionth; 7) direct mixing humidifier (heat exchanger); 8) gas – liquid heat exchanger; 9) separator; 10) additional gas – liquid heat exchanger; 11) cold column of second stage; 12) shell-and-tube liquid – liquid heat exchanger; 13) hot column of second stage; 14) gas – liquid heat exchanger; 15) separator; 16) additional gas – liquid heat exchanger. Thick line – cold process water; thick broken line – hot process water; thin line – cold circulating hydrogen sulphide; thin broken line – hot circulating hydrogen sulphide; –o–o coolant water; –×–×– -heating steam.

are 30° and 120–130°, the pressure in the system is 17 atm, and the molar ratio of the hydrogen sulphide and water streams is 2.1 : 1. The initial process of concentration is illustrated in Fig. 13. One quarter of the stream of water and hydrogen sulphide from the first stage is passed to the second stage. The product is removed from the water and hydrogen sulphide streams simultaneously, and this minimises the heat-exchange apparatus required in the second stage of the cascade. The arrangement of the streams in the initial process of concentration ensures the most complete use of the heat of the streams of hydrogen sulphide and the water by direct heat exchange in the humidifier 7 and indirect heat-exchange in the shell-and-tube heat-exchangers. Live steam is blown through the outlet water to reduce the hydrogen sulphide content to one millionth.

The exchange assembly consists of a 30 m high column with bubble-cap trays; the diameter of the first stage is 3.3–3.6 m, and that of the second stage 2 m. A combined system in which the columns are connected in a cascade is used, and the initial concentration section is broken down into separate units, each consisting of two columns [a cold and hot column in the first stage and four columns (two cold and two hot) in the second stage]. This combined system facilitates servicing and repairs and makes it possible to shut down the separate columns[101,102].

The two-stage cascade for the initial process of concentration is used in the Savannah River plant, rather than the five-stage cascade as in the Dana plant, in an attempt to simplify the process and reduce the number of control points. The experience of seven years' operation has shown that the process of concentration is not greatly affected by variations in the stream ratio within +1%.

The corrosion problem was solved by using ordinary steel clad with stainless steel. The possibility of adding corrosion inhibitors, (in particular amines or ammonia), to the feed water has not yet been fully studied.

The following are the requirements for the initial process of concentration, per kg of heavy water: 40 tons of feed water, 150 tons of circulating hydrogen sulphide, 125 tons of coolant water, 6 tons of heating steam at 18.5 atm, and 630 kWh of electrical energy. The degree of extraction of deuterium from the feed water is ~ 18%.

Further concentration to 90–98% D_2O is carried out by fractional distillation in vacuo in two cascades, each consisting of six columns with bubble-cap trays. The final concentration to 99.8% is carried out in an electrolytic assembly consisting of 150 cylindrical baths. The capital expenditure on the initial concentration was 114 million dollars, that on the distillation assembly 2.5 million dollars, and that on the electrolytic assembly 1.5 million dollars[40,93]. The investment per unit of product is 362 dollars per year per kg of D_2O and the operating cost is 30 dollars per kg of D_2O.[93,103].

Plants using the dual-temperature water–hydrogen sulphide system have enabled the USA not only to satisfy all her internal demand for heavy water, but also to export in at a price of 62 dollars per kg. Up to the end of 1958 ~ 400 tons of heavy water had been sold to various countries, including England, France, India, etc.[104,105]. As a result of fluctuations in the demand for heavy water, the Savannah River plant decreased production of D_2O in October 1958 by two thirds[106]. To increase the demand, the US Atomic Energy Commission offered to lend heavy water at 4% per annum[47-49]. India was the first country to accept and borrowed 15 tons[107].

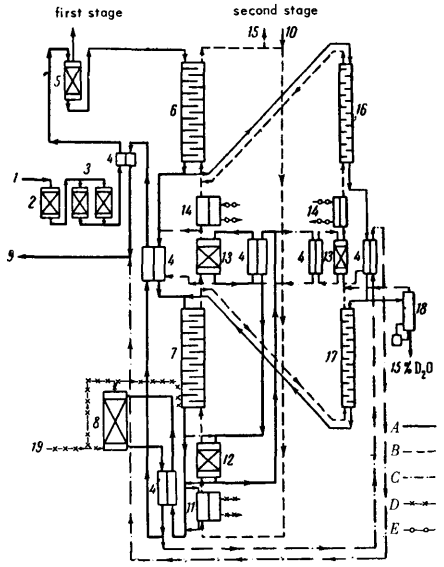


Fig. 14. German experimental two-stage assembly for preparing D_2O by dual-temperature exchange between water and hydrogen sulphide. 1) Fresh water supply; 2) 2) gravel filter; 3) ion-exchange water purifier; 4) heat exchanger; 5) degassing column; 6) cold column of first stage; 7) hot column of first stage; 8) apparatus for distilling off hydrogen sulphide; 9) removal of spent water; 10) supply of hydrogen sulphide; 11) heater; 12) saturator; 13) drier; 14) condenser; 15) removal of hydrogen sulphide for purification; 16) cold column of second stage; 17) hot column of second stage; 18) distillation apparatus for product; 19) steam supply. *A* – process water; *B* – hydrogen sulphide; *C* – process water used as heat-exchange medium; *D* – heating steam; *E* – coolant water.

The preparation of heavy water by dual-temperature exchange between water and hydrogen sulphide, often referred to simply as the hydrogen sulphide method, has attracted considerable attention in other countries interested in producing heavy water for themselves, particularly Western Germany, where laboratory studies have been completed and the construction of industrial plant has begun.

After considerable study and experiment for 2–3 years, the firm of Pintsch-Bamag constructed an experimental plant to produce 0.5 ton of heavy water per year by the dual-temperature exchange between water and hydrogen sulphide [47,35,73,90,108]. The process is illustrated in Fig. 14. [35] The total enrichment factor of 1000 is achieved in a two-stage cascade: the first has an enrichment factor of 16, the second of 64. The hot and cold columns of both stages of the cascade are divided into 4 columns in series, to reduce the total height. The temperature of the cold columns is 30°, that of the hot columns 120°, and the pressure 18–20 atm. The flow rates in the first stage are 2.17 tons h^{-1} of water and 8.8 tons h^{-1} of hydrogen sulphide; the molar stream ratio is 1 : 2.14. The material streams in the second stage are 16 times smaller. The number of theoretical separation stages in both stages of the cascade is 213.

It has recently been reported that the firm of Pintsch-Bamag has undertaken the construction of an experimental plant [109,110], scheduled for completion by the beginning of 1960, [111–113] in Batzbach [48], close to the existing plant of the firm Farbwerk Hoechst [110]. The construction of this experimental plant is the first step in providing Western Germany with large-scale plants for the production of heavy water by the hydrogen sulphide method [108]. A plant for the production of 40 tons of D_2O per year is now planned [111,112,114]. It is proposed to achieve an initial concentration of up to 15% D_2O by dual-temperature exchange in a three-stage cascade. The estimated cost of the plant is 12 million dollars [115].

Various firms, including SOD, a public company formed in France to produce heavy water, have shown interest in the dual-temperature exchange between water and hydrogen sulphide [45,116,117]. An experimental one-stage assembly was built in Lacq for the initial concentration of heavy water by a two-temperature method using natural gases containing up to 15% of hydrogen sulphide, in columns 0.3 m in diameter and 6 m high filled with 15 × 15 Raschig rings: the temperature of the cold column is 30°, that of the hot column 120°, and the pressure is 15 atm. It is calculated that 17 tons of heavy water per year can be produced in Lacq by preliminary enrichment of the water by exchange with hydrogen sulphide [45,117].

Sweden has planned to produce heavy water for use in power reactors [118]. The "ASEA" concern has plans to build a large-scale plant to produce 25 tons of D_2O per year, increasing to 100 tons per year [119,120]. The initial estimate of the cost of construction is 4–6 million dollars and the estimated cost of the heavy water is approximately two thirds of the present American price [120]. 300 000 dollars have been assigned to the project for 1959. [121] An experimental plant comprising columns 1 m in diameter and 15 m high has been set up in Kvarntorp to provide experience [4,122].

Plans have been made in Spain for laboratory studies and the construction of an experimental plant to produce heavy water by the hydrogen sulphide method, in order to gain experience before constructing a large-scale plant [123,124].

The Organisation for European Economic Cooperation has considered a plan to build a common European plant in Iceland to produce 500 tons of heavy water per year by the hydrogen sulphide method. The estimated cost of the plant was 200 million dollars and it was expected that the price of the heavy water would not be greater than the present American one [35,125,126]. England, and possibly the USA, were prepared to take part in the construction of the plant. After more detailed discussion it was decided to build initially a plant in Iceland able to produce 100 tons of D_2O per year [48,127]. The cost of construction will be 36 million dollars.

Other Systems

Urey has suggested the use of a liquid mercaptan RSH in place of gaseous hydrogen sulphide in the dual-temperature process [128]. This would eliminate corrosion, reduce the energy required for transporting the exchange materials, and facilitate the recovery of heat in the opposed streams.

Studies directed by Urey and carried out by Hutchison and Gillies [33b,129] on the possibility of using isopropanethiol showed, however, that the rate of isotopic exchange is insufficient. The firm of Pintsch-Bamag studied the

TABLE 8. Temerature dependence of the separation factor for the exchange between water and hydrogen halides.

Temperature, °C		0	25	100	125	227
System	H_2O—HCl	2.87	2.51	1.98	1.87	1.59
	H_2O—HBr	3.57	3.07	2.34	2.17	1.79
	H_2O—HI	4.55	3.80	2.78	2.56	2.06

possibility of using dithioethyleneglycol in a dual-temperature process[18,35], and found that the temperature dependence of the separation factors satisfies the requirements of the dual-temperature method, and that the rate of exchange is slightly higher than the rate of the extraction processes in the liquid–liquid system. On the basis of these data, plans were made for a plant to produce 36 tons of D_2O per year. However, calculations for this plant showed that because of the large volume of the exchange apparatus, the high cost of the dithiol used in the initial charging, and the loss of dithiol in the drainage water, the construction of the plant was inadvisable, since the capital expenditure and energy consumption would be approximately double that when hydrogen sulphide is used as circulating material[35].

The possibilities of a two-temperature process with the phosphine–water system were studied by Weston and Bigeleisen,[130,131] who found, however, that the exchange rate was too low.

Augood studied the possibility of using hydrogen halides as exchange substances[16]. The temperature dependence of the separation coefficients is favourable (Table 8) but the hydrogen halides are very soluble in water, which makes their recovery from the drainage water difficult, and have a marked corrosive action; these features make them unsuitable.

Taylor has suggested using the three-component cyclohexane–benzene–hydrogen system[33b,132] for the dual-temperature preparation of heavy water. The process is based on the fact that in the presence of a catalyst the equilibrium

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}\ , \qquad \text{(VII)}$$

is displaced towards the formation of cyclohexane at 100° and towards the formation of benzene at 300°, and that the separation factors of the exchange reactions

$$C_6H_{12} + HD \rightleftarrows C_6H_{11}D + H_2\ , \qquad \text{(VIII)}$$

$$C_6H_6 + HD \rightleftarrows C_6H_5D + H_2\ , \qquad \text{(IX)}$$

differ appreciably, and are equal to 2.3 and 3.0 at 184° and 100° respectively for reaction (VIII) and 1.30–1.35 at 300°–350° for reaction (IX). The process is illustrated in Fig.15. The deuterium is concentrated in the cyclohexane by exchange with hydrogen at 150° in the exchange column *II*. Dehydrogenation at 300° in the dehydrogenation column *III* yields the deuterium-rich hydrogen of the cyclohexane, thanks to the lower separation coefficient of the exchange reaction between hydrogen and benzene.

The benzene can be reconverted to cyclohexane in the hydrogenation column. The operating pressure in the system is 15 atm, and the degree of extraction is fairly high (φ_{max} = 0.48). All the extracted deuterium comes from the hydrogen stream. The difficulty in using this three-component system lies in the lack of a suitable catalyst to ensure hydrogenation and dehydrogenation without the formation of side products. Morever, the level of production is determined by the quantity of hydrogen available.

This review of possible systems for the dual-temperature process shows that the water–hydrogen sulphide and water–hydrogen systems deserve most attention, and more convenient exchange systems are unlikely to be found[62–64]. Some technological and economic data for these two systems are given in Table 9.[35]

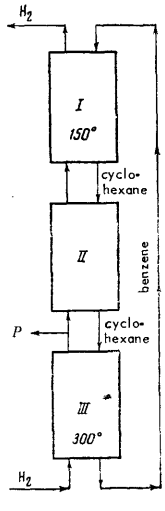


Fig. 15. Dual-temperature exchange in the cyclohexane – hydrogen – benzene system. I) Benzene-hydrogenation column; II) exchange column; III) cyclohexane-dehydrogenation column; *P*) removal of product.

TABLE 9. Comparison of dual-temperature methods for preparing heavy water.

Data	System of deuterium-exchange substances	
	H_2O—H_2S	H_2O—H_2
Temperature, °C	30, 120	40, 200
Pressure, atm	20	200
Ratio of separation factors	1.24	1.7
Effective degree of extraction	0.16	0.33
Stream ratio	1:2.08	1 : 2.42
Raw material used per kg of D_2O	38 tons of H_2O	26 000 km^3 of H_2
Additional raw material per kg of D_2O	100 000 km^3 of H_2S	8.7 tons of catalyst suspension
Approximate capital expenditure, dollars per kg of D_2O per year	240—285	240—360*
Power consumed per kg of D_2O:		
steam, tons	7	2.1
electrical power, kWh	800	200
Cost of power, dollars per kg of D_2O	36.7	10.5
Approximate cost of 1 kg of D_2O**, dollars	75—80	41—54

* Including 48 dollars per 16 kg of platinum.

** Including 10% depreciation costs, 20% extra charges for operating expenses (wages and salaries), and 10% profit.

TABLE 10. Breakdown of cost of heavy water from Savannah River plant.

Items of expenditure	Dollars per kg of D_2O	% of total operating costs
I. Operating costs		
Feed water	0.88	2.95
Hydrogen sulphide	0.97	3.25
Electrical power	2.93	9.84
Steam	9.71	32.62
Coolant water	0.26	0.87
Maintenance	1.08	3.63
Wages and salaries	5.78	19.42
Various prod. expenses	0.45	1.54
Overhead expenses	7.70	25.87
Total:	29.77	
II. Deductions for capital investmt. at 6% per annum	22.99	
III. Extra charges of the Atomic Energy Commission	8.11	
Cost of heavy water	60.87	

At first sight it might appear that the water-hydrogen system is preferable, but all the calculations are based on the use of hydrogen, purified from catalyst poisons, from plants synthesising ammonia at 200 atm: that is a significant proportion of the cost is related to the synthesis of ammonia. If allowance is made for this, the capital and operating costs for this method are no less than those for the hydrogen sulphide one. Morever, the productivity of the former method, like that of the distillation of hydrogen, is limited by the level of production of hydrogen. According to Weiss this method cannot yield more than 650 tons of heavy water per year.

Table 9 shows that the cost of heavy water from the dual-temperature exchange between water and hydrogen sulphide under European conditions is 75–85 dollars per kg. The cost of heavy water from the American Savannah River plant is 62 dollars per kg. The difference is due to the higher cost of power in Europe. Data on the operating expenses of the Savannah River plant (Table 10) show that the cost of power amounts to more than 40% of the total operating costs. The possibility of reducing the cost of power by using cheap natural sources of steam led the Organisation for European Economic Cooperation to choose a site for the production of heavy water in Hengill (Iceland), where the estimated cost of steam is at most one tenth of that in Western Germany, for example.

When examining the possibilities of the different methods for producing heavy water in large quantities, it should be noted that the dual-temperature exchange between water and liquid hydrogen sulphide is the only method known at present to give a low-cost product in unlimited quantities, and this will undoubtedly become the principal method for the production of heavy water. Hydrogen from nitrogen-fertiliser plants will probably also be used in a number of cases to produce deuterium by the low-temperature distillation of hydrogen, and the isotopic exchange between ammonia and hydrogen may also find some application.

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NUCLEAR MAGNETIC RESONANCE AND THE STRUCTURE OF MATTER

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A diamagnetic substance placed in a static magnetic field and also subjected to an alternating magnetic field of certain frequency will absorb energy from the alternating field. This phenomenon is known as nuclear magnetic resonance because it is due to the nuclear magnetic moments present in the molecules of diamagnetic substances. Nuclear magnetic resonance was first observed