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PRODUCTION OF HEAVY WATER
STATUS REPORT

March 1969

AEC RESEARCH &
DEVELOPMENT REPORT

BNWL-884

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PRODUCTION OF HEAVY WATER - STATUS REPORT

Prepared for
U.S. Heavy Water Reactor Base Program

By
J. A. Ayres

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PREFACE

This report was prepared for the U. S. Heavy Water Reactor Base Program. Its purpose is to review the status of technology in the subject area, and to identify required research and development for heavy water reactors and related systems.

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PRODUCTION OF HEAVY WATER - STATUS REPORT

J. A. Ayres

INTRODUCTION

The U. S. Heavy Water Reactor (HWR) Base Program was established in 1967 to provide technology and related information necessary to build heavy water power reactors in the U. S. , should that need arise. To establish a viable program, a number of status of technology reports were prepared as input to an overall HWR Program Plan.⁽¹⁾ One important status of technology report was that for production of heavy water.

Many summary reports on heavy water production have been written during the past twenty years, but some were written as magazine articles, or speeches, or summaries and were necessarily brief^(2, 9) --too brief to include all important information. Some were written to describe one or a limited number of procedures and hence were not suitable for a comparative evaluation of all possibilities. The "complete" reports⁽¹⁰⁻¹⁵⁾ do not include the recent important advances in technology.

The principal aim of this report is to include all available information required to define a research and development program for production of cheap heavy water. No attempt was made to be brief.

I. ECONOMIC CONSIDERATIONS

A. SUPPLY AND DEMAND OF HEAVY WATER

Table 1 lists the plants that are producing D_2O and those plants that are being built and will be in production soon. Table 1 does not include some small plants and plants not mentioned in the literature.

In the U.S., two plants, Dana and SRP, were constructed. These are designed for a total of about 1000 tons/year, but for economic reasons (as explained later), the maximum production at the present time is 180 tons/year.

Two Canadian plants at Glace Bay (Deuterium of Canada, Ltd.) are scheduled to go into operation within one to two years.⁽¹⁶⁻¹⁹⁾ The first unit (DC-1) is about two years behind schedule and the present target for startup is October 1968.⁽¹⁶⁻¹⁸⁾ Both these plants plan to use sea water as feed.⁽¹⁸⁾ Canadian General Electric plans to build a 400 to 500 tons/year plant at Pointe Tupper on Canso Strait, Canada.⁽¹⁸⁾

The demand for heavy water, at least in the next 30 years, * will depend on the number of HWR's built during this time, the amount of D_2O required per MWe, and the amount of D_2O removed from the stream by losses and degradation.

If we take the figures cited by Canada^(2, 19-21) for the amount of D_2O required through 1985 and assume no new D_2O production units are built beyond those scheduled, we can plot these predictions (Figure 1) against the supply. It is obvious from this figure that the D_2O units now or soon to be in production are insufficient. A minimum schedule to meet the demand requires construction of 14 new units of 400 tons/year each, the first unit being started by 1970. Any delay in starting the first unit will require additional units to provide required reactor inventories.

* At a later date D_2O may be required for fusion reactors, but this will not be considered in this discussion.

TABLE 1. Existing and Planned D₂O Production Plants

Country	Identification	Type	Discontinued	Capacity and Status		Planned or Proposed
				In Operation (year), T/year		
USA	SRP	GS	360	180	(1952)	
	Dana	GS	540			
	Boulder	H ₂ distillation	(pilot)(a)			
	Morgantown	H ₂ O distillation	15			
	Alabama					
Wabash River						
	Hydrocarbon Research	H ₂ distillation				34
Canada	DC-1	GS		200	(1969)	
	DC-2	GS		200	(1969-70)	
	CGE	GS		400	(1969-70)	
	Trail	H ₂ -H ₂ O electrolysis of H ₂ O	6			
France	Lacq	GS	~ 0.5			
	Toulouse	H ₂ distillation	2			
	Mazingarbe	NH ₃ -H ₂ mono	3			
	Mazingarbe	NH ₃ -H ₂ mono		(a) 20	(12/67)	
	Mazingarbe	NH ₃ -H ₂ bithermal			(11/67)	
Germany	Hoechst	H ₂ distillation		6		Semi-industrial
	Walter and Schindewolf	NH ₃ -H ₂				
	DEGUSSA	H ₂ -H ₂ O	(a)			
Switzerland	Ems (Sulzer)	Electrolysis		2.5-4.0		
		H ₂ distillation				
		H ₂ O distillation				
Norway	Norsk-Hydro	Electrolysis of H ₂ O		20		
England	John Brown	NH ₃ -H ₂				-
India	Nangal	H ₂ distillation		14	(1962)	200
	Nangal	GS				
Japan		H ₂ distillation		(a)		10
Pakistan	Fenchoganj	H ₂ distillation or NH ₃ -H ₂				15
Spain	Sabinango	H ₂ -H ₂ O Electrolysis		(a)		0.5
Russia		Electrolysis of H ₂ O		2 to 4 (4000 m ³ gas/hr)		
		H ₂ distillation				
Sweden		GS	(a)			
			0.0015.			

(a) Pilot plants built primarily to study process variables. Produced only very small quantities of D₂ or D₂O (usually about 0.01 to 0.1 tons/year) and usually at a low D₂O concentration. (300 ppm to 2%)

ERRATA

Page 7. Note at bottom of page applies only to discussions in Sec. IB, where $D/H < 0.01$. At higher concentrations,

$$\text{mole\% or \%} = \frac{\text{moles D}}{\text{moles (D+H)}} \times 100$$

$$\text{and ppm} = \frac{\text{moles D}}{\text{moles (D+H)}} \times 10^6$$

Page 40. In Table 7, last 3 lines should be

<u>Total Operating Cost</u>	7.90	5.75	5.35
<u>Capital Charges</u>	<u>9.45</u>	<u>8.10</u>	<u>7.80</u>
Total Production Cost	17.35	13.85	13.15

Delete Notes (a) and (b)

Page 51. Second paragraph should read:

One of the most extensive studies of the bithermal process is being made by Rae^(2, 5, 6) and co-workers of the AECL, they have tentatively chosen temperatures of -40 and +70 °C. Therefore,

$$\alpha = 5.90/2.80 = 2.1 \quad (21)$$

Page 55, line 5.

Change; at 30 °C is 85% to at 30 °C is 70%

Page 59, Figure 17.

$$y = \frac{\text{moles NH}_3 \times 100}{\text{moles (N}_2 + 3\text{H}_2)}$$

Page 112, line 4.

Reference should be (90)

Page 131, line 4.

The eight cells containing iron cathodes and nickel anodes are connected in siéves as shown in Figure 46.

Page 139, 2nd line from bottom.

Change 20 g of PD to 20 g of Pd

Page 149. Third paragraph should read:

Research to develop improved methods for producing D₂O has proceeded along several lines

References 25 and 27 are transposed.

Reference 52. Third author's name is misspelled. It should be Vaniscotte.

FIGURE 1. Estimated Supply and Demand of D_2O

B. OCCURRENCE OF DEUTERIUM

Deuterium (D or ${}^2_1\text{H}$) and compounds of deuterium (D_2O , HDO , HD , CH_3D , etc.) occur in nature as isotopic mixtures with normal hydrogen (${}^1_1\text{H}$) to the extent of 1 mole D per 7000 moles H. Thus, natural water contains about 0.000140 mole fraction (140 ppm) D_2O as HDO . The concentration is surprisingly invariant. Kot⁽²²⁾ states, "The amount of heavy water in natural water is almost the same irrespective of its source—in Altai glaciers, at the bottom of the ocean, in water from willows or redwood trees." Kirshenbaum⁽²³⁾ lists the deuterium content in natural waters, principally in North America (Table 2). He found the seasonal variation was only about 3%.

TABLE 2. Deuterium Content of Various Natural Waters⁽²³⁾

Source	Average Content in Water, mole % D
Columbia River	0.0139
Kootenay Lake	0.0139
Lower Arrow Lake	0.0139
Steamboat Springs	
Condensate	0.0139
Runoff	0.0141
Hetch Hetchy Aqueduct	0.0146
Hudson River	0.0147
Great Salt Lake	0.0147
Lake Ontario	0.0147
Niagara	0.0148
St. Lawrence River	0.0148
Searles Lake	0.0148
Wabash River	0.0148
Norris Lake	0.0148
Coosa River	0.0148
Lake Superior	
Ice	0.0148
Water	0.0148
Monongahela River	0.0149
Hot Springs, Arkansas	0.0149
Phillips Petroleum	0.0149
Pacific Ocean	0.0149
Atlantic Ocean	0.0150
Gulf of Mexico	0.0151
Associated Oil	0.0151

Engineers at the Atomic Energy of Canada, Ltd., (AECL) surveyed the Canadian waters (Figure 2) and found the deuterium content to be between 0.0130 and 0.0152 mole %.* This survey is being continued. One hundred locations are being sampled for surface waters every two months for two years, and precipitation samples at fifteen locations are sampled monthly. Five ocean locations are included.

Bancroft states "...concentration variations (result) from natural fractionation by evaporation and precipitation. The rain falling on coastal regions is somewhat leaner than ocean water because HDO is less volatile than H₂O. Successive precipitations from the same vapor supply are leaner, reaching about 133 ppm at the Columbia River head waters. Water vapor for the center of the continent comes largely from the Gulf of Mexico, in the range 140 to 145 ppm at the time it reaches Canada. The Great Lakes cause some enrichment by evaporation, 149 ppm in the St. Lawrence River at Cornwall, Ontario compared to about 144 ppm for the rivers feeding the Great Lakes and the Ottawa River at Ottawa. Downstream of Cornwall, the St. Lawrence is mixed with deuterium-leaner tributaries. Nova Scotia surface waters show 146 ppm. Natural fractionation is temperature-dependent, yielding leaner precipitation during winter and fluctuations from storm to storm."⁽²⁾

Roth reports values of deuterium content of various natural waters, including precipitation.⁽²⁴⁾ Table 3 is a partial listing of these values. These data are interesting because they represent such a wide variety of sources (springs, oceans, seas, ice from the polar regions, snow, rain, hail, water at different levels of the sea, and salt water reservoirs).

The values in Table 3 are uniformly higher than those of Kirshenbaum and Bancroft. This results from differences in the standard of comparison, since values are almost always measured

* In this discussion, x mole% or x‰ means $\left(\frac{x \text{ moles deuterium} \times 100}{\text{moles hydrogen}}\right)$, and x ppm means $\left(\frac{x \text{ moles deuterium}}{10^6 \text{ moles hydrogen}}\right)$.

TABLE 3. Deuterium Content of Waters in Various Parts of the World⁽²⁴⁾

<u>Sample</u>	<u>D₂O Content, ppm</u>
Oceans	
North Sea	161.3
Atlantic, near Quiberon	162.8
Atlantic, near Long Island	159.9
Antarctic, No. 1	157.1
Antarctic, No. 2	159.8
Antarctic, No. 3	160.9
Indian Ocean	161.0
Lakes and Inland Seas	
Dead Sea	162.6
Baltic Sea	156.1
Mono Lake, USA	152.8
Kenujarvi (Finland)	146.8
Lake Geneva	147.5
Loch Ness	154.5
Lake Michigan	153.2
Rivers	
Weser	152.0
Rhine	151.7
Po	149.4
Niger	157.7
Iijoki (Finland)	147.0
Vienne (France)	153.7
Isère	146.4
Springs	
Ain el Arione (Tunisia)	159.3
Mineral Springs of Tiberiod	159.2
Caldanaccia (France)	152.8
Le Monstier (Alps)	146.3
Precipitation	
Rain (Ramat Chien, Middle East)	163.8
Rain (Murchison Bay)	129.3
Spitzberg	
Rain, New York	150.2
Hail, Belgium	150.1
Snow, Switzerland	142.3
Rain, Monaco	160.4

<u>Sample</u>	<u>D₂O Content, ppm</u>
Snow (Swiss Glacier)	148.9
Summer Snow (Switzerland)	153.6
Hail (Vosges)	141.9
Snow (France)	151.6
Snow (High Alps)	139.1
Snow (9 samples at Saclay)	144.6
	to
	153.1
Rain (9 samples at Saclay)	149.5
	to
	160.3

Effect of Depth

Mediterranean	
Surface	161.0
100m	161.8
500m	162.0
1000m	162.1
2500m	161.5

against some standard. Roth reports the deuterium content of standard mean ocean water (SMOW) to be

$$D/H = 161.4 \times 10^{-6}$$

Bancroft⁽²⁾ uses 156.5 as the SMOW value.

Water resulting from distillation processes, especially where reflux occurs, could have a considerably higher D₂ content. Roth discusses the possible relationships between deuterium content and the various physio-chemical processes (evaporation, freezing, precipitation) occurring in nature. Weingaertner et al. report that bitterns contain 0.0250 mole% D₂O.⁽²⁵⁾ Variation in deuterium content over a narrow range is found in other compounds containing hydrogen and deuterium. Samples of natural gases from Canadian oil fields showed deuterium contents from 117 to 133 ppm.⁽²⁾

C. COST OF HEAVY WATER

The cost of D₂O is closely related to the demand. If an established market for large amounts of D₂O existed, industrial concerns would probably investigate procedures for producing D₂O more cheaply, and the

technology developed during these investigations would lead to more efficient processes. Similarly, if large quantities of D_2O were available at a low price ($< \$10/lb$), cost of a HWR would be less, the HWR would be more competitive, more HWR's would be built, and a market for D_2O would be established. At present, the market and the supply for D_2O are uncertain.

At the present established price, if a 1000 MWe reactor requires 500 tons of D_2O (see appendix) at \$57,000/ton, the D_2O cost alone will be \$28,500,000 or about 20% of the total cost of the reactor, and this cost will increase the unit price of electricity produced by the HWR. In addition, the D_2O is a capital item that can be lost or downgraded. A leak that might be of minor importance in a light water reactor could be a large expense in a HWR. Systems and controls to prevent leaks or other possible losses of D_2O and systems to recover D_2O add to the total capital and operating expense of HWR's. The degree of control required is directly related to the price.

In spite of the uncertain market for D_2O , a limited amount of research and development on methods to produce D_2O at a reasonable cost has been in progress since shortly after Urey and his co-workers discovered deuterium in 1932. The price has steadily decreased from the early value of several hundred dollars per pound to the present price of about \$28.50/lb.

A comparison of the costs of D_2O produced by different processes at different times is complicated by several factors, especially by the lack of agreement on capital charges and by inflation. Capital charges have been assumed from 10 to 24%, and cost of construction has changed over the past 25 years by a factor of three to four. This is illustrated in Figure 3 a reproduction of the Nelson Refinery Cost Index⁽²⁶⁾ from the Engineering News Record of March 21, 1968. Operating costs have also increased, although not so dramatically.

FIGURE 3. Cost Index for Period 1950-1970⁽²⁶⁾

The costs for producing D_2O by different methods are discussed in greater detail in the appropriate sections. For economic comparisons in this report, capital charges are arbitrarily assigned as 14%, and costs are based on 1967 U.S. dollars. Canadian dollars are taken as equivalent to \$0.91 U.S. dollars.

The principal difficulties in separating deuterium from hydrogen are: (1) the great similarity of hydrogen to deuterium, and (2) the very low concentrations found in nature. These difficulties imply a very small amount of separation per stage and a very large number of stages. The plants will be large, and capital costs will be high. As will be seen later, capital costs can account for from 50 to 80% of the total.

The deuterium concentration in the feed is very important since the yield (and hence size of plant, capital costs, and total production costs) will vary directly with feed concentration.

Several authors have tried to estimate the value of increased feed concentration. Kumar and Datta⁽²⁷⁾ use the equation of Cohen as modified by Benedict and Pigford.⁽²⁸⁾

$$C_p = C_E (2X_p - 1) \ln \frac{X_p (1 - X_o)}{X_o (1 - X_p)} + \frac{(X_p - X_o) (1 - 2X_o)}{X_o (1 - X_o)} \quad (1)$$

where C_p = unit cost of enriched material

C_E = cost of separative work

X_o = D_2O fraction in water

X_p = D_2O fraction in the final product

and similar equations of London⁽²⁹⁾ and Cerrai et al.⁽³⁰⁾ to estimate the economic advantage of using bittorns water, which contains 0.0257% D_2O , about twice the normal value. The use of these equations is of questionable value unless a direct correlation is made with a specific design. For example, if one assumed the feed to be equivalent to the

product from the first stage, the value of the increased concentration would be equivalent to the cost reduction obtained by eliminating all (or part) of the first stage. Otherwise, untenable assumptions are made, and the evaluation includes no consideration of decreased efficiency of smaller scale, higher losses in waste, or effects of change in type of process used in different stages.

Figure 4 is probably a more realistic curve showing effect of initial feed concentration on total cost. Approximately 60% of the total cost is used for Stage 1 to increase the original concentration from 140 to 840 ppm. The final concentration (from 15 to 99.8%) is usually effected by a different process. For comparison, the values as calculated by Kumar and Datta are shown as a dotted line. For the first 10 to 12 ppm, the discrepancy is not too great.

Bancroft⁽²⁾ states that within a narrow range, the value of increased (or decreased) concentrations can be considered equivalent to 0.6%/ppm. Over the range of 120 to 160 ppm, this is probably as good an estimate as the complicated equations used by Kumar and Datta.

The following discussion considers the candidate processes in detail giving general principles, history, present status, and economics.

FIGURE 4. Percentage of Total Cost of D₂O as a Function of Feed Concentration

II. HISTORICAL SUMMARY OF D₂O PRODUCTION IN THE U. S. A.

Deuterium was discovered and first concentrated by Urey et al.⁽³¹⁾ using the fractional distillation of hydrogen process. Later, Urey and Washburn⁽³²⁾ discovered that when ordinary water was electrolyzed, heavy water concentrated in the electrolyte. Lewis and Macdonald⁽³³⁾ prepared the first samples of pure D₂O by electrolyzing 20 liters of water in successive stages to obtain 0.3 cm³ of water having a specific gravity of $d_4^{25} = 1.1059$, essentially pure D₂O. Taylor and coworkers⁽³⁴⁾ later electrolyzed 2310 liters in seven successive stages to obtain 83 cm³ of 99.0% D₂O. Electrolysis was the method first used for producing D₂O on an industrial scale. These plants produced only small amounts of D₂O and were limited to locations where electricity was very cheap (as in Norway).

When the first nuclear reactors to produce plutonium were being designed and built, the Office of Scientific Research and Development, not wishing to rely entirely on the principle of graphite moderation, decided to investigate the feasibility of producing D₂O in sufficient amounts to construct D₂O-moderated reactors as an alternative.^(10, 35) In 1941, they asked Professor Urey and others to investigate methods for producing large amounts of heavy water. An early survey showed three general methods to be most feasible: distillation, electrolysis, and chemical exchange. Fractional distillation of water was chosen for development, because the U. S. had an enormous backlog of experience in fractional distillation techniques, and almost no development work would be required.

Catalytic exchange of hydrogen with water was chosen as an alternate process because large amounts of electrolytic hydrogen were available (at Trail, B. C.). Electrolysis was chosen as the finishing process (concentration from 50% to 99.7%).

Water distillation plants were designed, constructed, and operated by E. I. du Pont de Nemours, Inc., at Morgantown Ordnance Works (MOW), Alabama Ordnance Works (AOW), and Wabash River Ordnance Works (WROW) in 1943. The first D_2O was produced at these plants in 1944. The hydrogen-water exchange plant was built at Trail, B.C. in 1943 by Consolidated Mining & Smelting Company and Stuart Oxygen Company.

In 1949 and 1950 Hydrocarbon Research, Inc., under contract with USAEC, studied the ammonia-hydrogen exchange process using natural gas as a feed. Their studies showed such a process could be economically competitive if the hydrogen was taken from feed to an ammonia plant, processed, and returned to the ammonia plant: a so-called "parasitic" process. A detailed design was prepared, but the plant was never built.

The dual-temperature chemical exchange between H_2S and H_2O (GS process*) was one of the candidate processes considered in 1942 but was not utilized because it appeared that some difficult corrosion problem might arise when H_2S contacted the materials of construction, especially since there was a shortage of stainless steel at this time. In 1949 the USAEC wished larger quantities of D_2O for construction of reactors that might prove more economical than the light water, graphite-moderated reactors then used exclusively in the U.S., for manufacture of plutonium. The GS process appeared to be a very attractive candidate for producing large amounts (hundreds of tons per year) of D_2O because of low energy requirements and rapid exchange rate.

Material problems were no longer so critical as in 1942. The AEC, therefore, asked the Guerdler Corporation, and later du Pont, to design and operate a H_2S - H_2O plant. Du Pont was also asked to study corrosion and material problems connected with the GS process. The pilot plant was constructed at the Wabash River Ordnance Works (Dana) and was successfully operated in 1950. Several problems of corrosion,

* GS (Guerdler Sulfide)

maintenance, and plugging occurred, preventing continuous use of the plant, but these difficulties pointed out the information required for designing large-scale plants, and subsequent research showed that these difficulties were not insurmountable.

In 1951-1952, the Guerdler Corporation constructed a large-scale plant for du Pont at Dana. In 1951 du Pont constructed a similar plant at Savannah River (SRP).

The SRP, being the newest, incorporated several improvements in design. The SRP had two stages in contrast with Dana's five. Dana required somewhat smaller towers because it more nearly duplicated the ideal cascade (Figure 5), but it was more complicated.⁽³⁶⁾ Corrosion was a more serious problem at Dana, especially corrosion of carbon steel and 410 stainless steel portions at points of high velocity, spray impingement, or turbulence.

Both plants started operation in 1952-53 and operated at full capacity (540 tons/year each) for a short time. Dana was shut down permanently in 1959. It is doubtful that it will ever be started up again. It would be much cheaper to build a new plant, utilizing present technology, than to repair and restart Dana. Figure 6 shows the operating history of Dana and SRP.⁽³⁷⁾ SRP consisted of three units, each capable of producing 180 tons/year, and operated at full capacity from 1953 to 1957. In October 1957, one unit was shut down; in October 1958, another unit was shut down; since then, SRP has operated at 1/3 capacity, producing 180 tons/year. The two units that were shut down were placed in standby condition and could conceivably be started again, but it would require up to an estimated \$20,000,000 to do this.⁽³⁸⁾

FIGURE 5. Comparison of SRP and Dana with Ideal Cascade⁽³⁶⁾

FIGURE 6. Production of Heavy Water⁽³⁷⁾

III. CANDIDATE METHODS FOR D_2O PRODUCTION

Although hydrogen closely resembles deuterium in physical and chemical characteristics, slight differences do exist. Deuterium acts as a more inert isotope with slightly slower reaction rates. Heavy water appears to be more ordered than light water (more viscous, higher melting point, higher boiling point, higher heat of formation). However, the differences are all small, and any exchange, based either on chemical or physical differences, will effect only a slight separation, with the more inert deuterium compound remaining in the residue or unreacted portion. The separation, therefore, involves removing a very large amount of material to obtain a small amount of product, and providing a cascade with a sufficient number of stages to effect the desired concentration.

A. GENERAL CONSIDERATIONS

The most common reactions for concentrating D_2O from 140 ppm to reactor grade (99.8%) D_2O may be classified as: chemical exchange, distillation, and electrolysis. Other techniques such as sorption, ion exchange, diffusion, hydration, and freezing have been suggested but have never been developed to pilot plant or production stage.

In distillation, the amount of separation per stage is designated as the separation factor, α

$$\alpha = \frac{X_H(1-X_T)}{X_T(1-X_H)} \quad (2)$$

Thus, a mixture of H_2O and D_2O containing X_F mole fraction D_2O in a single-stage distillation will produce a distillate with a mole fraction X_H and a residue with a mole fraction X_T .

Similarly, if two phases containing D_2O are mixed, the equilibrium concentrations of D_2O in Phase A (X_a) and Phase B (X_b) are determined by the

separation factor

$$\alpha = \frac{X_a(1-X_b)}{X_b(1-X_a)} \quad (3)$$

The overall separation (w) of a cascade consisting of several stages will be

$$w = \frac{X_P(1-X_W)}{X_W(1-X_P)} \quad (4)$$

where

X_P = atom fraction of desired isotope in the product

X_W = atom fraction of desired isotope in waste.

The minimum number of stages required (n) is

$$n = \frac{\log w}{\log \alpha} \quad (5)$$

This ratio increases rapidly as $\alpha \rightarrow 1.0$.

The optimum number of stages that can be used in a practical plant will be greater than the minimum and can roughly be taken as twice the minimum.

The total flow rate in a cascade (J) can be calculated from the following equation. (28)*

$$J = A \cdot B \quad (6)$$

where

$$A = \frac{2(\sqrt{\alpha} + 1)}{(\sqrt{\alpha} - 1) \ln \alpha}$$

$$B = W(1-2X_W) \ln \frac{X_F(1-X_W)}{X_W(1-X_F)} + P(2X_P-1) \ln \frac{X_P(1-X_F)}{X_F(1-X_P)}$$

* An ideal cascade is assumed in which $\alpha = \beta^2$, where β is the heads

separation factor, $\frac{X_H(1-X_F)}{X_F(1-X_H)}$

$$= W(2X_W - 1) \ln \frac{X_W}{1 - X_W} + P(2X_P - 1) \ln \frac{X_P}{1 - X_P} - F(2X_F - 1) \ln \frac{X_F}{1 - X_F}$$

F = molar feed rate, X_F = mole fraction deuterium in the feed

W = molar waste rate, X_W = mole fraction deuterium in the waste

P = molar product rate, X_P = mole fraction deuterium in the product

A is a function only of α and increases rapidly as $\alpha \rightarrow 1.0$.

B is a function of the throughput and is large when the concentration of product differs greatly from concentration of feed. Benedict terms B the "separative duty" because it has the same form as heat duty of an evaporator and is a magnitude of the job of separation.

The size of the plant and, to a large extent, the capital costs are an inverse relationship of α . Equation 6 relates α to the amount of liquid processed (J). Figure 7 plots α against A . Since the plant size depends on A , the graph can be used to estimate effect of α on relative size of the plant. In a close separation cascade ($\alpha \rightarrow 1.0$), the first term in Equation 6 becomes

$$A = 8/(\alpha - 1)^2 \quad (7)$$

and plant size varies inversely with $(\alpha - 1)^2$.

The separation factor also determines the degree of removal of deuterium from the feed. In a separation process $[(\alpha - 1)/\alpha] \times 100\%$ of the deuterium is recovered as the final product, and $(1/\alpha) \times 100\%$ is sent to waste. In the specific example of distillation of water, where $\alpha = 1.05$, only 5% of the D_2O is removed, and 95% is discarded with the waste.*

* For a complete discussion and derivation of these equations, see Benedict and Pigford (Reference 28).

FIGURE 7. Effect of Separation Factor on Size of Plant (A versus α)

B. CHEMICAL EXCHANGE

In chemical exchange, two different chemical compounds in intimate contact ionize, and the ions exchange in such a manner that one compound becomes relatively enriched in the desired isotope and the other becomes relatively depleted. For example,

The concentration of each species at equilibrium is expressed as the equilibrium constant

$$K = \frac{[\text{H}_2\text{S}]}{[\text{HDS}]} \cdot \frac{[\text{HDO}]}{[\text{H}_2\text{O}]} \quad (9)$$

where $[\text{H}_2\text{S}]$ = concentration of H_2S , etc.

In an actual chemical separation, pure H_2O , HDO , H_2S , or HDS are not present. Instead, there will be H_2S with a mole fraction, X_1 , of HDS before mixing and a mole fraction, X_2 , of HDS after mixing, and H_2O with a mole fraction, X_3 , of HDO before mixing and a mole fraction, X_4 , of HDO after mixing.

If we designate X_a as the concentration of HDO in H_2O at equilibrium, then $X_a \equiv [\text{HDO}]$ and $1 - X_a \equiv [\text{H}_2\text{O}]$. Similarly if X_b is taken as the concentration of HDS in H_2S at equilibrium $X_b \equiv [\text{HDS}]$ and $1 - X_b \equiv [\text{H}_2\text{S}]$, and Equation 9 is identical with Equation 3. Therefore, $\alpha = K$. However, in an exchange between two compounds not having the same number of replaceable hydrogens, $\alpha \neq K$. For example, in an exchange between NH_3 and HD , $\alpha = 2/3K$.

The equilibrium constant and, hence, the separation coefficient, change with temperature, usually in an inverse relationship, i. e.,

$$\alpha_c / \alpha_h > 1 \quad (10)$$

where α_c equals the separation coefficient at a lower temperature, and α_h equals the separation coefficient at a higher temperature.

The separation coefficient changes with temperature in accordance with the equation

$$\log \alpha = \frac{A}{T} + B \quad (11)$$

where log is logarithm to base 10, A and B are constants, and T is temperature in °K. As the temperature increases, the logarithm of α decreases and α approaches a value of 1.0*

* This is based on the assumption that $\alpha \geq 1.0$. If $\alpha < 1.0$, α will increase with increasing temperature. In both cases, α will tend to approach the value of 1.0, and no appreciable concentration can be effected. For example in the reaction

At 30 °C, the equilibrium constant to express the transfer of deuterium from H_2S to H_2O will be 2.27, $\log \alpha = 0.356$, and $\log \alpha$ will decrease with temperature to approach a value of 0.00. On the other hand, the equilibrium constant to express the transfer of deuterium from H_2O to H_2S will be less than 1, $\log \alpha$ will be negative and thus

$$\alpha (\text{H}_2\text{S} + \text{HDO} \rightarrow \text{HDS} + \text{H}_2\text{O}) = \frac{1}{\alpha} (\text{HDS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{HDO}) \quad (12)$$

$\log \alpha$ will increase with temperature to approach a value of 0.0000.

In this paper, we will adopt as a standard convention, $\alpha \geq 1.00$. In chemical exchange between a vapor or gas and a liquid, this will usually be the α for transfer of deuterium from the vapor or gas to the liquid.

If α is greater than 1.0, water will be preferentially enriched with deuterium. That is, at equilibrium, the concentration of deuterium in the water will be higher than the concentration of deuterium in the hydrogen sulfide.

The equilibrium constant (K) and the separation factor (α), which is a function of K, express the amount of product that can be obtained under given conditions at equilibrium. Neither α nor K give any information as to how fast the reaction will proceed nor how much product will be formed in a given time. Therefore, even though α is very high, the product may form at such a slow rate that the reaction cannot serve as the basis for any practical procedure. For example, if α is 1.5 and the initial concentration is 0.014%, the reaction must be repeated sixteen times to obtain a product concentration of 10%. Unless the reaction is completed rapidly, the yield will be very low.

The rate of reaction is expressed as the amount of reaction taking place in a unit of time; for example, g/sec or mole/hr. The rate is related to the temperature by the equation

$$\log k = -\frac{A}{T} + B \quad (13)$$

where k is the rate constant, log is logarithm to base 10, A and B are constants, and T is temperature in °K.

According to Equation 13 and the discussion in the previous paragraph, k increases with temperature while α decreases with increasing temperature. Thus, while it may be desirable to operate at a low temperature to obtain a high separation factor, the reaction at this temperature may proceed so slowly that little or no exchange will occur in any reasonable time.

Some reactions are so sluggish at all temperatures where $\alpha > 1$ that they are useless. Sometimes a small amount of compound may be added to speed up or catalyze the reaction. The catalyst may form an intermediate compound with one or more of the reactants, and this intermediate compound may decompose to form the product. Many different types of catalytic action are possible, but in all cases, the reaction is accelerated while the catalyst remains essentially unchanged. Since the catalyst is not depleted and can be reused indefinitely, relatively expensive catalysts (Pd or Pt) may be used.

These considerations are used as bases for two types of chemical exchange:

- Monothermal. Monothermal chemical exchange is very similar to distillation. Two species, such as NH_3 and H_2 , are contacted countercurrently in a column at a given temperature, t . The ammonia strips deuterium from the hydrogen. To increase the number of stages above one, part of the enriched ammonia is cracked to form enriched hydrogen which serves as reflux. The separation factor is the α corresponding to temperature, t .
- Bithermal. Since the equilibrium constant and separation factor change with temperature (usually decrease), water may be contacted with hydrogen sulfide at a low temperature (where α is relatively high) to strip deuterium from the hydrogen sulfide and at a higher temperature (where α is relatively low) to give up part of the deuterium to the hydrogen sulfide.

The separation coefficient (α) is the ratio

$$\alpha = \alpha_c / \alpha_h \quad (14)$$

1. Exchange Between Hydrogen Sulfide and Water (H₂S-HDO)

The only method that has been used successfully to produce large amounts (several hundred tons/year) of D₂O is a bithermal process utilizing the chemical exchange reaction between hydrogen sulfide and liquid water.

Roth et al. report what is probably the best value of α for this reaction:

$$\alpha = 1.001 \exp (221/T) \quad (16)$$

and calculate values given in Table 4.⁽³⁹⁾

TABLE 4. Separation Coefficient for H₂S-H₂O Reaction at Various Temperatures⁽³⁹⁾

<u>t, °C</u>	<u>α</u>	<u>t, °C</u>	<u>α</u>
0	2.52	80	1.94
10	2.39	90	1.90
20	2.30	100	1.86
30	2.22	110	1.82
40	2.15	120	1.79
50	2.09	130	1.76
60	2.04	140	1.73
70	1.99	150	1.71

The bithermal process (GS) has been developed extensively and will be described first. The monothermal process has not been developed because no one has come up with an economic method for producing chemical reflux.

a. Bithermal HDO-H₂S Exchange (GS Process)

The GS process as developed at the SRP and Dana plants consists of contacting H₂S gas with H₂O liquid at 30 and 130 °C.⁽³⁶⁾ The overall separation coefficient is thus

$$\alpha = \frac{2.22}{1.76} = 1.26 \quad (17)$$

A complicated system of heat exchangers reduces steam consumption and reduces operating costs. Figure 8 is a flow diagram of one unit of the SRP.⁽³⁶⁾ The feed (water containing 140 ppm D₂O) flows down through the cold tower (CT-1) at 30 °C countercurrently to H₂S, and is progressively enriched with D₂O. Part of the enriched water is withdrawn as feed for the cold tower (CT-2A) in the second stage, while the remainder flows down the first stage hot column (HT-1). Hydrogen sulfide flowing up through HT-1 becomes enriched in deuterium. Part of the enriched H₂S is drawn off to feed the second stage hot column (HT-2B), and the remainder flows upward through CT-1 where it is depleted and is then returned as feed to HT-1. Thus the H₂S flow is cyclic. The H₂O after being depleted in HT-1 is sent to a steam blower, stripped of H₂S (down to about 1 ppm), and sent to waste.

The flow patterns in the second stage are similar to those in the first stage and are shown clearly in Figure 8. The D₂O concentration is increased by a factor of four to five in the first stage and by a factor of 200 to 250 in the last two stages. The final product from the cascade is H₂O containing about 10% D₂O. The volume has been reduced by about 3 orders of magnitude, and the choice for final concentration of the D₂O is based on convenience and simplicity rather than economics. Therefore, when the SRP and Dana plants were built, distillation (DW process) was used for concentration to 90% and electrolysis (E process) for the final concentration to 99.8%. Table 5 is a breakdown of costs for the GS, DW, and E processes. The final concentration from 10 to 99.8% accounted for only 6.8% of the total cost. In 1958, the E plant was shut down, and the entire concentration from 10 to 99.8% was done by distillation (Figure 9).

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FIGURE 9. History of Operation of SRP GS Plant⁽³⁷⁾

TABLE 5. Cost of Stages of D_2O Production at Savannah River⁽³⁶⁾

	Percentage of Cost		
	<u>GS</u>	<u>DW</u>	<u>E</u>
Direct production cost	90.5	4.2	5.3
Direct maintenance cost	95.4	2.0	2.6
Utilities	94.5	4.8	0.7
Total direct cost	93.2	4.2	2.6

Proctor and Thayer in 1962 critically re-examined the GS process and found several areas where improvements could be made to reduce the unit cost.⁽⁴⁰⁾ They considered cheaper fuel (gas at 16¢/1000 Btu rather than coal at 36¢/1000 Btu); direct gas-fired heating to replace a central steam plant; simpler and cheaper heat recovery exchangers, which would also simplify piping and reduce pumping costs; larger diameter towers (16 ft diameter rather than the 8 ft diameter at SRP); sieve plates to replace bubble caps and thus increase efficiency, reduce column size, increase throughput, and decrease pressure drop; elimination of the electrolysis unit, and direct makeup of H_2S . Table 6 shows their calculations for cost of D_2O as produced in the SRP and in the new plants. The total cost can be broken down into two headings, operating costs and capital charges. For this comparison, capital charges were taken to be 14% and the dollars quoted are 1960 U.S. dollars. Since this is only a comparative study of two processes, no attempt will be made at this time to convert to other values. The flow diagram of the improved process is shown in Figure 10. A 200 ton/year unit requires only 12 towers as compared with 60 needed for a SRP design of the same capacity. Figure 11 details the heat recovery circuit.

TABLE 6. Comparison of Costs of D₂O Produced at Savannah River and in GS Plants of New Design^{(a)(40)}

	Savannah River	New Plants	
	500 tons/year	50 tons/year	200 tons/year
Feedwater	\$ 0.40	\$ 0.00	\$ 0.55
H ₂ S makeup gas	0.30	0.05	0.05
Total materials	0.70	0.65	0.60
Salaries and operating labor	1.30	2.60	1.00
Maintenance			
Labor	1.33	2.45	1.30
Materials	0.52	0.30	0.25
Total direct maintenance	1.85	2.75	1.55
Utilities			
Steam or natural gas	4.35	2.00	1.85
Electric power	1.35	1.00	0.85
Cooling water	0.20	0.15	0.15
Total utilities	5.90	3.15	2.85
Miscellaneous	0.15	0.15	0.15
Total direct cost	9.90	9.30	6.15
Administrative and general expense	3.60	3.45	1.75
Operating cost (excluding capital charges)	\$ 13.50	12.75	\$ 7.90
<u>Capital Charge, 14%/annum</u>			
GS Process	\$ 15.40	\$ 7.55	\$ 7.25
Piping	(5.20)	(1.70)	(1.65)
Towers	(4.05)	(1.95)	(1.90)
Heat exchangers	(1.95)	(1.85)	(1.95)
Structure	(1.55)	(0.40)	(0.20)
Instrumentation	(0.85)	(0.75)	(0.55)
Switchgear and control buildings	(0.40)	--	--
Turbines	--	(0.50)	(0.60)
Other	(1.40)	(0.40)	(0.40)
Vacuum distillation plant	0.35	1.15	0.55
Electrolytic plant	0.20	--	--
Steam and electric power plant	2.10	0.55	0.30
Water treatment and distribution	1.00	0.60	0.35
H ₂ S manufacturing plant	0.15	--	--
Gas storage facilities and flare	0.25	0.80	0.30
General facilities	0.85	1.25	0.60
H ₂ S inventory at 50¢/lb delivered	--	0.10	0.10
Total capital charge at 14%	\$ 20.30	\$ 12.00	\$ 9.45
<u>Total Production Cost/lb D₂O</u>			
Operating cost and capital charges at 14%	\$ 33.80	\$ 24.75	\$ 17.35

(a) Costs are in 1960 U. S. Dollars

FIGURE 10. Flow Diagram for an Improved 200 ton/year GS Process Heavy Water Unit⁽⁴⁰⁾

Notes:

1. Dotted lines indicate regions in which heat transfer takes place between liquid streams or liquid and vapor streams.
2. Take-off and return lines between stages have been omitted to simplify the diagram.

FIGURE 11. Improved Heat Recovery Circuit for the GS Process⁽⁴⁰⁾

In 1965, Proctor, as part of an AEC contract with du Pont, updated his study to include additional considerations, especially cheaper heat and larger plant size.⁽⁴¹⁾ He assumed that the largest practical tower size is 16 ft in diameter, and a large plant will be a combination of 200 ton/year plants.

Table 7 shows his comparison of a 200 ton/year, a 2000 ton/year, and a 4000 ton/year plant. The greatest savings result from more efficient use of facilities and manpower in the larger plants. Again these are 1960 U. S. dollars and capital charges are 14%. If Proctor and Thayer are correct in their analyses, it is possible to decrease the cost of D₂O to about 40% $\left[(13.85/33.80) \times 100\% \right]^*$ of the SRP costs by building a new GS plant of suitable size and using present technology.

Proctor concludes that availability of very cheap heat (even at \$0.00/1000 lb steam) would have only a minor effect on D₂O costs - probably \$2.50 to \$3.00 a pound, or a further reduction of 25% in D₂O costs (to 32% of present SRP costs). He bases this conclusion on the statement, "In any dual temperature process, the gas and liquid streams must be heated and cooled repeatedly for the process to function correctly, and a large amount of heat exchange equipment is necessary, regardless of fuel cost or heat recovery considerations."

The major conclusion one may draw from the Proctor and Thayer studies is that if any large amount of D₂O is required (2000 tons/year or more), a new large GS plant will be more economical than existing plants. This conclusion is obvious from a comparison of Tables 6 and 7. The total cost for D₂O as produced in a new plant is approximately the same as the operating cost alone (and 0% capital charges) for existing plants.

Additional technological considerations not considered, or discarded, by Proctor and Thayer should be examined more critically.

* U. S. 1960 dollars

TABLE 7. Effect of Plant Size on Costs for Production of Heavy Water by GS Process⁽⁴¹⁾

Item	Operating Costs, \$/lb D ₂ O		
	200 tons/year	2000 tons/year	4000 tons/year
Materials	0.60	0.60	0.60
Salaries and labor	2.55	1.50	1.25
Utilities	2.85	2.85	2.85
Miscellaneous	0.15	0.10	0.10
Indirect	<u>1.75</u>	<u>0.70</u>	<u>0.55</u>
Total Operating Cost ^(a)	7.90	5.75	5.35
Capital Charges ^(b)	<u>13.10</u>	<u>11.15</u>	<u>10.70</u>
Total Production Cost	21.00	16.90	16.05'

(a) No escalation on operating costs

(b) 37% escalation on capital costs (1960-67 from Nelson Price Index)⁽²⁶⁾

- If very cheap heat can reduce cost of D₂O even further (to \$11/lb on a comparative basis), then serious consideration should be given to locating GS plants at sources of such heat (e.g., at a large nuclear reactor, where waste heat is normally sent to a dump condenser). This is discussed in greater detail in Section III, C, 2 of this report.
- Larger column sizes should be considered. Canadian General Electric plans to use columns 28 ft diameter, field-fabricated towers in their Port Hawkesbury plant.⁽⁴²⁾
- An exhaustive study should be made of column and plate design to obtain more efficient reflux, changes to reduce pressure drop or increase efficiency, and changes in concentrations, velocities, or temperatures.

Aside from the studies described above, there is no new published work in the U. S. on improvements in the GS process since installation of the SRP plant.

Other nations have erected or plan to erect pilot plants or full-scale production units (See Table 1). Rae⁽⁵⁾ has written an excellent summary of the economics involved in designing a GS process and discusses the Canadian installations and plans as of 1967.

In France, work on heavy water is coordinated by the Société pour l'Obtention du Deuterium (SOD).^{*} This combine constructed a GS pilot plant (one stage) at Lacq (Basses-Pyrénées) to take advantage of a large source of natural gas containing 15% H_2S . Lacq also had two other advantages: the power in this area was cheaper than in other parts of France, and the H_2S had a high deuterium content. When the H_2S was scrubbed with water, a feed water enriched in deuterium (189 ppm D_2O) could be obtained. They encountered trouble, mainly because the feed gas contained impurities, (CO_2 and small amounts of CH_4) which concentrated in the system and created composition transients. However, they saw no difficulty they considered insuperable and planned to construct a corrosion test facility. The entire project was dropped later when other methods, especially NH_3-H_2 chemical exchange, appeared to be more promising.

In Sweden, the Allmana Avenska Elektriska Aktiebolaget (ASEA) has studied methods of heavy water production for AB Atomenergei, the semi-State company of Sweden. In 1955 the ASEA built a small pilot plant to study variables in the GS process,⁽⁴³⁾ and in 1959 they erected a larger pilot plant to produce very dilute D_2O .⁽⁴⁴⁾

^{*} A consortium composed of the Commissariat à l'Energie Atomique (CEA), the Air Liquide, the Compagnie Française de l'Eau Lourde, the Office National Industriel de l'Azote, and the Société Nationale des Pétroles de l'Aquitaine.⁽³⁹⁾

This was essentially only a one-stage plant to study some problems of D_2O production on a larger scale. In an economic study of large scale production, they estimated D_2O could be produced in a 200 ton/year plant for about \$27.50/lb.⁽⁴⁵⁾ Since there was no apparent market for large amounts of D_2O , they did not actually construct a plant.

Deshpande et al.⁽⁴⁶⁾ investigated the economics of producing D_2O in India by the GS process. They considered the modifications suggested by Proctor and Thayer and concluded D_2O could be produced there for \$22.50/lb.

Of all nations, Canada has the greatest need for D_2O in the immediate future, since it manufactures and sells HWR's. Consequently it has the most aggressive program underway to produce D_2O .

Deuterium of Canada, Ltd. (DCL)* is building two plants at Glace Bay, Nova Scotia, each capable of producing 200 tons of D_2O per year.⁽¹⁶⁻¹⁹⁾ Each plant is a single unit of five stages (in contrast to SRP, which consists of 24 units of two stages each, and the recommended design of Proctor and Thayer of 4 units of three stages each). The first stage tower is 20 ft diameter by 200 ft high. The use of a single unit will reduce unit cost of D_2O , but will increase the seriousness of any mishap. The Province of Nova Scotia has furnished financial assistance and has provided cheaper power ($25\text{¢}/10^6$ Btu).⁽¹⁸⁾ DCL plans to use sea water as feed, thus taking advantage of the higher D_2O content (152 ppm) of the feed.⁽¹⁸⁾ Fresh water is not available at Glace Bay, but can be piped in at some additional expense.⁽¹⁸⁾ Since $NaCl + H_2S$ is corrosive to stainless steel, Deuterium of Canada plans to use Inconel for at least part of the internals of the first stage towers.⁽¹⁸⁾

* A combine, 50.002% owned by Industrial Estates, Ltd., a Nova Scotia Provincial development corporation, and 49.998% owned by Deuterium Corporation of U.S. J. Spevack, owner of Deuterium Corporation of the U.S., holds some basic patents on the GS process.

Carbon dioxide will be removed from the sea water to prevent scaling at 130°C, the temperature of the hot tower. With five stages, the product will be 99.7% D₂O. Only a very small distillation column will be required to bring the concentration to 99.85% (nuclear grade). Other features include improved heat recovery and addition of hydrosulfide to the feed water both to add makeup H₂S and to increase concentration of sulfide ion.⁽¹⁸⁾

The plant operation has been delayed by labor troubles and material supply problems.⁽¹⁸⁾ It is now scheduled to start operation during October 1968.⁽¹⁸⁾ The plant was originally estimated to cost \$33 million, but as of 1967, costs were re-estimated to be \$43 million (1967) Canadian dollars and operating costs were estimated to be \$7.00/lb. D₂O.⁽¹⁸⁾ This can be compared with Proctor and Thayer estimates for SRP (Table 8) and new plants by converting to U. S. 1967 dollars.

TABLE 8. Comparison of Costs for SRP and New Design GS Plants

	SRP Type ^(a)	PT 200	PT 2000	DCL 200
Capital cost, \$/lb-year ^(b)	(210.00)	(93.50)	(79.75)	(98.00)
Capital charges, \$/lb D ₂ O at 14%	29.40	13.10	11.15	13.75
Operating costs ^(c)	<u>13.50</u>	<u>7.90</u>	<u>5.75</u>	<u>6.50</u>
Total	42.90	21.00	16.90	20.25

(a) Assuming a new plant would be built exactly to the SRP design.

(b) Capital charges given in Proctor and Thayer escalated 35%, (1960-1967 escalation).

(c) No escalation on Proctor and Thayer figures for operating costs.

The DCL cost will be very close to that predicted by Proctor and Thayer for a 200 ton/year plant. DCL has contracted to furnish 5000 tons of D_2O to the AECL during the next 12 years at an average price of \$16.50/ton (U.S. 1967 dollars).^(18,19) In building the first 200 ton/year unit, DCL oversized all components except the first stage towers, so capital costs for the second unit may be less than \$43 million. All that will be required will be erection of heat exchangers, gas humidification, and dehumidification equipment, and two more pairs of hot and cold towers.

Canadian General Electric (CGE) is also building a large GS plant in Canada, at Port Tupper on Canso Strait.^(2,18,19,42) Very little is published about the design except that it is sized to produce 400 tons/year and will use very large first stage towers (28 ft diameter). CGE does not plan to use sea water, but will use fresh water containing 135 to 140 ppm D_2O .

b. Monothermal HDO- H_2S Exchange

The GS Process has several advantages. The feed (H_2O) is cheap, universally available, and unlimited; the reaction is ionic and therefore proceeds rapidly without a catalyst; the temperatures (30 to 130 °C) and pressures (20 kg/cm²) are moderate; and the corrosion problems (at least with fresh water feed) are not insuperable. One disadvantage of the GS process is the low α of 1.27. Only about $20\%[(\alpha - 1)/\alpha]$ of the deuterium is removed, and 80% is lost with the waste. This is not too big a problem since the feed is free, but it does mean more water must be treated (at least 35,000 lb water must be treated to yield 1 lb of D_2O), and capital costs, pumping costs, cooling water, and steam will all be much higher than for a similar process with a higher α .

An attractive variant on the GS process is the monothermal $\text{H}_2\text{S}-\text{H}_2\text{O}$ exchange. Here the α would be $\alpha_{30^\circ\text{C}} = 2.22$; recovery would be 55%; and volume of water would be reduced by a factor of 2.5 (from 35,000 lb H_2O /lb D_2O to 14,000 lb H_2O /lb D_2O). The pressure could be lower (between 1 and 2 kg/cm²); only one temperature would prevail throughout the system; and capital costs would be markedly decreased.

The difficulty in developing a monothermal chemical exchange system is to provide reflux. Such a reflux might be provided⁽⁴⁷⁾ by a reaction such as

The reaction must proceed in one direction under certain easily attainable conditions and in the reverse direction under another set of easily attainable conditions. The overriding criterion is expense. It must be possible to complete the reaction in both directions for about \$100/lb mole of D_2O (\$0.007/lb mole H_2O). No work has been done on this concept.

2. Ammonia-Hydrogen Chemical Exchange (NH_3 -HD)

This method utilizes the reaction

Since NH_3 contains three replaceable hydrogen isotopes and H_2 contains only two, $\alpha = 2/3$ K. Probably the best value for α is that determined by Ravoire et al.⁽⁴⁸⁾ who measured separation factors

between hydrogen and ammonia at atmospheric pressure over the temperature range -70 to +200 °C. They found for liquid ammonia over the range -70 to -25 °C.

$$\log \alpha_l = \frac{233}{T} - 0.2283 \quad (19)$$

To evaluate α above -25 °C, they used the separation factor for gaseous ammonia

$$\log \alpha_g = \frac{218}{T} - 0.1841 \quad (20)$$

and multiplied the values by a correction factor, α_v . Some values for α_l are listed in Table 9. Equations 19 and 20 are plotted in Figure 12.

TABLE 9. Separation Coefficients for Ammonia-Hydrogen Chemical Exchange

Temp °C	α_g	α_l	Temp °C	α_g	α_l
-60	6.89	7.32	0	4.11	4.21
-40	5.63	5.90	+20	3.63	3.69
-20	4.75	4.92	+40	3.25	3.28
			+60	2.95	2.96

The data of Ravoire et al. agree fairly well with those determined by Bigeleisen and co-workers. ⁽⁴⁹⁾

At first glance, the NH_3 -HD chemical exchange appears very attractive since the separation coefficients are so high, much higher than for the GS process. However, the exchange proceeds only with a catalyst and, even then, proceeds much more slowly than does an ionic reaction such as the H_2S -HDO exchange. In 1950, Wilmarth and co-workers found that KNH_2 catalyzes this reaction; ⁽⁵⁰⁾ even now after extensive research, no improved catalyst has been discovered. ^(2, 51) Amides of cesium and rubidium are effective but are too expensive to use. ⁽⁵²⁻⁵⁵⁾ Even potassium amide is expensive, since potassium itself is expensive and the preparation (dissolution of potassium in ammonia) is dangerous. The amide reacts with water or oxygen under violent and even explosive conditions. ^(2, 5, 49, 51, 56)

FIGURE 12. Equilibrium Constants for the NH_3 -HD Exchange Reaction

Bar-Eli and Klein⁽⁵⁷⁾ state catalysis of the exchange reaction is due to both free amide ion and undissociated alkali amide. They postulate a two-step mechanism with formation of an intermediate complex composed of a hydrogen, a catalyst, and a solvent molecule. Delmas et al.⁽⁵⁸⁾ disagree with this interpretation and state that catalysis is due entirely to the amide ions. Kenyon⁽⁵⁹⁻⁶¹⁾ and co-workers found that cyclic secondary amines, such as pyrrolidine and, to a lesser extent, other primary or secondary aliphatic amines, such as dimethylamine, enhance the catalytic action of KNH_2 .

The NH_3 -HD exchange can be dangerous. Not only is the catalyst explosive, but also hydrogen and (especially) ammonia can cause violent explosions. Large amounts of these materials must be handled and stored under pressure. However, industry has a great deal of experience in handling these materials. Plants producing up to 1500 tons of NH_3 per day are becoming commonplace.

One of the most serious drawbacks to the process is the limitations on supply of deuterium. Large amounts of hydrogen are required--100,000 scfm for a 200 ton/year plant. Hydrogen is too expensive to be discarded, and one of the following alternatives must be used.

1. Water may be the source of deuterium. For example, the depleted H_2 could be passed through a column counter-current to a stream of water to remove deuterium from the water; the depleted water would be discarded, and the enriched H_2 would serve as feed. The plant is independent: it can be constructed anywhere with no limitations on plant size. However, the $\text{H}_2\text{O}-\text{H}_2$ exchange adds another step to the process, and necessitates columns for humidification and dehumidification of the hydrogen stream (since no trace of water can be brought into contact

with the KNH_2).^(2, 39, 56) These extra operations increase the cost of the process to such an extent that it is no longer competitive.* At the present time, the independent process does not appear economical.⁽²⁾

2. If H_2 is the source of deuterium, the depleted hydrogen must be used in some other process, such as ammonia synthesis. Thus, the hydrogen is only borrowed, and the D_2O production process is dependent (parasitic) on some other process. This imposes a limitation on the size of the plant. For example, if the D_2O production is dependent on ammonia synthesis, the maximum size of the D_2O plant will be governed by the size of the largest ammonia plant. Since the largest ammonia plants now in common use are 1500 tons NH_3 /day, the largest D_2O plant will be 120 tons/year, which is small.

For the dependent process, several sources of supply have been visualized. Use of synthesis gas from an ammonia plant has already been discussed. If even larger ammonia plants are built, or if several large plants are built at one location, a larger D_2O production plant can be built, and the unit cost will be reduced.

The use of pure hydrogen rather than synthesis gas as feed would make the NH_3 - H_2 exchange much more attractive from an economic standpoint. Not only does the inert N_2 increase the amount of gases to be pumped around the system, but it also markedly lowers the gas velocity that can be used without flooding, with the result that the cross-sectional area of a tower required for accommodating a certain flow of synthesis gas will be almost three times that required for the same flow of hydrogen.⁽⁶²⁾ With H_2 as feed, tower sizes could be reduced, with corresponding decreases in both operating and equipment expense.

* A description of the complicated procedure required for the preliminary enrichment of H_2 is described in Section III, B, 3, e.

Solid oxide electrolyte cells have been proposed for dissociation of water vapor at high temperatures to produce cheap hydrogen (\$0.20 per 1000 scf)..⁽⁶³⁾ Such a development could have a significant influence on the production of heavy water. Production of pure H_2 from water vapor at a low price would remove the size limitation from the dependent chemical exchange processes (NH_3-H_2 , H_2O-H_2) and from hydrogen distillation, would reduce purification requirements, and would reduce the overall size of the plant and capital costs.

Recent technological advances⁽⁶⁴⁾ have reduced the price of electrolytic hydrogen to such an extent that production of very large amounts of pure hydrogen in the future appear to be highly probable. Electrolytic cells can operate at current densities as high as 1600 A/ft^2 , and very cheap dump power may be available, at least during certain periods, at large nuclear power plants.

Either the monothermal or bithermal variation of the NH_3 -HD exchange may be used. Each is being actively pursued by different groups.

a. Bithermal NH_3 -HD Exchange

An examination of Figure 12 shows that α varies considerably with temperature, the curve being especially steep in the lower temperature region. As with all bithermal processes, the highest separation factor will be obtained by operating at the greatest possible difference between the temperatures of the cold and hot towers and at the lowest temperature in the cold tower.

The upper temperature for the NH_3-H_2 exchange reaction is limited by pressure considerations. In addition, the values of α flatten out at the higher temperatures, and vapor pressure of ammonia increases rapidly, so not much is gained by going above 40°C .

The lower temperature is limited by the freezing point of NH_3 (-78°C). Very low temperatures (near the freezing point of NH_3) are not attractive since refrigeration costs and heat losses will represent too large an expense. Furthermore, although α is very high at low temperatures, the exchange rate also decreases with temperature, so longer contact times and higher towers are necessary.

One of the most extensive studies of the bithermal process is being made by Rae^(2, 5, 6) and co-workers of the AECL, they have tentatively chosen temperatures of -40 and $+50^\circ\text{C}$. Therefore,

$$\alpha = 6.05/3.10 = 1.95 \quad (21)$$

Figure 13 is a flow diagram of their process as they visualize it (1968), based on a 1000 ton/day NH_3 plant (70 ton/year D_2O).

Bancroft⁽²⁾ states that a dependent NH_3 -HD plant can produce D_2O at about the same price as the GS plants (presumably DCL and CGE plants), if the deuterium content of the feed is at least 123 ppm D/H (Figure 14). Higher deuterium content of feed, availability of larger NH_3 plants, or large sources of H_2 will all increase the economic advantage of the process.

Rae et al. have built a small pilot plant which they are using to obtain fundamental data, such as transfer coefficients.^(2, 65) They intend to continue the studies and in two to three years fabricate a pilot plant to produce sizeable amounts of D_2O .⁽⁶⁵⁾

Walker and Poole have proposed a modification of the flows in the NH_3 -HD bithermal exchange plant to reduce plant size.⁽⁶²⁾ In their scheme, illustrated in Figure 15, four columns are used: the transfer tower, the cold tower, a small cold reflux tower, and a hot tower. The transfer tower and the hot tower operate at 20°C , and the cold towers operate at -70°C . Synthesis gas ($\text{N}_2 + 3\text{H}_2$) circulates only in the transfer tower. A recirculating H_2 stream flows countercurrently to a recirculating NH_3 stream in the other three towers. Walker and Poole state that this modification will result in a decrease of plant volume by a factor of four.

FIGURE 13. Flowsheet for AECL Proposed $\text{NH}_3\text{-H}_2$ Exchange Unit to Produce 70 ton/year $\text{D}_2\text{O}^{(2)}$

FIGURE 14. Cost of Heavy Water as a Function of Synthesis Gas Feed Deuterium Content for a 70 ton/year $\text{NH}_3\text{-H}_2$ Exchange Plant⁽²⁾

FIGURE 15. Modification of NH_3 -HD Chemical Exchange Plant⁽⁶²⁾ to Effect Economy Through Reduction of Plant Size

b. Monothermal NH_3 -HD Exchange

The separation coefficient for the monothermal process is very high. At 30°C , it is 3.5; at lower temperatures it is even higher. The calculated recovery of deuterium from the H_2 feed stream at 30°C is 85%, and the required amount of liquid to be treated, the number of plates required, and hence the size of the plant are much smaller than for many competitive processes such as bithermal NH_3 - H_2 , GS, or H_2O distillation.

Again, the difficult part of the process is furnishing the chemical reflux. This can be done by cracking and resynthesizing the NH_3 . This, in itself, adds appreciably to the cost of the D_2O produced and requires the additional operations of addition and removal of catalyst. In the monothermal process, the flow of liquid NH_3 is discontinuous. The catalyst (KNH_2) must be removed from the NH_3 leaving the bottom of the exchange tower and added to the NH_3 added to the top. The catalyst may be recovered either by evaporation^(66, 67) or by electrolysis^(68, 69) of the NH_3 solution before it goes to the cracking unit. The recovered KNH_2 will be enriched in deuterium and must be depleted in a separate column before it is added to the makeup stream. These additional operations may be so expensive that the apparent economic advantage of monothermal operation may vanish.

By far, the greatest amount of work done on the monothermal NH_3 -HD exchange has been by the French.^(39, 48, 51-55, 66-78) After an extensive evaluation of hydrogen distillation, GS process, and bithermal and monothermal NH_3 -HD exchange, they have evidently discarded all but the monothermal NH_3 -HD exchange and are pursuing this approach with the intent of developing the process on a production scale. In 1965, Lefrancois et al. concluded that only the GS and the NH_3 -HD exchange processes were competitive; that distillation of H_2 , H_2O , or NH_3 was useful only for the final concentration steps, and that electrolysis of water is economic only as a dependent process.⁽⁵¹⁾

The choice of $\text{NH}_3\text{-H}_2$ exchange was based on the economics of production in France and other European countries. Fuel costs in France are about four times as high as in the U.S., electricity is about twice as high.⁽⁷⁰⁾ The $\text{NH}_3\text{-H}_2$ plants can be built even in relatively small sizes (20 to 50 tons/year) for a cost of \$100/lb-year.⁽⁷⁰⁾ Additionally, the French considered the $\text{NH}_3\text{-H}_2$ process would benefit most from future technological advances, and the plants could fit in well as dependent auxiliaries to existing industries (NH_3 production) in France.⁽⁷⁰⁾ The CEA together with the Houilleres du bassin du Nord et du Pas-de-Calais (HNPC), Societe Air Liquide, and Sulzer Brothers have investigated the problems connected with both monothermal and bithermal $\text{NH}_3\text{-H}_2$ exchange processes, have settled on the former as the most economic, have constructed five pilot plants, including two of large size, and have built and are operating a 20 ton/year production plant.

A small pilot plant at the Usines Chimiques de Mazingarbe (UCMa) was built in 1957 and was operated at 500 kg/cm^2 at temperatures between $+5$ and -50°C . The central column was 4 cm ID by 1 m in height (1250 cm^3 volume). The plant was operated intermittently to study the effects of process variables (pressure, time, flow, type of contact) on the enrichment. The flow of gas ($\text{N}_2 + 3 \text{ H}_2$) was varied from 7 to 100 m^3 (STP) per hour; the volume of liquid ($\text{NH}_3 + 40 \text{ g KNH}_2$ per liter) in the column varied from 125 to 600 cm^3 . As plates, they used fritted disks with porosities of 20, 50, and 100μ and, later, different types of perforated plates that could be used on an industrial scale. Their results showed:

- The exchange efficiency increased as the plate pore diameter decreased.
- The efficiency increased as the ratio of gas to liquid flow decreased. At low gas velocities, the efficiency was proportional to the height of the liquid on the plate.

- The efficiency was very low at low temperatures. For example, at -50°C with a liquid height of 5 cm and pores of 1 mm diameter, the efficiency was about 1% for a gas ($\text{N}_2 + 3 \text{H}_2$) flow of $13 \text{ m}^3/\text{hr}$, a catalyst concentration of 4%, and a pressure of 500 kg/cm^2 .
- The most effective contact system adaptable to a large-scale plant was an ejector designed by Sulzer Brothers. The working principle of the ejector is shown in Figure 16. (79)

In 1963, as the next step, the French group built a larger pilot plant with a column 35 cm ID, 2.5 m in height ($24,000 \text{ cm}^3$ volume), and capable of using a gas flow up to $5000 \text{ m}^3/\text{hr}$ (4 tons/year). (74)

With this plant, they were able to evaluate effects of geometry both at -30°C , (the temperature they consider optimum for plant operation) and at 35°C (the temperature of the catalyst recovery column). The tower could operate only intermittently (a maximum of three to four minutes after reaching temperature).

In supporting laboratory studies at Saclay and at Mazingarbe, they obtained data on:

- Precise values for α and for exchange rates. (48, 74, 76)
- Solubility of KNH_2 in NH_3 as a function of temperature. (75)
- Kinetics of the exchange reaction. (76)
- Kinetics of cracking NH_3 under pressure
- Corrosion of candidate materials (plastics, metals, joints) with and without stress.
- Determination of impurities in the synthesis gas.
- Deuterium content of the gas as a function of time.
- Solubility of NH_3 in the synthesis gas as a function of temperature. (Figure 17)
- Solubility of synthesis gas in NH_3 (with and without KNH_2) as a function of temperature.
- Physical constants (viscosity, density, surface tension, etc.) of the fluids.

1. Pressure tube
2. Gas channel
3. Gas pump
4. Separation chamber
5. Overflow tube
6. Liquid reservoir
7. Reaction chamber
8. Ejector
9. Baffle plates
10. Separator inlet
11. Separator plate
12. Pump discharge
13. Holes (sized to maintain desired liquid level)

FIGURE 16. Sulzer Ejector⁽⁷⁹⁾

FIGURE 17. Solubility of NH_3 in a Mixture of Gases ($\text{N}_2 + 3\text{H}_2$) in Presence of Liquid NH_3 at 300 and at 500 kg/cm² (78)

- Reactions (with O_2 , H_2O , CO , CO_2) leading to destruction of KNH_2 dissolved in NH_3 ,⁽⁷⁷⁾
- Two-stage purification of the gas.
- Evaporation of solutions (KNH_2 in NH_3) to concentrate and recover the catalyst.^(66, 69)
- Design of pumps for compressing and circulating $NH_3 + KNH_2$.
- Improved inhibitor systems.

Figure 18 is a flow diagram of the 20 ton/year pilot plant at Mazingarbe, which started operation in December, 1967.^(70, 71, 73, 74) The size of the plant was based on the size of the ammonia plant at Mazingarbe (650 tons/day), one of the largest in France at the time the design studies were made. The synthesis feed gas is compressed to 350 kg/cm^2 and purified in two operations to remove oxygen, water, and other impurities. The final purification is accomplished in the spray tower, T4, where final traces are removed by contacting with NH_3 . The feed gas is depleted in the reaction towers (T_1 and T_2) which operate at -25°C . The enriched NH_3 from the bottom of the reaction tower is sent to the evaporator. Most of the vaporized enriched NH_3 goes to the cracking unit where it is cracked, and the gases are sent as reflux to the reaction tower. Some of the enriched ammonia is removed as product (1.37%) and sent to the final concentration stages (NH_3 distillation, decomposition into N_2 and H_2 , burning, and purification). The residue from the evaporator, a concentrated solution of enriched KNH_2 in NH_3 , is sent to the scrubbing tower (T3) where most of the deuterium is removed by a countercurrent flow of gas at low pressure at 37°C . The gas containing most of the D_2 is combined with the reflux stream to the reaction towers. The KNH_2 solution, depleted in deuterium, is sent to the top of the reaction towers in proper proportion to provide the correct catalyst concentration. Additional details of the plant and its operation are given in References 71 and 74. The extra steps (cracking, evaporation of NH_3 from the catalyst, removing deuterium from the catalyst) are very expensive. Only by operation of full-scale

plants or large pilot plants will the data be available to make the necessary evaluation of the comparative economics of monothermal and bithermal processes. ⁽⁷²⁾

As a step in making the evaluation, the French have constructed a bithermal pilot plant (November 1967) and are now obtaining operating data. ⁽⁷²⁾

Very recently, larger NH_3 plants were constructed in France. ⁽⁷⁰⁾ One plant, having a capacity of 1000 tons/day was built in 1966. Three others of similar size are being constructed (1968), and three others (including one for 1500 tons/day are being proposed. At a ratio 7 tons D_2O /year for each 100 tons NH_3 /day, large D_2O plants could be built at centralized locations. ⁽⁷⁰⁾ The total production of NH_3 in France will soon be sufficient to permit construction of sufficient D_2O plants to produce 500 tons/year. As larger plants are built, the costs will decrease. However, the French feel they have shown that even the small plants (30 to 60 tons/year) can be operated at a profit, ⁽⁷⁰⁾ and this will be of value to the smaller countries who need D_2O but do not have sufficient resources to build the large plants. ⁽⁷⁰⁻⁷³⁾

3. Hydrogen-Water Exchange (H_2O -HD)

Hydrogen-water exchange is potentially a very attractive process because both water and hydrogen are relatively noncorrosive, and the separation factors are high. The exchange can be in either the vapor phase

or liquid phase

Cerrai et al.⁽³⁰⁾ determined several values for Equation 22 that differed only slightly from the theoretical. Their results may be expressed as

$$\log K = 188/T - 0.095 \quad (24)$$

Kirshenbaum⁽²³⁾ calculates for Equation 23 the following values for K: 4.69 at 0 °C and 2.47 at 125 °C. These results fit the equation

$$\log K = 238/T - 0.200 \quad (25)$$

Figure 19 is a plot of the equilibrium constants for Equations 22 and 23 against temperature.

The reaction is nonionic and requires a catalyst to proceed at a suitable rate. So far, the greatest drawback has been development of a suitable catalyst.

Of all potential D₂O production processes, hydrogen-water exchange is probably the most difficult to assess, because so many variations are possible, so many have been studied, and each has its advantages and disadvantages. The process may be monothermal or bithermal; either water or hydrogen may be used as feed material; the reaction may be in the vapor or liquid phase; and the catalyst may be either fixed, suspended, or dissolved. The process of greatest economic interest is one using water as a feed material since this would be an independent process that would not be limited in size. However, several difficult technical problems remain to be solved before this can become feasible. Since, according to Figure 19, the concentration of deuterium in water is always higher than in hydrogen at all reasonable temperatures, the efficiency of exchange from water to hydrogen will be low.

a. Monothermal Vapor-Phase H₂O-HD Exchange

Although both monothermal and bithermal processes have been evaluated, the only modification that has been used for production of tonnage lots of D₂O is the monothermal vapor phase exchange, which formed the basis for the plant at Trail, B. C.

FIGURE 19. Separation Factors for the Reactions: $\text{H}_2\text{O} + \text{HD} \rightleftharpoons \text{HDO} + \text{H}_2$

Early laboratory studies led to the development of two types of catalysts for the $\text{H}_2\text{O}-\text{H}_2$ reaction: Pt on a carrier such as charcoal (Urey et al. ⁽¹⁰⁾) and Cr_2O_3 (Taylor et al. ⁽¹⁰⁾). All studies showed that both Cr_2O_3 and Pt catalyzed the reaction effectively at temperatures of interest (50 to 100 °C) if the water was present only in the vapor phase, but the catalytic effect dropped to very low values if liquid water was present. It was recommended therefore that the vapor phase catalytic exchange be used.

This process was chosen in 1941 as one of the first processes for commercial development because enough experimental work had been done to give reasonable assurance of success. Moreover, at that time, Consolidated Mining and Smelting Company of Canada, Ltd. (Cominco) was operating a large electrolysis plant at Trail, B.C., and the catalytic exchange could be integrated with the electrolytic plant to form a cascade of alternating units of electrolytic cells and chemical exchange towers. The electrolytic plant normally produced H_2 for the manufacture of NH_3 . The D_2O plant was planned as a dependent, or parasitic, unit attached to the H_2 production plant. The H_2 produced was depleted of deuterium and then sent on to the ammonia fabrication tower. Essentially, as with the NH_3-H_2 parasitic process, the D_2O unit borrowed the H_2 and later returned it.

Some pilot plant studies were completed, and a catalytic exchange plant was constructed at Trail, B.C., by the U.S. Government with the help of Cominco, Columbia University (SAM), Badger and Co., Inc., and several other organizations. The plant, as completed in 1944, included two stages. The first stage, consisting of a cascade of alternating catalytic exchange units and electrolytic cells, produced 2.4% D_2O . This product served as feed to the second stage, a battery of electrolytic cells, and was concentrated to 99.8% D_2O .

Figure 20 illustrates one unit of the catalytic exchange tower in the first stage or "primary plant." Hydrogen gas from the cathode of an electrolytic cell flowed upward through the tower while water flowed downward.

Figure 21 illustrates countercurrent flow of gas and liquid. ⁽¹⁰⁾ The temperature in the tower was 65 °C, and the pressure was slightly less than atmospheric. Catalyst beds and bubble trays were arranged alternately so that liquid water did not touch the catalyst. The presence of liquid water in the catalyst bed reduced the efficiency of the catalyst by several orders of magnitude, probably because diffusion rates through the liquid were so low. The gas and vapor passing upward through the bubble plate were heated to prevent condensation and then passed through a catalyst bed (flow was downward to prevent disturbance of catalyst granules) and up through the next bubble plate and so on. The depleted hydrogen at the top of the column was sent on to the ammonia synthesis plant. The enriched water from the bottom of the tower was sent to an electrolytic cell for further enrichment.

Since the electrolytic cells were already in place, it was necessary only to construct the exchange towers and modify the existing plant to obtain correct flow patterns. The cost of the new construction and modification was \$2,350,000; operating costs were \$60,000/year; and the capacity was 10 T/year. Therefore, neglecting capital charges for the electrolytic cells, the cost of producing D₂O at Trail was (at 14% capital charges) \$19.50/lb D₂O. With suitable modifications and improvements, the process may produce D₂O at a reasonable price. ^(10,11) However, it is dependent on a supply of pure hydrogen, since the catalysts are easily poisoned by impurities normally present with commercially produced hydrogen.

b. Development of Catalysts for Liquid Phase H₂O-HD Exchange

The reaction between liquid water and hydrogen is represented in Equation 23.

Although studies by Urey, Taylor, and their co-workers showed that the catalytic efficiency was decreased by several orders of

FIGURE 20. One Unit of the Catalytic Exchange Tower in the Primary Plant

FIGURE 21. Schematic Diagram of HD-H₂O Catalytic Exchange Unit Showing Countercurrent Flow Through Tower⁽¹⁰⁾

magnitude when liquid contacted the catalyst beds, Roth et al.⁽³⁹⁾ conclude from their studies that the catalysts were equally effective in vapor and liquid phases. However, since the reaction was diffusion-controlled, the presence of liquid acted as a barrier to contact of the catalyst by the gas. Several methods may be used to increase gas diffusion rates: use of a soluble catalyst, extensive dispersion (e.g., colloidal suspension) of the catalyst, more efficient gas-liquid contactors, and increase of hydrogen pressure. Roth et al. showed that at pressures below 50 kg/cm^2 , reaction rates increased rapidly with increasing pressure (Figure 22).⁽³⁹⁾

Recent catalyst research has developed along several different lines. In 1955, the Institute Francais du Petrole (IFP) evaluated different catalysts for liquid-gas exchange. Their results (Figure 23)⁽³⁹⁾ showed colloidal platinum was by far the best, with Ni on Cr_2O_3 satisfactory at higher temperatures. The colloidal Pt catalyst, as with all Pt catalysts, is easily poisoned; the initial investment and cost of recovery would add materially to the cost of the D_2O . Becker estimates the investment for platinum catalyst would be about \$18/lb-year.

Fixed catalysts do not give satisfactory reaction rates even at high pressures. However, acceptable exchange rates can be obtained with dispersions of the catalyst in water⁽⁸⁰⁻⁸³⁾ although rates are still much lower than can be obtained in gas phase reactions. In one study at 30°C , with a platinum catalyst on activated charcoal powder suspended in the water, and with a column of normal sieve plates, the plate efficiency was 1%.^(12, 80) Even at this very low efficiency, liquid-phase exchange is much more economically attractive than gas phase.

Savic and co-workers⁽⁸⁴⁾ measured catalytic activities of several compounds and compared the results with those obtained with platinum on activated charcoal. Their results are shown in Table 10.

FIGURE 22. Influence of Pressure on Exchange Velocity
for $\text{H}_2\text{O-HD}$ Reaction ($\text{Ni-Cr}_2\text{O}_3$ catalyst)⁽³⁹⁾

FIGURE 23. Rates for the Reaction,
 $\text{HD} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{HDO}$,
 with Different Catalysts

TABLE 10. Reaction Rates with Heterogeneous Catalysts⁽⁸⁴⁾

Catalyst	Surface Area $S, \text{ m}^2/\text{g}$	Amount H_2 Adsorbed at $110^\circ \text{ C}, \text{ cm}^3/\text{g}$	Mean Pore Volume, mm^3	Effective Density, g/cm^3	Rate Constant k , sec^{-1}	Half-time of Exchange, sec	Equal Area Activity, $A = 10^3 k/S$
Ni-W	26.2	0.50	0.033	7.0	2.22	0.31	85
Cr-W	29.8	0.08	0.026	9.0	1.19	0.58	40
Co-W	37.0	0.21	0.040	12.5	0.32	2.17	9
Fe-W	21.7	0.03	0.023	8.2	0.00	--	0
Ni-Cr	256.8	3.90	0.352	1.5	4.65	0.15	18
Co-Cr	201.3	3.25	0.261	2.0	0.60	1.15	3
Fe-Cr	113.0	1.69	0.140	4.9	0.00	--	0
Ni-Mo	147.7	7.45	0.149	2.7	2.26	0.31	15
Cr-Mo	195.0	1.90	0.203	4.2	0.21	3.38	1
Co-Mo	96.6	3.75	0.119	2.4	0.15	4.50	1.6
Fe-Mo	49.5	0.20	0.046	4.5	0.00	--	0
NiO	45.2	10.62	0.052	6.0	0.39	1.76	9
CoO	50.3	3.40	0.056	3.7	0.00	--	0
Pt(a)	580.0	0.70	0.476	2.5	0.88	0.79	-

(a) Platinum on activated charcoal with 2.54% Pt. The surface area is measured for both platinum and charcoal.

The rate constant, k (Column 6), was calculated from Equation 26.

$$k = \frac{1}{t} \ln \frac{C_o - C_\infty}{C_t - C_\infty}, \text{ or } e^{-kt} = \frac{C_t - C_\infty}{C_o - C_\infty} \quad (26)$$

where C_o = starting concentration, C_t = concentration at time t , and C_∞ was calculated from the values of C_o and the equilibrium constant ($K = \alpha$). The half time ($T_{1/2}$) was

$$T_{1/2} = 0.693/k$$

They found that activity decreased in the order $\text{Ni} > \text{Cr} > \text{Co} > \text{Fe}$ and $\text{WO}_4 > \text{CrO}_4 > \text{MoO}_4$. Nickel tungstate was by far the most effective, and the iron compounds were of no measurable value.

Hydroxyl ion catalyzes the exchange reaction,^(85,86) but the reaction rate is still so low that the process is not economic.

Schindewolf^(85,86) investigated several homogeneous catalyst systems to determine relative rates for the H_2O -HD reaction. Ruthenium chloride in 4M HCl and cobalt cyanide in cyanide solution have some catalytic effect, but rates are very low. Basic systems (OH^- in H_2O , NH_2^- in NH_3 , OH^- ions in methyl alcohol) are more effective than either Ru or Co, but not as effective as the heterogeneous catalysts. At OH^- concentrations below 1M and hydrogen pressures below 100 atm, the rate of H_2O -HD exchange in a NaOH solution is proportional to the hydroxyl ion concentration and the hydrogen pressure. Table 11 lists data for different homogeneous catalysts and, for comparison, data for exchange with Pt on charcoal in water.

TABLE 11. Reaction Rates for Catalyzed H₂O-HD Exchange^(a)
(Homogeneous Catalysts and Pt-Charcoal)⁽⁸⁵⁾

<u>Catalyst</u>	<u>Temperature, °C</u>	<u>Rate mole/liter-sec</u>
Ru-chloride in 4M HCl	85	8×10^{-6}
Co-cyanide in 0.5M KCN	30	9×10^{-8}
Sodium hydroxide in water	115	1.5×10^{-7}
Potassium amide in ammonia	-53	$\sim 2 \times 10^{-5}$
Pt on-charcoal in water	30	1×10^{-4}

(a) Hydrogen pressure 1 atm, 1 liter solution or suspension with 0.01M, catalyst

Potassium amide, a very strong base in an ammonia system, is more effective than NaOH in a water system. Platinum on charcoal is much more effective than any of the homogeneous catalysts studied. Schindewolf suggests as an improvement a combination of catalysts that attack the hydrogen in different ways; for example, a transition metal (M) and a base (B).

Potassium hydroxide and other strong alkalis are corrosive to steel. Ishida and Benedict⁽⁸⁷⁾ evaluated diethylamine, which they considered as the most promising of all organic bases, but the rates were lower than for KOH.

Barthelemy⁽⁸⁸⁾ had some promising results with buffered Fe-EDTA solutions but obtained no consistent quantitative results. Benedict suggests quaternary amines or other paramagnetic ions might catalyze the reaction, but so far no evaluation of this idea has been made.

Recycle of a heterogeneous catalyst is expensive. The catalyst must be removed quantitatively, treated to remove adsorbed deuterium, and then reused.⁽⁸⁹⁾ Becker states that discovery of a suitable homogeneous catalyst could lead to production of very cheap heavy water. This seems to be such a promising line of attack that

additional work should be made. Recently developed procedures could be used to recover the catalyst by ion exchange or evaporation prior to stage conversion. The cost of recovery should be low; for example, Alcoa⁽⁹⁰⁾ states 1000 lb of pure water can be prepared for about \$0.03. The cost for catalyst recovery should be only about \$0.30/lb D₂O.

c. Monothermal Liquid-Phase H₂O-HD Exchange

If hydrogen or synthesis gas is used as feed, a monothermal liquid catalytic H₂O-H₂ exchange with phase conversion may be a profitable method to prepare D₂O.⁽⁹¹⁾ Becker⁽¹²⁾ states that heavy water produced by this method should be substantially cheaper than that produced by the GS process. The principal disadvantage is the relatively low reaction rate resulting from use of heterogeneous catalysts.

d. Bithermal H₂O-HD Exchange

Bithermal modifications of vapor phase catalytic exchange have been suggested by several workers, but for various reasons are not considered economical.

Harteck and Suss⁽⁹²⁾ proposed a stepwise equilibrium in the gas phase with repeated phase separation by condensation, but such a process is too expensive to be competitive.

Cerrai et al.⁽³⁰⁾ suggested low-temperature columns with a high-temperature reaction chamber (Figure 24, HTR). The steam and hydrogen are reacted in the HTR in the presence of a Pt catalyst (supported on charcoal or silica gel) at a temperature above 500 °C. The resultant vapor-gas mixture flows through Columns S and M, maintained at 70 to 100 °C, countercurrent to a stream of water which acts as feed. In Column M, deuterium exchange takes place in the presence of the supported catalyst beds to enrich the feed water. Part of the enriched water is taken as product to serve as feed for other stages or other processes. The rest of the water flows through Column S, which contains no catalyst. Here, exchange occurs only between liquid water and vapor. Benedict analyzes the economics of the process and suggests improvements.⁽¹¹⁾ The steam

FIGURE 24. Flow Diagram of a Hypothetical Bithermal H_2O -HD Catalytic Exchange Unit(30)

cost would be very low, about \$1.50/lb D_2O , but capital investment would probably be high. Neither Benedict nor Cerrai give any estimate of the probable capital cost. The high capital cost, according to Benedict, results from the relatively inefficient exchange with a heterogeneous catalyst and the need for elaborate contact towers. If a catalyst that would not be inactivated by liquid water were available, it would be possible to use simpler columns, and the capital expense would be reduced greatly. A homogeneous catalyst would permit use of ordinary packed columns, although some modification would be required to prevent continuous attainment of equilibria at temperatures between T_1 and T_2 .

The bithermal H_2O -HD exchange in which liquid water containing a suspended catalyst is cycled countercurrently to a hydrogen stream appears promising, ^(12, 80-82) but as yet suffers from lack of a suitable catalyst. In one pilot plant experiment to evaluate such a procedure, ^(12, 81) the operating conditions were:

Pressure	200 atm
Temperature of hot column	200 °C
Temperature of cold column	30 °C
Gas throughput	600 m ³ (STP)
Mole ratio (D_2 in gas)/(D_2O in liquid)	2.5
Catalyst concentration	25 g/l
Weight ratio (Pt/charcoal)	0.1

Figure 25 is a diagram of the pilot plant. The two series-connected cold towers had an overall length of 28 m, and the hot tower had a length of 17.5 m. The columns contained sieve plates; each plate had 276 holes, 1 mm in diameter.

FIGURE 25. Diagram of Pilot Plant for the System Hydrogen/Aqueous Catalyst Suspension, Built by Friedrich Uhde G.m.b.H., Federal Republic of Germany(12)

The enrichment factor* was measured periodically during the 3-month operating period and was at all times very close to 1.28, the value calculated.

The slow reaction rate at the lower temperature makes this type of process of marginal interest until a more effective catalyst is developed.

e. Single-Stage H₂O-HD Exchange for Preliminary Enrichment

The single-stage catalytic exchange of H₂O and HD has sometimes been considered as a method to provide a source of deuterium for a plant using some other process (e.g., NH₃-H₂ exchange).⁽²⁾

Figure 26 shows the complicated series of towers and equipment required for this preliminary enrichment of hydrogen. Raw water must be treated, preferably deionized. The catalyst is added to the water which then is passed downward through the chemical exchange tower (at 250 °C, 3000 psi). The depleted water passes through a filter or hydroclone to remove the catalyst and then goes to waste. The catalyst is expensive and must be recovered efficiently, treated by some method (such as contacting with a depleted gas stream) to remove the deuterium,⁽⁸⁹⁾ and then re-used. Depleted hydrogen from the first stage serves as feed to the first (cold) column in the NH₃-H₂ exchange.

Since the deuterium is transferred from H₂O to H₂, the separation coefficient will be the reciprocal of the α of Equation 23, and it will be advantageous to operate at as high a temperature as possible. However, the temperature should not be so high that the catalyst is destroyed or that material surfaces effect reversal of the isotopic equilibrium as the gas cools. Roth et al.⁽³⁹⁾ suggest

$$* A = \frac{N_1(1-N_o)}{N_o(1-N_1)}$$

where N_o = concentration of HDO in liquid at start

and N_1 = concentration of HDO in liquid at time of measurement

FIGURE 26. Catalytic H_2O -HD Exchange as First Stage in a D_2O Production Plant

operation at 600 °C or above. At this temperature, rates are sufficiently high, and α does not change much with temperature. Very little data on actual operations are available, and the process has many unknowns that must be resolved before it can be used. Bancroft⁽²⁾ states that H₂O-HD exchange necessary to provide feed to a bithermal NH₃-HD plant would account for 37% of the total cost of the D₂O.

Schindewolf and Hornke are more optimistic about the economics of H₂O-HD exchange with a homogeneous catalyst (NaOH or KOH).⁽⁸⁶⁾ They investigated the kinetics of the reaction in pilot plant studies and concluded the rates were sufficiently high to be of interest. Hydrogen containing 100 ppm D₂ was bubbled through a high-pressure autoclave containing enriched (0.3% D₂O) aqueous solution of NaOH. The autoclave measured 7.5 cm in diameter by 45 cm high and was filled with solution to a height of 18 cm. The hydrogen at 150 atm bubbled through a 1 mm diameter tube at a rate of 6 liters/hr. With 0.4 g/liter NaOH, at 200 °C, the plate efficiency (E), as expressed by Equation 28 was 25%.

$$E = \frac{C - C_0}{C_\infty - C_0} \quad (28)$$

where

C_0 = initial concentration (100 ppm)

C_∞ = maximum attainable concentration as calculated from equilibrium constant

C = concentration in effluent hydrogen

From similar studies, he concludes these experimental conditions are equivalent to a single-stage sieve plate column with a gas velocity of 250 m³_{eff}/hr-m². In an actual plant, only a few plates would be required and the column would be relatively small. The NaOH at these low concentrations could economically be discarded. If normal water was used as feed, the hydrogen could be enriched to a maximum of only 75 ppm, but pure H₂ with 75 ppm D₂ would probably

require smaller exchange columns in the subsequent concentration (e. g., by NH_3 -HD exchange) than synthesis gas with 150 ppm D_2 .

f. Future Directions

The economic status of the catalytic H_2O -HD exchange process depends almost entirely on the development of a suitable catalyst. The fixed catalyst beds using $\text{Ni-Cr}_2\text{O}_3$ or Pt on charcoal are satisfactory only for gas-phase towers with very pure H_2 as feed.

All catalysts used so far are too easily poisoned. For the liquid-phase towers, the catalyst must be made available and therefore must be present as either a colloidal suspension or a solution. The efficiency of colloidal suspensions is still so low that development of an economic process is questionable. The real need is for a homogeneous catalyst. Becker⁽¹²⁾ points out that development of a homogeneous catalyst resistant to poisoning could lead to very cheap D_2O . If a homogeneous catalyst is used, the feed may be either H_2 from an electrolytic plant or synthesis gas from an ammonia plant. The process may be bithermal, or monothermal with phase conversion as was done at Trail. Since all of these methods are parasitic, they are limited in size to probably 100 tons/year maximum. Water cannot be used as feed unless some method is developed for economically removing and handling the catalyst without too much loss or destruction of the catalyst. This may not be an insuperable problem since new procedures have been developed to desalt 1000 gal of water for about \$0.25. It may be possible to use these processes and recover the catalyst for less than \$1.00/lb D_2O .

A somewhat related, but probably unattainable goal, is the one mentioned by Benedict:⁽⁴⁷⁾ the discovery of a catalyst that would permit use of conventional adsorption towers. Perhaps research is indicated to find some combination of tower design, mechanical agitation, and catalyst that would make such an idea possible.

C. DISTILLATION

When a mixture is distilled, the component having the lowest boiling point is removed preferentially. Hydrogen and deuterium are sufficiently different in atomic structure that the boiling point of a compound containing hydrogen differs from that of the same compound with one or more hydrogens replaced by deuterium. Thus H_2 , HD, and D_2 all have different boiling points, and fractional distillation will remove first H_2 , then HD, and finally D_2 . This relatively simple method of isotope separation is the oldest procedure for concentrating deuterium, since Urey⁽³¹⁾ and his co-workers used fractional distillation of hydrogen in 1939 to concentrate and identify it as an isotope of hydrogen.

Distillation of hydrogen-containing compounds as a procedure for preparation of D_2O has attracted a great deal of attention because it is a simple process, uses well developed procedures and equipment, and does not require addition of chemicals that may be expensive, corrosive, or difficult to remove.

In distillation, the separation coefficient will be the ratio of the vapor pressures of the compounds being separated. Table 12 lists data of the separation coefficients for the four most common hydrogen-containing compounds at the triple point (lowest usable temperature for distillation) and at the boiling point.⁽²³⁾ For all four compounds, α decreases with temperature, and from this standpoint it is preferable to distill at low pressures. However, at low pressures, larger columns are required to obtain satisfactory flow rates, and operating equipment becomes more complex, so some compromise is necessary. Column design also becomes important to have an adequate number of plates without excessive pressure drop.

TABLE 12. Vapor-Pressure Ratios of Hydrogen and Deuterium Compounds Under Different Conditions⁽²³⁾

<u>Compounds</u>	<u>At Triple Point</u>	<u>At Boiling Point Under Normal Con- ditions</u>
H ₂ O/HDO	1.12	1.026
NH ₃ /NH ₂ D	1.08	1.036
CH ₄ /CH ₃ D	1.0016	0.9965
H ₂ /HD	3.6	1.75

1. Distillation of Hydrogen

Preparation of heavy water by fractional distillation of hydrogen isotopes has been reviewed by many workers at different laboratories, and all have concluded that this is potentially a means of producing cheap D₂O, but there are many unsolved problems. (2, 7, 8, 11, 39, 51, 93-95)

The separation coefficient is relatively high (Figure 27). For example, at the normal boiling point, α is 1.75 as compared to a value of 1.026 for water at its normal boiling point. The disadvantages that so far have sufficed to prevent H₂ distillation from becoming a competitive process are:

- Extremely low temperatures are required. Since hydrogen boils at -253 °C, the distillation must be done at some temperature not much above -250 °C. This poses formidable problems of insulation and refrigeration. Very large columns are required to handle the gas volumes for a plant of practical size (100-1000 T/year). No experience for operating at these temperatures with such large volumes is available.
- The feed must be very pure hydrogen. Since hydrogen produced commercially in large amounts is always accompanied by impurities, a series of purification steps is required. The purification is expensive and any residual impurities will cause trouble, since all

FIGURE 27. Separation Coefficient for Hydrogen Distillation⁽¹⁰⁾

gases except He have a boiling point higher than H_2 and will freeze out in various parts of the system and impede or block flow.

- Hydrogen exists in two forms, ortho and para. At room temperature, the hydrogen is 75% ortho- H_2 , but at $-235^\circ C$, it is all para- H_2 . The conversion from ortho to para is exothermic. If the mixture (25% p, 75% o) normally present at room temperatures is cooled to low temperatures and suddenly changes to the para form, enough heat will be given off to vaporize all of the hydrogen. A rapid transformation could cause instability and excessive loss in the system.
- The total production will be limited by the available hydrogen source (as with dependent NH_3 -HD plants). Maloney et al.⁽¹⁰⁾ discuss various sources of hydrogen for distillation plants and enumerate the impurities resulting from each source. It should be noted that this limitation may not be as important now with present large and potentially even larger sources of hydrogen available.*

As a first approximation, the separation coefficient obtained by distilling isotopic substances will be equivalent to the ratio of the vapor pressures. A normal mixture of hydrogen isotopes will contain H_2 , HD, and D_2 with almost all the deuterium present as HD. Figure 28 shows vapor pressures of the isotopes as a function of temperature.^(12, 96) Since deuterium exists principally as HD, and the vapor pressure of HD lies between those for H_2 and D_2 , the separation coefficient will depend on the ratio p_{H_2}/p_{HD} . The separation coefficient is actually slightly lower as shown in Figure 29, a plot of ratio of vapor pressures and α as a function of total vapor pressure.^(12, 96)

* See discussion on page 50.

FIGURE 28. Vapour-Pressure Curves
for the Isotopic Hydrogen Molecules
with Ortho and Para Modifications^(12, 96)

FIGURE 29. Ratio Between Vapour Pressures of Hydrogen and HD, and Elementary Separation Factor, α , as Functions of the Vapour Pressure of Hydrogen (12,96)

When normal hydrogen is distilled, the HD distills without disproportionating into H_2 and D_2 . The end product will then be HD. The engineers designing the early units proposed this HD be burned to provide feed for some plant using a different process for final concentration. Later, it was discovered that HD could be changed to H_2 and D_2 by contact with a catalyst at a higher temperature (room temperature).

In 1941, Urey and co-workers at Columbia University evaluated the H_2 distillation process.* Later, they worked with engineers at du Pont to design a pilot plant for producing 15 tons/year D_2O . They proposed that the product, HD, be burned to provide feed for an electrolysis unit that would concentrate deuterium to 99.8%. The cost of D_2O by this method was estimated to be \$66/lb, including capital charges at 20%.

In 1949, Clusius and Starke designed a unit suitable for large-scale production (Figure 30).⁽⁹⁷⁾ The French at CEA used this basic design with some improvements and constructed two pilot plants to produce 0.1 and 2.0 tons/year D_2O .^(39, 93) The large pilot plant (Figure 31), located at Toulouse, used as feed, pressurized synthesis gas containing approximately 75% H_2 , 24.5% N_2 and small amounts of A (0.25%), CH_4 (0.2%), CO (100 ppm), CO_2 (50 ppm), O_2 (< 5 ppm), and traces of water. The gas passed through absorbers (to remove H_2O) and through a series of condensers cooled with nitrogen at reduced pressure to remove all but 2% of the nitrogen and most of the other gases. The gas at 15 kg/cm² pressure and 63 °K was passed through reversing heat exchangers to remove the residual impurities. Figure 32 shows a working cycle of these heat exchangers, one exchanger is being cleaned by depleted hydrogen while the other is used to cool the feed stream. The flow through these exchangers was reversed periodically to vaporize and remove condensed impurities. The hydrogen was distilled first in a large column to

* This work was dropped when the decision was made to proceed with large-scale production of D_2O by distillation of water.⁽¹⁰⁾ Water distillation was admittedly more expensive but it presented fewer areas requiring development.

FIGURE 30. Flow Diagram of the Hydrogen Distillation Plant Designed by Clusius and Starke for Production of Deuterium⁽⁹⁷⁾

FIGURE 31. Flow Diagram of the 20 ton/year Hydrogen Distillation Pilot Plant Built by the French for Production of D_2O

FIGURE 32. Block Diagram (a) and Flow Diagram (b) of Reversible Heat Exchangers Provided in the Hydrogen Distillation Plant at Toulouse for Purification of Hydrogen⁽³⁹⁾

preconcentrate the deuterium. The liquid containing about 10% HD was then sent to a smaller column, where it was concentrated to essentially 100% HD. The HD was passed through a high-temperature catalyst bed and transformed to H_2 and D_2 and then to a final concentration column. The French workers found that hydrogen boiled easily with no foaming or excessive fog formation.⁽³⁹⁾

The pilot plant was designed in 1954, started up in February 1957, and used for various experiments to check design and operation. In 1958 the plant was modified and used for pilot runs, and from the end of 1959 until April 1961 it treated $4000\text{ m}^3/\text{hr}$ of synthesis gas.⁽⁴⁾

One of the main objectives of the plant was to obtain data necessary for designing a large industrial plant to produce 30 to 50 tons/year. The French estimated the capital equipment would be about \$200/lb-year, and the total cost would be comparable to D_2O as produced by the GS process. Since 1959, the French stopped work on the H_2 distillation, presumably because they were convinced the monothermal NH_3-H_2 chemical exchange was more economical.

Malkov et al.⁽⁹⁴⁾ describe the work in Russia to develop a H_2 distillation process. The Russian scientists constructed two pilot plants, one using relatively pure hydrogen as feed and the other using synthesis gas. With the aid of the information gained in these preliminary studies, they constructed an industrial plant capable of producing several tons of D_2O per year (as 10% HD). Malkov estimated capital costs for a large-scale plant to be about \$150/lb-year and operating costs about \$15/lb, giving a total cost (at 14% capital charge rate) of \$36/lb D_2O (1958 \$U.S.).

Figure 33 is a diagram of the Russian plant showing insulation.⁽⁹⁴⁾ The distillation column and the heat exchangers operated at temperatures below 80°K form one unit (Figure 33A), and the remainder of the heat exchangers and filters, all operating at temperatures above 80°K form another unit (Figure 33B). The

FIGURE 33. Side and Top Views of Russian Hydrogen Distillation Pilot Plant⁽⁹⁴⁾

- A Low Temperature Block, Including Distillation Column and Heat Exchangers Operated at Temperatures Below 80 °K
- B Block Containing Heat Exchangers and Filters Operated at Temperatures Above 80 °K

colder unit is insulated with two layers, an inner shield cooled with liquid nitrogen and an outer shield filled with hydrogen to prevent air condensation.

Kanda and co-workers at Japan⁽⁹⁸⁾ studied some of the parameters of H_2 distillation and constructed a small pilot plant to evaluate operating problems. In preliminary experiments with a small column, they found the distillation proceeded smoothly, high flow rates could be obtained without flooding, and yields were 90 to 95%. Their value for a HETP in a column with Stedman packing was 53 mm, considerably higher than the value of 30 mm for distillation of N_2-O_2 .

The Japanese pilot plant (Figure 34) processed electrolytic hydrogen. The distillation column was 2 in. ID by 4 ft high (24 theoretical plates) and operated with a reflux ratio of 4. The insulating space was packed with Santocel* and evacuated to 1.0 to 0.1 mm Hg. From their studies, they concluded a hydrogen distillation plant should be built, with H_2O -HD chemical exchange to provide enriched feed.

Bailey and others at A. D. Little investigated problems of feed gas purification and insulation.⁽⁹⁹⁾ They concluded:

- Nitrogen condenses as a gas-transportable fog, extensively under laminar flow conditions, and appreciably with turbulent flow. A filter must be placed after the reversing heat exchangers to remove this nitrogen.
- The best type of insulation consists of an inner vessel filled with silica aerogel powder with an atmosphere of hydrogen, and an outer vessel filled with perlite powder in a nitrogen atmosphere.

A small hydrogen distillation plant has been built at India to produce 14 tons/year of D_2O .

* Trademark, Monsanto Chemical Co., St. Louis, Mo.

FIGURE 34. Experimental Pilot Plant Used by Kanda and Co-workers to Investigate Procedures for Concentrating Deuterium by Distillation of Hydrogen⁽⁹⁸⁾

In 1954, the Department of Atomic Energy in India realized the need for a plant to produce heavy water to supply the reactors they planned to build. ⁽¹⁰⁰⁾ A large block of power was available at Bhakra Dam, and there was a regional need for large amounts of fertilizer. They calculated about 25,000 m³ (STP) of hydrogen per hour must be produced to synthesize the NH₃ required (at least 85,000 tons of NH₃ per year).

The Indian government accordingly requested three firms (Costain-John-Brown-UK, St. Gobain-France, and Vitro Engineering Division-USA) to propose procedures and tender bids. These three firms each proposed a different process: ammonia distillation, catalytic H₂O-HD exchange, and hydrogen distillation.

Table 13 reproduces cost data for these three processes. ⁽¹⁰⁰⁾ The ammonia distillation, although simple, required much higher capital costs, and catalytic exchange required higher operating costs (principally because so much steam was required for the specific tower design chosen). Consequently, hydrogen distillation was chosen because it was the most economical. It is interesting to note here that lack of a suitable catalyst for the catalytic exchange required much more elaborate tower design and much higher steam consumption. The estimated costs for producing D₂O from enriched hydrogen in this plant are given in Table 14.

The plant was erected and full-scale operation was started in 1962. A detailed description of operational history was given in a Geneva paper. ⁽⁹⁵⁾ The plant operated successfully for long periods without trouble; one run was as long as 10 months. The plant was shut down several times, usually for short periods to correct difficulties (deposition of nitrogen and oxygen in piping and valves) and plant modifications. Table 15 lists the typical costs incurred (Column 2) during actual operation of the Nangal plant along with estimated costs (Column 3) as calculated from Table 14. The actual costs are considerably lower.

TABLE 13. Cost Data for Candidate D₂O Production Schemes⁽¹⁰⁰⁾

	<u>Ammonia Distillation</u>	<u>Catalytic Exchange</u>	<u>Hydrogen Distillation 5000 Nm³ H₂/hr</u>
Overall D ₂ O recovery efficiency, %	35.75	52.6	55.6
Production level, metric tons D ₂ O per year	9.15	14.3	15.0
Erected cost of the plant, \$ x 10 ⁶	3.03	4.392	4.255
Unit investment cost, \$/kg year	337	283	284
Total annual charges, \$ x 10 ⁶	0.733	1.1	1.002
Unit capital charges, \$/lb	30.4	25.5	25.6
Unit operating cost, \$/lb	5.9	9.3	4.7
Unit cost of D ₂ O, \$/lb	36.3	34.8	30.3
Power consumption, kW-hr/kg D ₂ O	3380	177	2000
Steam metric tons/ kg D ₂ O	--	9.1	--
equivalent, kW-hr/kg D ₂ O		6000	

If a \$2,750,000 plant cost and a 16.8% capital charge are assumed, and if the appropriate multiplying figure (2.85/2.20) is used to change costs from 1958 to 1967, the capital costs for the plant would be \$19.10/lb D₂O to give a total cost of \$27.37/lb D₂O. The feed containing 600 ppm HD was furnished by the electrolytic plant. No figures are given for the cost of operating the electrolysis plant or the cost for producing this enriched feed. This cost can be estimated by assuming (Figure 4) that this preliminary enrichment represents 35% of the total production cost. This would place the total at

$$\frac{\$27.37}{0.65} = \$42.30/\text{lb D}_2\text{O}$$

TABLE 14. Estimated Costs for Producing D₂O from Enriched Hydrogen at the Nangal Plant⁽¹⁰⁰⁾

	<u>Cost</u>	<u>Total Cost</u>
Erected cost of the plant, \$ x 10 ⁶	2.75	
Annual charges		
Capital charges at 16.8%, \$ x 10 ⁶	}	
Depreciation at 10%, \$ x 10 ⁶		
Interest at 45%, \$ x 10 ⁶		
Insurance and taxes 2.3%, \$ x 10 ⁶		
Operating charges:		
Power, \$ x 10 ⁶	0.150	
Inert gas, \$ x 10 ⁶	0.012	
H ₂ loss, \$ x 10 ⁶	0.090	
Labor (operational and maintenance), \$ x 10 ⁶	0.050	
Overheads, \$ x 10 ⁶	0.025	
Maintenance (material), \$ x 10 ⁶	0.055	
Miscellaneous (cooling water, chemicals, lubricant) \$ x 10 ⁶	0.015	
Total operating charges, \$ x 10 ⁶		0.377
Total annual charges, \$ x 10 ⁶		0.839
Yearly production of heavy water, tons/yr (8000 hr/yr)		14.00
Unit capital cost, \$/lb	14.8	
Unit operating cost, \$/lb	12.4	
Total unit cost of heavy water, \$/lb		27.2

TABLE 15. Actual and Estimated Operating Costs to Produce D₂O from Enriched Hydrogen in the Nangal Plant (India)⁽⁹⁵⁾

<u>Item</u>	<u>Average Cost, \$/lb</u>	
	<u>Actual</u>	<u>Estimated</u>
Power	2.82	4.86
Nitrogen	0.08	0.41
Hydrogen	1.30	3.02
Labor (Operational and Maintenance)	3.53	1.64
Miscellaneous (cooling water, chemicals, lubricants, etc.)	0.54	2.27
Total	\$8.27	\$12.20

A larger plant would be more economical. If the cost of hydrogen feed could be reduced, or if the cost for this feed could be shared with some other process, and if continued progress could be made in increasing the efficiency of hydrogen distillation, this process could become competitive. Gami and Rapial discuss the feasibility of operating at reduced pressure with a series of three columns (0.4, 0.56, and 0.83 kg/cm² absolute). This poses the problem of air ingress, but Gami and Rapial think this is not an insuperable problem.

Purification of hydrogen did not appear to be too great a problem; the impurities were removed by adsorption or by reversible heat exchangers. However, no system removed oxygen and nitrogen completely. The residual oxygen varied between 0.05 to 0.15 ppm, and residual nitrogen varied between 0.1 to 0.6 ppm. These impurities deposited in the cold region but did not concentrate at one spot and hence did not tend to cause choking. Moreover, they did not adhere to the metal surface and could be blown out. Presence of oxygen in the hydrogen is potentially dangerous and may require periodic shutdowns to clean the system.

The plant appeared to be very flexible, and many parts could be shutdown for a few hours without adversely affecting plant operation. The overall recovery of D₂ was 85 to 90%.

Newton describes hydrogen production and purification on an industrial basis.⁽¹⁰¹⁾ Of interest is the fact that the largest plants he mentions have a capacity of 4 tons/day, which corresponds to 2 tons/year of D₂O. A D₂O production plant would be 10 to 1000 times as large. Impurities are all removed by adsorbents, which are periodically reactivated. Table 16 lists the common impurities associated with different sources of hydrogen, and the removal agents.

As mentioned in previous paragraphs, uncontrolled o-p conversion is highly undesirable, because the heat released will cause instabilities that may result in considerable loss of hydrogen. Two methods of obviating this uncontrolled release of heat are:

TABLE 16. Concentration Levels and Removal Systems for Impurities in Hydrogen Sources⁽¹⁰¹⁾

Impurity	Electrolysis ^(a)	Impurity level for different sources, vol. %			Removal System
		Partial oxidation of oil or gas	Steam reforming of natural gas	Refinery off gas	
H ₂ O	(b)	(b)	(b)	(b)	Activated alumina, molecular sieves
Aromatics	-	-	-	<0.3	Oil scrub
CO ₂	-	<0.01	<0.0005	<0.06	Caustic scrub, molecular sieves.
C _n H _{2n+2} ^(c)	-	-	-	5, max	Partial condensation, adsorption, distillation
O ₂	<0.01	-	-	-	Catalytic reaction
N ₂	<0.01	0.04	<0.1	<0.06	
Ar	-	0.02	-	-	Adsorption on
CH ₄	-	0.48	5 to 10	18, max	activated carbon
CO	-	0.10	<0.001	<0.06	at low temperatures
Other	<0.01 ^(d)	-	-	<0.2 ^(e)	Adsorption on activated carbon

(a) Also contains traces of oxides of nitrogen

(b) Saturated

(c) Except methane

(d) Cl₂

(e) H₂S, SH⁻, S⁼

(1) prevent the reaction from occurring, and (2) make the reaction occur in a controlled manner. The ortho form is unstable at very low temperatures but may exist if no catalytic surfaces are present. Thus, the hydrogen may be liquefied and distilled without releasing the heat of conversion in an uncontrolled manner if care is taken to eliminate any material that may act as a catalyst. A safer method, and one that must be used if liquid hydrogen is to be stored for any length of time, is the release of the heat of conversion gradually as the hydrogen is being cooled. The aim is to remove the heat at as high a temperature as possible. Lawson describes the controlled release of heat of conversion with catalysts in a staged converter. Hydrous iron oxide and chromic oxide are satisfactory, but the recently developed Apachi* catalyst, is much superior and can be used indefinitely (with periodic reactivation).

Hydrogen distillation as a process for producing D_2O was studied at the National Bureau of Standards Cryogenic Laboratory in Boulder, Colorado. Timmerhaus et al.⁽¹⁰²⁾ discuss their findings concerning design considerations for a production plant. As part of the program, a pilot plant (Figure 35) was constructed to concentrate deuterium from the normal concentration of 0.03% HD to 3.0% HD. The plant operated at 1.3 atm to eliminate possibility of air leakage into the hydrogen stream. The calculated recovery was 85%, and the designed production was 45 lb/year.

Many features of hydrogen distillation are encouraging. The hydrogen boils smoothly with no foaming and no entrainment if vapor velocity and plate height are maintained at correct values. A very low pressure drop, small holdup, stable column operation, and small plate spacing all indicate that relatively small columns can be used in the production plant.

* Developed by Air Products under a U. S. Air Force contract.

FIGURE 35. Pilot Plant Used by Timmerhaus et al. to Concentrate Deuterium by Distillation of Hydrogen⁽¹⁰²⁾

In summary, hydrogen distillation is potentially an economic method of producing D_2O , but not enough actual data are available to determine just what the unit costs will be. Some of the problems are not as difficult as they were once thought to be, but many still need to be solved. More research and development is required before hydrogen distillation can compete with the GS process, at least in the U. S.

2. Distillation of Water

Distillation of water has never been considered an economical process for manufacture of D_2O . It was used early in the project (1942) by USAEC to prepare several tons of D_2O , principally because the process was simple and could be developed with a high assurance of success.^(10, 11) The equipment required was of standard design; no critical materials were required for construction of the plants; and production could be started sooner than with other processes. Later, when sufficient time was available to develop an alternate more economical procedure, water distillation was not considered.

Deuterium is present in normal water to the extent of 130 to 150 ppm (see Table 2) and exists almost entirely as HDO in accordance with the equation:

When natural water is fractionally distilled, H_2O will come off preferentially, and the HDO will concentrate in the liquid. As the H_2O is removed, the deuterium content of the residue increases and the relative amounts of H_2O , D_2O , and HDO change in accordance with the equilibrium constant, Equation 29. At high concentrations of deuterium, the liquid is essentially all D_2O and HDO.

It was early proposed by Lewis and Cornish⁽¹⁰³⁾ that the vapor pressure of HDO is the geometrical mean of vapor pressures of H_2O and D_2O

$$p_{HDO} = \sqrt{p_{H_2O} \cdot p_{D_2O}} \quad (30)$$

Later measurements indicated Equation 30 is at least approximately correct. (104)

If Equation 30 holds, then

$$\alpha = p_{\text{H}_2\text{O}}/p_{\text{HDO}} = (p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}})^{1/2} = p_{\text{HDO}}/p_{\text{D}_2\text{O}} \quad (31)$$

The separation coefficient should be equal to the square root of the vapor pressure ratios at either low concentrations of deuterium (when the water is composed almost entirely of H_2O and HDO) and at high concentrations (when the water is composed almost entirely of HDO and D_2O).

Merlivat and co-workers determined values of $\alpha_{\text{H}_2\text{O-HDO}}$ by evaporating natural water (about 300 ppm HDO) in a one-plate still attached directly to a mass spectrometer. (105)

For studies between 0 and 60 °C, they used a flask immersed in a thermostatted bath and connected directly to a mass spectrometer. A large volume of water was used to ensure that the withdrawal of the gas sample did not affect the equilibrium. The temperature of all portions of the equipment leading from the flask to the mass spectrometer was higher than that of the flask to prevent condensation. The liquid was stirred vigorously at all times with a magnetic stirrer. At temperatures around 100 °C, a one-plate still was operated under equilibrium conditions, and the vapor and liquid phases were analyzed. At temperatures above 200 °C, the water was agitated in an autoclave. Simultaneous measurements of temperature and pressure were taken to assure equilibrium. Portions of the liquid phase were removed by means of capillaries equipped with 3-way valves. Samples were withdrawn, analyzed, and compared with the solution initially placed in the autoclave. They found that Equation 31 is approximately but not entirely correct.

Table 17 lists vapor pressures for H_2O and D_2O , the vapor pressure ratios ($p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}}$), the square roots of the vapor pressure ratios, and the separation factors for concentration of deuterium by distillation. The separation factors are practically identical to the square roots of the vapor pressure ratios for temperatures below 275 °C. Above 275 °C up to the critical temperature, α (as measured by Merlivat) again increases while $(p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}})^{1/2}$ continues to decrease. The separation factors are discouragingly low. For example,

at 50 °C, $\alpha = 1.05$. The very low separation factor means many theoretical plates are required, very large volumes of water must be distilled, columns will be very large, and steam requirements will be high. The requirements have been calculated by Benedict who uses the following values:

feed concentration $x_F = 0.000149$

product concentration $x_P = 0.998$

TABLE 17. Vapor Pressures of H₂O and D₂O and Separation Coefficients for Concentration of Deuterium by Distillation.

Temp., °C	^(a) P _{H₂O} kg/cm ²	^(b) P _{D₂O} kg/cm ²	P _{H₂O} /P _{D₂O}	(P _{H₂O} /P _{D₂O}) ^{1/2}	α ^(c)
3.8		0.00681			
10	0.01252	0.01050	1.1924	1.092	1.091
20	0.02384	0.02051	1.1624	1.078	1.079
30	0.04327	0.03804	1.1375	1.066	1.069
40	0.07521	0.06728	1.1179	1.057	1.060
50	0.12577	0.11418	1.1015	1.050	1.053
60	0.20308	0.18665	1.0880	1.043	1.046
70	0.31718	0.2951	1.0748		
80	0.48276	0.4527	1.0664		
90	0.71478	0.6757	1.0578		
100	1.03323	0.9836	1.0505	1.025	1.029
120	2.0245	1.9511	1.0376		
140	3.6855	3.587	1.0275		
160	6.3027	6.185	1.0190		
180	10.224	10.106	1.0117		
200	15.851	15.766	1.0054	1.0027	1.003
225	25.998	26.026	0.9989	0.9994	0.999
250	40.538	40.78	0.9940	0.997	0.997
275	60.608	61.22	0.9900	0.995	0.996
300	87.60	88.68	0.9878	0.994	0.997
325	122.96	124.79	0.9853	0.993	0.998
350	168.58	171.63	0.9821	0.991	0.999
371	213.96	221.49(crit)			
374	217.72(crit)				

(a) International Critical Tables

(b) V. A. Kirillin (Ed in chief). Heavy Water, Thermo-physical Properties
State Power Press, Moscow-Leningrad. 1963. (in Russian)

(c) Ref. 105

To be consistent with the previous discussions, we have changed the value of X_F to 0.000140.

The minimum number of plates will be (Equation 32)

$$n_{\min} = \frac{\log \frac{0.998 \times 0.99986}{0.00014 \times 0.002}}{\log 1.05} = 309 \quad (32)$$

The actual number of plates will be about twice this or, according to Benedict,⁽¹¹⁾ about 700.

The minimum consumption of steam will be

$$\frac{\alpha}{\alpha-1} \cdot \frac{X_P - X_F}{X_F} = \frac{1.05}{0.05} \cdot \frac{0.99786}{0.00014} = 150,000 \text{ lb} \quad (33)$$

In a practical plant, the steam requirement will be between 200,000 and 250,000 lb steam per pound of D_2O produced.⁽¹¹⁾

The recovery of D_2O from the feed will be

$$\frac{\alpha-1}{\alpha} = 0.05 \quad (34)$$

Approximately 95% of the D_2O will be sent to waste. This is really not a disadvantage since the feed material is free and unlimited in supply.

Three large water distillation plants were built by du Pont for the U.S. government in 1943 and were started up during 1944.^(10, 11)

The plants were built at the following locations: Morgantown, W. Va. (MOW); Childersburg, Ala. (AOW); and Newport, Indiana (WROW). The design and production capacities for the three plants are listed in Table 18.

Less than 2% of the D_2O was recovered from the water. The plants cost \$14,500,000. The heavy water was concentrated to 90% D_2O ; further concentration to 99.8% was done by electrolysis.

TABLE 18. Design and Capacities of Manhattan District Water Distillation Plants. ⁽¹⁰⁾

<u>Plant</u>	<u>H₂O processed, lb/hr</u>	<u>D₂O capacity, tons/month</u>	
		<u>Design</u>	<u>Actual</u>
MOW	177, 000	0. 4	0. 28
AOW	387, 000	0. 8	0. 32
WROW	556, 000	1. 2	0. 66

Table 19 gives some idea of the size of the plants. Figure 36 is a diagram of the MOW unit. Table 20 gives information about the towers at MOW.

The first three stages (five towers) each contained 70 to 90 bubble plates; stages 4 through 8 were packed columns with 72 ft packing (5/8 in. Raschig rings). The last column shows the concentration of D₂O (equivalent weight percent) obtained in each stage at MOW.

In October 1945, after operating two years and producing 22.8 tons D₂O, the plants were shut down. ^(10, 11) Total operating costs were \$9,536,000. Fixed charges were 14% x 2 x 14,459,000 = \$4,050,000. Total charges were \$13,586,000 or \$300/lb D₂O. The du Pont engineers figured that the plants could be improved to produce D₂O at a cost of \$150/lb at the present location, or \$109/lb at the location where cheap power (natural gas) is available. Today, the capital costs would, of course, be much higher today because of escalation (factor of 3).

Benedict ⁽¹¹⁾ analyzes the distillation costs and discusses possible improvements.

The bubble cap plates were relatively inefficient. Benedict proposes Spraypak packing, which would allow a throughput 7.2 times that through the plate columns used at the three old units. Cost and pressure drop per theoretical plate (4.7 mm Hg) are about the same.

TABLE 19. Equipment at Manhattan District Water Distillation Plants⁽¹⁰⁾

WROW			AOW		MOW	
Stage	No.	Description	No.	Description	No.	Description
1	15	15 ft diam x 80 plates	10	15 ft diam x 80 plates	5	15 ft diam x 80 plates
	15	12 ft diam x 90 plates	10	12 ft diam x 90 plates	5	12 ft diam x 90 plates
2	3	10 ft 6 in. diam x 72 plates	2	19 ft 6 in. diam x 72 plates	1	10 ft 6 in. diam x 72 plates
	3	8 ft diam x 83 plates	2	8 ft diam x 83 plates	1	8 ft diam x 83 plates
3	1	5 ft 6 in. diam x 72 plates	1	4 ft 6 in. diam x 72 plates	1	3 ft 4 in. diam x 72 plates
4	1	2 ft 6 in. diam x 72 plates	1	2 ft diam x 72 plates	1	18 in. diam x 72 plates ^(a)
5	1	18 in. diam x 72 plates ^(a)	1	16 in. diam x 72 plates ^(a)	1	10 in. diam x 72 plates ^(a)
6	1	18 in. diam x 72 plates ^(a)	1	16 in. diam x 72 plates ^(a)	1	10 in. diam x 72 plates ^(a)
7	1	18 in. diam x 72 plates ^(a)	1	16 in. diam x 72 plates ^(a)	1	10 in. diam x 72 plates ^(a)
8	1	18 in. diam x 72 plates ^(a)	1	16 in. diam x 72 plates ^(a)	1	10 in. diam x 72 plates ^(a)
Calandrias						
1	15	1500 ft ²	10	1500 ft ²	4	1500 ft ²
2	3	750 ft ²	2	750 ft ²	1	2200 ft ²
3	1	200 ft ²	1	132 ft ²	1	750 ft ²
4	1	50 ft ²	1	33 ft ²	1	75 ft ²
5	1	20 ft ²	1	14 ft ²	1	20 ft ²
6	1	20 ft ²	1	14 ft ²	1	8 ft ²
7	1	20 ft ²	1	14 ft ²	1	8 ft ²
8	1	20 ft ²	1	14 ft ²	1	8 ft ²
Condensers						
1	15	Jets	10	Jets	5	Jets
2	3	6000 ft ²	2	6000 ft ²	1	6000 ft ²
3	1	1600 ft ²	1	1070 ft ²	1	600 ft ²
4	1	400 ft ²	1	264 ft ²	1	140 ft ²
5	1	160 ft ²	1	112 ft ²	1	60 ft ²
6	1	160 ft ²	1	112 ft ²	1	60 ft ²
7	1	160 ft ²	1	112 ft ²	1	60 ft ²
8	1	160 ft ²	1	112 ft ²	1	60 ft ²

(a) Packed

FIGURE 36. Flow Diagram of Water Distillation Unit of the MOW Primary Plant⁽¹⁰⁾

TABLE 20. Towers at MOW Distillation Plant. ⁽¹¹⁾

Tower	Number in parallel	Diam	Number of plates	Pounds of vapor per hour	Pressure, mm Hg		Atom % D, bottom
					Top	Bottom	
1A	5	15 ft	80	(177, 000)	67	238	
1B	5	12 ft	90	177, 000	236	536	0. 117
2A	1	10. 5 ft	72	(21, 200)	129	340	
2B	1	8 ft	83	21, 200	340	645	1. 40
3	1	3. 3 ft	72	3050	124	343	3. 8
4	1	1. 5 ft	72 ^(a)	725	127	440	10. 0
5	1	10 in.	72 ^(a)	190	127	340	11. 5
6	1	10 in.	72 ^(a)	185	124	328	21. 2
7	1	10 in.	72 ^(a)	200	124	333	56. 4
8	1	10 in.	72 ^(a)	200	127	308	89
Total	18		757	202, 750			

(a) Number of theoretical plates in packed column.

In the Manhattan District plants, high-pressure steam (233 °F) was produced and throttled down. Benedict proposes as improvements: (1) use of low pressure (22 psia) exhaust steam from the turbines of a power plant, or (2) use of a vapor recompression system.

Benedict then calculates costs of producing D₂O by distillation of water in a plant of improved design built in 1955 operating with 22 psia exhaust steam. The steam would cost \$0.15/1000 lb. Other operating costs and capital cost would be the same as for the Manhattan District plants, but production rates would be 7.2 times as great; the escalation factor for plant construction (1943 to 1955) is 2.2.

$$\text{Investment costs } \frac{50.4}{7.2} \times 2.2 = \$155/\text{lb-year}$$

Capital charges (at 14%)	\$21.70
Steam (178 x \$0.15)	26.70
Other operating expenses ($\frac{\$53}{7.2}$) =	<u>7.40</u>
	\$55.80

Recent advances make the water distillation seem even more competitive. A new type of distillation unit developed by Alcoa is said to be able to produce 1000 lb of ultrapure water from brackish or salt water at a cost of \$0.03.⁽⁸⁹⁾ Use of similar design could reduce steam costs to $178 \times \$0.03 = \5.34 and total costs to \$34.74. The overriding expense is the capital charge. With escalation, this would be \$34 in 1967 and total cost would be about \$47/lb of D_2O . Unless some method is found to reduce the capital cost by a factor of at least 3, water distillation will not be a competitive process.

The very high capital costs result from the large volumes of water that must be distilled. A 500 ton/year plant must distill 20,000,000 lb of water per hour. Recently developed packing material may be used to reduce the HETP and pressure drop per theoretical plate.⁽¹⁰⁶⁻¹⁰⁸⁾ This would help, not only by reducing the overall column height, but also by reducing the maximum pressure in a column and thus increase the efficiency. For example, if the effective vapor pressure in a column could be reduced from 90 mm to 30 mm, α would increase from 1.052 to 1.066, and column volume would decrease by 40%.

Baertschi and Kuhn⁽¹⁰⁹⁾ describe some experiments that have been conducted with a typical high efficiency column. The Kuhn column consists of a large number of narrow parallel fractionating tubes with a complicated device to distribute the feed to the individual columns. Figure 37 illustrates the design and operation of the column. The feed is continuously evaporated in the boiler (1), and the steam is distributed by means of superheated capillaries in (2) to the various fractionating tubes. The overhead water in (3) is equally distributed by capillaries as reflux to the fractionating tubes; (5) is a differential manostat for maintaining proper pressure relationships. The lower part of the fractionating tubes is superheated by steam entering into the heating chamber (6) from the steam generator (7). Since the distillation is carried out under reduced pressure, maintained by the manostat (13), all the downflowing water is completely evaporated along the inner walls of the fractionating tubes in the

FIGURE 37. Pilot Plant Used by Baertschi and Kuhn to Concentrate Deuterium Oxide by Fractional Distillation of Water⁽¹⁰⁹⁾

region of (6) while the corresponding amount of heating steam is condensed at the outer surface of the tubes. The lower ends of the tubes are almost closed by superheated capillaries through which the proper small amount of the enriched D_2O steam is withdrawn into the common chamber (8), through the flow control valve (9), and finally, after condensation, into the storage flask (10). The steam ascending in the fractionating tubes leaves the upper open ends in (4) and is condensed completely in (11). The stripped condensate in (12) is pumped back into the container (3) from where a certain amount of feed is leaving the column by a barometric overflow (14).

The extremely low HETP that can be obtained with these columns during distillation of organic liquids could not be obtained with water, probably because water did not wet the walls to produce the necessary uniform thin film. In experiments to concentrate D_2O , the best attainable value for the HETP was about 2 cm.

A recent suggestion^(110, 111) to reduce capital costs entails utilization of a fractionating tower to replace the condenser at a large power plant such as a nuclear reactor. A 1000 MWe nuclear plant should provide about 2600 MWt as exhaust steam at low pressure (2.5 to 3.5 psia). This should be sufficient thermal energy to provide 200 tons/year D_2O by distillation of water. Figure 38 illustrates two schemes for utilizing this thermal energy to produce D_2O .⁽¹¹¹⁾

In the direct feed case (Figure 38 A) the exhaust steam from the turbine is sent to a large packed column. The steam travels upward countercurrently to the feed (distilled water). The condensate at the bottom of the column will become enriched. A portion is removed as product, and the remainder will be returned to the system. The depleted steam at the top of the tower is condensed in a barometric column and sent to waste (unless it can be used for some other purpose).

FIGURE 38. Alternate Schemes for Producing D₂O by Distillation of Water with Dump Heat from a Large-Scale Power Plant.(111)

- A. with direct turbine exhaust feed
- B. with indirect turbine exhaust feed

In the indirect heating scheme (Figure 38 B), the exhaust steam is part of a closed cycle, passing through the column in a coil or series of tubes. The feed (treated or raw filtered water) is heated, vaporized, and fractionated in the column.

In either variation, the packed column with the barometric condenser replaces the usual dump condenser. To be an economical process (D_2O price of \$20 to \$25/lb) the net cost of the column (cost of fractionating column assembly minus cost of dump condenser) must be not more than \$60/lb-year. The first variation is more efficient with a simpler (cheaper) tower design, but requires more expensive feed.

The product is at a concentration of some chosen value between 0.05 to 99.8 mole %. The concentration of the product should not affect the economic evaluation, providing tower efficiencies are optimum in all cases.

A detailed up-to-date economic study of the water distillation process should be made to determine whether the newer technology and utilization of cheap steam and recent technological advances will make this process competitive.

3. Distillation of Methane

Until recently, distillation of methane was not considered a promising method for producing D_2O . The vapor pressure ratio, CH_4/CH_3D , is only 1.0016 at the triple point ($-182.5^\circ C$) and 0.9965 at the boiling point ($-161.9^\circ C$) at 1 atm.⁽²³⁾ The separation coefficient at 1 atm is less than that for water by one or two orders of magnitude, and any plant based on such a value would be so enormous that D_2O could not be produced at a reasonable cost.

In 1963, however, Pogorski of Chemical Projects Ltd. of Canada discovered that the vapor pressures of CH_3D and CH_4 behaved anomalously as pressure was increased.^(112,113) The ratio p_{CH_3D}/p_{CH_4} increased with pressure and at $-85^\circ C$, attained

a value of 1.031. Table 21 lists vapor pressures of methane, $\Delta p (p_{\text{CH}_3\text{D}} - p_{\text{CH}_4})$, and α as functions of temperature. Pogorski explains the inversion on the basis of temperature effects on internal vibrations of polyatomic molecules. The same inversion occurs with H_2O and D_2O , but the ratio at comparable pressures is much smaller [at 255°C (43.5 kg/cm^2), $p_{\text{D}_2\text{O}}/p_{\text{H}_2\text{O}}$ is 1.007]. Pogorski also found that the vapor pressure was increased by several orders of magnitude if the system was perturbed.^(112, 113) For example, in a ternary system at -130°C , α was about 1.22. Figure 39 shows separation coefficients as calculated from Pogorski's data.

Pogorski suggests that chemical additives or the application of magnetic or electrical fields to the system might increase the α even further.

Separation factors of 1.20 are very attractive for straight distillation processes. Volume, capital costs, and power would be much less (factor of 15) than for water distillation. The supply of feed material is sufficiently large, especially in the vast oil fields of British Columbia and Alberta. One might visualize a process for selectively removing deuterium-rich fractions of the compressed gas before transportation by pipe lines to the consumer. Of considerable interest is the fact that the desired compound has the highest vapor pressure and will appear in the distillate.

4. Distillation of Ammonia

Ammonia, like water, is noncorrosive to steel, and distillation of ammonia would be an attractive procedure if the separation coefficients were sufficiently high.

Since there are three replaceable hydrogens, the separation coefficient will be

$$\alpha = p_{\text{NH}_3} / p_{\text{NH}_2\text{D}} \quad (35)$$

FIGURE 39. Coefficients for Separation of CH_3D from CH_4 by Distillation in a Binary (α_1) and in a Ternary (α_2) System

TABLE 21. Data for Distillation of Methane

Temperature, °C	P_{CH_4} , (a) psi	Δp ($P_{CH_3D} - P_{CH_4}$), psi ^(b)		Separation Coefficients	
		Binary System	Ternary System	Binary System (α_1)	Ternary System (α_2)
-160	17.1	negligible		---	
-155	24.5				
-150	34.9	0.55		1.014	
-145	48.2				
-140	65.0	1.1	18	1.018	1.28
-135	85.5				
-130	110.2	2.1	24	1.019	1.22
-125	139.7				
-120	174.4	3.6	28	1.021	1.16
-115	215.2				
-110	273.1	6.0	36	1.022	1.13
-105	317.3				
-100	379.6	9.7		1.026	
- 95	449.6				
- 90	546.0	15.3		1.028	
- 85	620.4	19.5		1.031	

(a) Interpolated from values in Table III, Reference 114

(b) Calculated from data in Reference 113

If the H and D atoms exchange in a normal manner, Equation 35 is equivalent to the following expression.

$$\alpha = (p_{\text{NH}_3} / p_{\text{ND}_3})^{1/3} \quad (36)$$

Stedman⁽¹¹⁵⁾ suggested the vapor pressure of monodeutero-ammonia might be anomalously low and that this might substantially increase the separation factor. However, Bigeleisen⁽¹¹⁶⁾ showed that the distribution of H and D atoms was random and the separation factor should be the value calculated from Equation 36.

Petersen and Benedict⁽¹¹⁷⁾ briefly review the literature on ammonia distillation and plot the results of previous investigators to show that the logarithm of $(p_{\text{NH}_3} / p_{\text{ND}_3})^{1/3}$ is a linear function of the logarithm of the system pressure. At one atmosphere, $(p_{\text{NH}_3} / p_{\text{ND}_3})^{1/3} = 1.04$.

Although distillation of ammonia offers several advantages (low latent heat, higher vapor pressure) over distillation of water, it has the disadvantage that a plant based on NH_3 distillation would be limited in size, probably to 70 to 100 tons/year. Therefore, unless the α is greater than that for water distillation the process will not be competitive as a primary process. Barr and Drews,⁽⁹⁾ in their analysis, concluded that distillation of ammonia would not be competitive unless some anomaly, such as the one suggested by Stedman, were found.

Petersen and Benedict⁽¹¹⁷⁾ investigated concentration of deuterium by distillation of NH_3 and concluded α was a function of both deuterium content and system pressure. Their equation is approximately

$$\ln \alpha = 0.045 - 0.013M - 0.0125p_s \quad (37)$$

where M = mole fraction ND_3 and

p_s = system pressure in atmospheres

The separation factor calculated from Equation 37 for 1 atm is very close to the value for $(p_{\text{NH}_3} / p_{\text{ND}_3})^{1/3}$ from Figure 40. In Figure 41, $\ln \alpha$ is plotted against system pressure for 2 values of M , 10 and 42 mole % ND_3 . The dependence on deuterium concentration is very slight. Even over such

FIGURE 40. Plot Showing Relationship Between System Pressure (p_s) and Cube Root of Ratio ($p_{\text{NH}_3} / p_{\text{ND}_3}$) (117)

FIGURE 41. Separation Factor (α) Versus System Pressure (p) for (a) 42 Mole % ND_3 and (b) 10 Mole % ND_3 (117)

a wide range as 10 to 42%, the variation is only about 10%. However, any extrapolation from the lowest value studied (10%) to the very low concentrations found in nature should be made with caution. More data are needed at very low concentrations before one can know for certain whether or not an anomalously high value of α can be obtained in the initial concentration of deuterium by distillation of ammonia.

Distillation of ammonia will not be an economical process for the initial concentration of deuterium (from 140 ppm) unless some method is discovered for increasing the separation factor. If the separation factor could be increased by addition of a suitable material, higher pressure, or by application of external force, distillation of NH_3 might become competitive. However, it should be noted that this process is useful for final concentration, as for concentration from 2 to 99.8% deuterium in the final stage of the NH_3 -HD isotopic exchange process (see Section III, B, 2).

D. ELECTROLYSIS

The separation coefficients for electrolysis are very high (6 to 30) and decrease sharply with increasing temperature. References in the literature to values of α tend to be confusing since widely different values are given without clear indication of temperature or temperature dependence.

1. Electrolysis of Water

Until 1943, all of the heavy water produced commercially was made by electrolysis, principally by the Norsk-Hydro Company.* The primary plant used nine stages of cells connected in a series cascade operated in steady flow without recycle, as shown in Figure 42. The product of the primary plant, 15% D_2O , was fed to a secondary (nine-stage) plant, which operated at steady flow to produce 99.8% D_2O . The partially enriched hydrogen formed at the cathodes was burned to produce enriched water, which was fed to the previous stage (Figure 42).

* Norsk-Hydro-Electrisk Kvaelstofaktieselskab, Rjukan, Norway

FIGURE 42. The Norsk-Hydro Plant for Producing D_2O by a Combination of Electrolysis of Water and $HD-H_2O$ Catalytic Exchange⁽¹²⁾

Electrolysis was used in both primary and secondary plants at Trail (Section III, B, 3a) to concentrate D_2O . The secondary plant, consisting entirely of electrolytic cells, concentrated the D_2O from 2.37% to 99.8%. A batch procedure was used in preference to a continuous process because fewer stages would be required, the plant would be more flexible, and operating problems would cause less delays.

The secondary plant at Trail, shown in Figure 43, included three stages, each consisting of a feed tank, electrolytic cell battery, carbonating tank, H_2 - O_2 combiner (burner), and evaporator. The feed from the primary plant was made about 0.5N in KOH and electrolyzed in the first stage to about 15% of the initial volume. The hydrogen and oxygen gases were combined and burned to form enriched water which was fed to a lower stage of the primary plant. The residual solution was carbonated to form a solution of K_2CO_3 and evaporated. The condensate was sent as feed to the second stage of cells. The condensate from the final stage was slightly acidified with H_2SO_4 and re-evaporated to form the product.

Electrolysis was also used at the MOW distillation plant for final concentration of the D_2O to the desired purity. Approximately 1.2 tons/month of D_2O were concentrated from 90% to 99.7% D_2O . The mode of operation was similar to the Trail plant described above.

The electrolysis generates heat, and to operate at high efficiency, the electrolyte is cooled usually to $40^\circ C$, where α has a value of 8 to 9.

This value for α is much higher than one would predict on the assumption that the only reaction is the exchange between H_2 and H_2O at the cathode surface, since the α for the exchange reaction is only about 3.5 to 4.0. Farkas⁽¹³⁾ lists three other possible contributing reactions in addition to H_2 - H_2O exchange:

FIGURE 43. Diagram of the Secondary Plant at Trail for Concentrating D₂O by a Cascade of Electrolytic Cells⁽¹⁰⁾

- Transport of the ions from the electrolyte to the electrodes
- Discharge of the ions at the electrodes
- Formation and liberation of molecular gases at the electrodes.

The first mechanism has been shown to be of negligible importance, since the hydrogen isotopes are in normal concentration ratios at the cathode boundary.

The high value of α probably results from a combination of the second and third mechanisms. The electrode transfers from the cathode metal to the hydrogen ion by a jump over the energy barrier, and since the height of this barrier is different for hydrogen and deuterium ions, the probability of discharge for deuterium ion is different (lower) from that for the hydrogen ion. Similarly, the formation and liberation of molecular gas from the discharged and adsorbed atoms proceed with activation energies that are different for the different isotopes. ^(13, 118)

The separation factor will depend on the condition of the experiment; the state of electrode surface, current density, overvoltage, and electrode metal all have an important effect on the amount of separation possible. Topley and Eyring ⁽¹¹⁹⁾ obtained the following values with different electrodes in alkaline solutions: Pb, 7.3; Fe, 7.3; Pt, 7.1; Ni, 5.5; Ag, 5.2. In acid solutions, values were: Pt, 5.7; Cu, 5.6.

Raman et al. ⁽¹²⁰⁾ determined the values and the temperature dependence of the separation factors in aqueous solutions at 30 to 60 °C. The highest separation factors were obtained with an iron-tin alloy (Fe; Sn, 7.85). Surprisingly, they found $d\alpha/dt$ to be positive for cathodes of tin and a tin-iron alloy containing more than 39.5% tin. As the tin content was increased, $d\alpha/dt$ slowly changed from negative for high iron alloys to positive for high tin alloys.

Conway ^(121, 122) discusses the mechanisms of electrolytic separation of deuterium and plots the Tafel lines for cathodic polarization of different metals in acidic H_2O and D_2O solutions

(0.1N HCl in H₂O and 0.1N DCl in D₂O). The amount of polarization, the differences in polarization for H₂O and D₂O solutions, the slopes of the Tafel lines, and the changes in slopes differ for different metals.

The electrolytic enrichment of D₂O proceeds according to the equation:

$$\begin{aligned} d \ln A_H &= \alpha (d \ln A_D) \text{ or} \\ d \ln (V \cdot [H]) &= \alpha d \ln (V \cdot [D]) \end{aligned} \quad (38)$$

where A_H and A_D are the total amounts of the H and D compounds present, V is the volume of solution, [H] is the molar concentration of hydrogen, and [D] is the molar concentration of deuterium. Thus, by measuring the amounts of H₂O and D₂O present at different times, one can calculate α . Equation 38 can be transformed to an expression similar to the Rayleigh equation:⁽¹³⁾

$$\left(\frac{[H_o]}{[H]} \right) \left(\frac{[D]}{[D_o]} \right)^\alpha = \left(\frac{V_o}{V} \right)^{\alpha-1} \quad (39)$$

Where V_o, [H_o], and [D_o] are the values at time = 0, and V, [H], and [D] are values at any later time.

Equation 39 can be used to calculate the concentration of deuterium in a batch operation where the volume is reduced from V_o to V. Figure 44 plots values of mole fraction of D₂O,

$\frac{[D]}{[H] + [D]}$, as a function of V_o/V for α values of 5 and 10.

Thus to concentrate D₂O from 140 ppm to 10% D₂O, if α is 10, it will be necessary to electrolyze the solution (in stages) until the final volume is 1/1500 that of the starting volume.

The relation between isotopic concentrations in the gas and in the liquid are given by Equation 40.

$$\alpha = \frac{[H]}{[D]}_{\text{gas}} / \frac{[H]}{[D]}_{\text{liquid}} \quad (40)$$

FIGURE 44. Concentration of D_2O in an Electrolytic Cell

The separation factor for electrolysis is very high and consequently the volume of feed will be much lower than for other processes. For example, the value for the first factor in Equation 6 is about 3 for electrolysis as compared to 200 for the GS process and 3200 for distillation of water. However, in spite of the extremely favorable separation coefficient, electrolysis is not and will probably never be an economic independent process for production of D_2O because current requirements are so high.

The Norsk-Hydro plant in 1942 consumed 91,000 kW and produced 640,000 ft³/hr STP of H_2 .⁽¹¹⁾ If one assumes a 40% recovery of the D_2 in the feed, the plant could have produced 8.5 tons/year D_2O if it had been devoted entirely to D_2O production. At \$0.003/kW-hr, the electrical power alone would have cost \$135/lb D_2O .

Benedict⁽¹¹⁾ makes a detailed assessment of the economics of electrolysis for production of hydrogen and D_2O . He assumes an α of 7, a feed concentration of 149 ppm, and a product of 99.7% D_2O . The concentration and amounts of D_2 , H_2 , H_2O , and D_2O are shown in the flow diagram (Figure 45). The hydrogen fractions from the first three stages contain such low concentrations of D_2 that it is not economic to burn them for recycle. For example, Benedict calculates it would cost \$93/lb D_2O to burn the gases from Stage 3 for recycle. Gases from Stages 4 through 15 are burned and sent to the next lower stage. About 60% of the D_2 is thus lost with the gases from the first three stages, and recovery is only 32% of feed $\left(\frac{0.488}{1.49}\right)$. About 58,000 kW-hr are required for each lb D_2O . If one assumes the hydrogen is sold, approximately 2500 kW-hr are required solely for the production of one lb of D_2O . At \$0.003/kW-hr, this power costs \$7.50/lb D_2O . Electrolysis may be an attractive procedure for making small amounts of D_2O in areas where electricity is very cheap. The amount will be limited since the amount of D_2O that can be produced will depend on the available electrolytic hydrogen plant, and the number of plants of sufficient size is limited.

FIGURE 45. Optimum Electrolytic Cascade, as Visualized by Benedict, for Production of 10,000 Moles of H_2 and 0.488 Moles D_2O as Byproduct ($\alpha = 7$)⁽¹¹⁾

Electrolysis is at present used principally for final concentration or upgrading of water with D_2O contents ranging from 0.1 to 95%.

Morrison et al.⁽¹²³⁾ describe the electrolysis unit at Chalk River for upgrading D_2O . The four cells containing iron cathodes and nickel anodes are connected in series as shown in Figure 46. The plant operates efficiently with few operating difficulties to concentrate water with D_2O content of 90% or above. A separation coefficient of 10 is obtained with no difficulty. (Operating temperature was not specified.)

The largest electrolysis plant is composed of the three Norsk-Hydro units, which produce about 20 tons/year of D_2O . The pre-enrichment plant produces 2% D_2O by a combination of electrolysis and catalytic H_2 - H_2O exchange. This enriched water is fed to the final system of 20 electrolytic stages.

An electrolysis plant in Nangal, India enriches the hydrogen to provide feed for a hydrogen distillation plant.⁽¹⁰⁰⁾ The electrolytic hydrogen, produced primarily for manufacture of NH_3 , passes through a three-stage electrolysis unit (Figure 47) where the deuterium content is increased by a factor of three. The economics of the H_2 distillation plant was discussed previously.

The very high separation factor makes electrolysis appear to be an excellent process for initial concentration to provide feed for water distillation or NH_3 - H_2 exchange. For example, if electricity were available at a price that H_2 could be produced for NH_3 synthesis, the following scheme (Figure 48) might be economical. The feed water at 140 ppm would be electrolyzed to 1/12 of the original volume. The residual water, containing 1400 ppm D_2O (Figure 48), would be fed to a distillation plant. The distillation plant would handle only 1/12 the amount of feed required at normal D_2O concentration. Plant size and costs would be much lower. According to Figure 4, the initial concentration by a factor of 10 accounts for over 60% of total cost. The electrolysis plant would be very simple, since no provisions for recycle, hydrogen

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FIGURE 47. Simplified Block Diagram of Nangal Plant for Producing D_2O as a Byproduct to Manufacture NH_3 ⁽¹²⁾

N = normal concentration of HD (as HDO)
in water = 300 ppm

FIGURE 48. Single-Stage Electrolysis of Water to Provide Enriched Feed for Water Distillation Plant

burning, evaporating, or KOH recovery are required. The distillate could be returned to the electrolysis tank. The principal limitation on the size of the plant would be the market for electrolytic hydrogen.

It has been suggested that the electrolysis of water be used in conjunction with some procedure for efficiently recombining the evolved H₂ and O₂, such as in a fuel cell. The energy produced would replace part of the energy spent for electrolysis.^(124, 125) Winsel considers such a process an electrochemical analog to a distillation column. Such an arrangement might be economical in a location where electricity can be produced very cheaply.

2. Electrolysis of Ammonia

Electrolysis of ammonia or ammonium salts has been suggested as an improvement over the more accepted electrolysis of water. Dirian et al. state that electrolysis of NH_4Br yields separation factors of 15 to 30.^(126, 127) If current requirements are not too great and equipment costs are not too high, this process might serve as an excellent method for providing concentrated feed to the $\text{NH}_3\text{-H}_2$ exchange, NH_3 distillation, or other process. No detailed cost estimates or performance data are given.

E. UNTESTED PROCEDURES

In addition to the procedures described above, some methods have been discussed, some have been used in the laboratory, and a few have been tested in preliminary pilot plant experiments. Many of these procedures seemed to have a potential, but the data obtained were usually inconclusive or unconvincing. In most cases, the real or supposed technical difficulties appeared to be so great that a concentrated effort seemed inadvisable. These procedures may be classified as distillation, electrolysis, chemical exchange, sorption or ion exchange, diffusion, and other.

Periodically, new ideas or novel procedures are suggested. These should be examined carefully before they are discarded. Sometimes, an idea is discarded because it has an apparently insuperable difficulty, and later study shows the supposed difficulty was not really so formidable. Barr and Drews⁽⁹⁾ listed and briefly commented on many possible procedures for producing D_2O . Their conclusions were usually pessimistic although tentative: e.g., "separation factors are expected to be low" and "(success) is unlikely".

Since only a very limited amount of new work has been done on this angle since Barr and Drews wrote their report, this section will be brief.

1. Distillation

Two distillation procedures, previously discussed, may be classified as unusual or untried procedures: distillation of methane and distillation of ammonia.

The preliminary data cited by Pogorski^(112, 113) for distillation of methane at higher pressures, especially in a perturbed system, appear so encouraging that additional work should be done and/or reported to demonstrate whether this system merits serious consideration. Very large sources of methane are available as raw material. Separation factors in the order of 1.1 for a process so simple and noncorrosive could very well lead to production of cheap heavy water. Holenberg discusses distillation of dissociable compounds such as pyridinium-HCl, pyridine-H₂S, and methylamine-H₂S. The α for Py-HCl is 1.113 for distillation at atmospheric pressure. None of the systems seem economically competitive. The Py-HCl system would be smaller, but heat requirements would be higher. The corrosiveness of this system might increase equipment costs.

2. Chemical Exchange

Many possible chemical exchange systems have been suggested:^(9, 11, 128) PH₃-H₂O, diborane-H₂, C_nH_{2n+2}-H₂, benzene (or cyclohexane)-H₂, CH₃CHO-H₂, RSH-H₂, RNH₂-NH₃, glycol-H₂O, benzene-HCl, enols-H₂O, HCl-H₂, H₂S-CH₃OH, RNH₂-H₂, SbH₃-H₂, AsH₃-H₂, HF-H₂O, HCl-H₂O, HBr-H₂O, HI-H₂O, monothermal H₂S-H₂O, UH₃-H₂. Table 22 is a list of possible exchange reactions with the separation coefficients at 20 °C as compiled by Varshavsky and co-workers.⁽¹²⁸⁾ In almost all cases, some factor seems to make the couple unworthy of consideration. Some compounds (HCl, HBr, HF) are very corrosive; some (SbH₃, AsH₃, H₂S) are very poisonous; many are expensive; and none have demonstrated extremely high separation factors.

TABLE 22. Chemical Exchange Separation Factors⁽¹²⁸⁾

Substance	Separation Factor α at 20 °C																			
	a	b	820°	850°	875°	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₆ H ₆	NH ₃	H ₂ O	HF	PH ₃	H ₂ S	HCl	AsH ₃	H ₂ Se	HBr	HI
H ₂	0.8484	418.7	3.54	3.10	2.83	1	0.329	0.316	0.312	0.298	0.303	0.305	0.364	0.615	0.649	0.693	0.752	0.801	0.843	1.05
CH ₄	0.5071	894.5	10.74	8.04	6.63	3.04	1	0.959	0.947	0.904	0.902	0.924	1.10	1.87	1.97	2.10	2.28	2.43	2.56	3.18
C ₂ H ₆	0.4640	932.8	11.20	8.33	6.77	3.16	1.04	1	0.988	0.943	0.959	0.964	1.15	1.94	2.05	2.19	2.38	2.53	2.67	3.31
C ₂ H ₄	0.4632	936.8	11.33	8.42	6.84	3.20	1.05	1.01	1	0.953	0.970	0.975	1.16	1.97	2.08	2.22	2.41	2.56	2.70	3.35
C ₆ H ₆	0.4128	984.7	11.89	8.70	6.99	3.36	1.11	1.06	1.05	1	1.02	1.02	1.22	2.06	2.18	2.33	2.52	2.69	2.83	3.52
NH ₃	0.5611	889.4	11.68	8.81	7.23	3.30	1.09	1.04	1.03	0.982	1	1.01	1.20	2.03	2.14	2.29	2.48	2.64	2.78	3.46
H ₂ O	0.6344	852.1	11.62	8.87	7.34	3.28	1.08	1.04	1.02	0.978	0.995	1	1.19	2.02	2.13	2.28	2.47	2.63	2.77	3.44
HF	0.7340	757.3	9.73	7.66	6.47	2.75	0.905	0.868	0.857	0.818	0.832	0.837	1	1.69	1.78	1.90	2.06	2.20	2.32	2.88
PH ₃	0.5337	696.8	5.76	4.62	3.95	1.62	0.536	0.514	0.508	0.484	0.493	0.496	0.592	1	1.05	1.13	1.22	1.30	1.37	1.70
H ₂ S	0.6291	633.1	5.46	4.47	3.88	1.54	0.508	0.487	0.481	0.549	0.467	0.470	0.561	0.948	1	1.07	1.16	1.23	1.30	1.57
HCl	0.7245	572.1	5.11	4.26	3.75	1.45	0.476	0.456	0.451	0.430	0.438	0.440	0.525	0.888	0.936	1	1.09	1.16	1.22	1.51
AsH ₃	0.5312	639.3	4.71	3.85	3.34	1.33	0.438	0.420	0.415	0.396	0.403	0.405	0.484	0.817	0.863	0.922	1	1.06	1.12	1.39
H ₂ Se	0.6099	580.2	4.42	3.68	3.23	1.25	0.411	0.395	0.390	0.372	0.378	0.381	0.445	0.768	0.810	0.866	0.939	1	1.05	1.31
HBr	0.7192	517.3	4.20	3.57	3.18	1.19	0.391	0.375	0.371	0.353	0.359	0.362	0.432	0.729	0.770	0.822	0.891	0.905	1	1.24
HI	0.7178	453.7	3.38	2.93	2.64	0.955	0.315	0.302	0.298	0.284	0.289	0.291	0.347	0.587	0.619	0.661	0.717	0.764	0.805	1

On the other hand, some seem intriguing and might merit further study.

Taylor et al., (129-131) investigated chemical exchange reactions and obtained some promising results, but these studies were discontinued before sufficient data could be obtained or reported. Table 23 lists the data they obtained on possible exchange reactions.

TABLE 23. Separation Coefficients and Rates for Candidate Chemical Exchange Systems⁽¹²⁹⁾

Exchange Couple	Catalyst	$T_{1/2}$ ^(a)	Separation	Coefficient
HDC-H ₂ S	none	sec	α_{25}/α_{100}	1.22
H ₂ O-HD	Pt, hetero	5.2 min	α_{25}/α_{100}	1.44
NH ₃ -HD	0.1M KNH ₂	sec	α_{25}/α_{60}	1.48
HDO-RSH	none	10 sec	- - - -	- - -
HDO-CH ₃ C≡CH	0.1M NaOH	3 sec	α_{25}/α_{80}	1.20
	or ion exchanger			

(a) Time required for 50% of reaction to take place.

The water-propyne exchange was rapid, and the separation coefficient was about equal to the one for the GS process. The use of ion exchange resin to obtain the necessary hydroxyl concentration looks very attractive since the system would be relatively noncorrosive, and cheaper construction materials could be used.

The monothermal H₂S-H₂O has been suggested as a possible improvement over the GS process.⁽⁴⁷⁾ If operation is at 30 °C, α would be 2.2 as compared to 1.3 for the GS process; plant size would be reduced by a factor of about 10. Such a system would require chemical reflux similar to that provided by cracking NH₃ in the NH₃-HD system. Dissociation of H₂S or H₂O is not economical; research must develop a reaction that is reversible without expenditure of too much energy.

Amine-hydrogen exchange would be simpler than NH_3 -HD exchange since it could operate at higher temperatures and lower pressures. (132, 133)

3. Adsorption and Ion Exchange

Adsorption, discussed previously, is sometimes considered because it is a very simple and effective method for separating similar materials, including isotopes.

Many modifications of adsorption and ion exchange have been suggested. (134-148) Glueckauf and Kitt^(134, 135) adsorbed hydrogen isotopes on 20 g Pd black mixed with 2 g asbestos in a column 44 by 0.8 cm. Palladium is one of the most effective adsorbents for hydrogen, having an α of about 2 (Equation 41).

$$\log \alpha = \frac{215}{T} - 0.47 \quad (41)$$

The deuterium is less adsorbed and will break through first. In a larger column containing 460 g Pd it was possible to separate the deuterium from 16 liters of gas, containing 40% D_2 . They obtained three fractions: 5800 ml of 97.5% D_2 , 2520 ml of 12.1% D_2 , and 6460 ml of 1.6% D_2 . After adsorption, the deuterium may be preferentially displaced by hydrogen or removed by heating. Botter et al.,⁽¹³⁶⁾ reported on use of chromatographic adsorption for separating the hydrogen isotopes. They found this method was satisfactory on the very small scale in which they were interested. Adsorption was rapid (the separation was completed in about 10 min) and efficiencies were high. They obtained deuterium in 99.7% purity with 80 to 84% yield. A 1 m column had 1200 theoretical plates, so the HETP was about 0.8 mm. A column containing 20 g PD on alumina or Fe_2O_3 adsorbed about 1 liter of H_2 .

Haubach et al., ⁽¹³⁷⁾ discuss separation of hydrogen isotopes on alumina at low temperatures. The method has potential, but it will be necessary to find a suitable adsorbent system such that separation factors and rates are both high. Recently, it has been shown that chromatographic adsorption columns can be built in large sizes, and large-scale production of D_2O by this method may be feasible. ⁽¹³⁸⁾

No progress has been reported on any adsorption system that will produce D_2O economically. Usually, the adsorbent (Pt or Pd) is so expensive, separation factors are so low, or exchange rates are so low that capital costs are very high. (Any capital cost greater than \$150/lb-year D_2O will not compete with the GS process, and any capital costs greater than \$100/lb-year will not compete unless all other costs are very low.)

The costs of completing a cycle (adsorption and desorption) must be low. For example, any cycle requiring heating and cooling of a large mass of adsorbent bed over a wide temperature range will probably not be competitive.

On the basis of the figures quoted by Glueckauf, about \$100,000,000 worth of Pd are required to adsorb the natural hydrogen mixture (300 ppm HD) corresponding to one pound of D_2O . Any batch procedure will probably not be economical and any continuous procedure will require a very rapid cycle time. Schmieschek ⁽¹³⁹⁾ suggests adsorbing the deuterium on Pd wires and desorbing by heating the wires electrically.

Seailles ⁽¹⁴⁰⁾ describes a process combining electrolysis with adsorption; the electrolytic cells contain porous diaphragms and Pd plates. The hydrogen is preferentially electrolyzed, adsorbed on the Pd, and oxidized to water, which is then removed. The D_2O concentrates in another section of the cell.

Pogorski^(112, 113) has suggested adsorption of methane isotopes at high pressures, but the literature contains no data that can be used to evaluate this method.

Augood⁽¹⁴¹⁾ studied absorptive fractionation processes for concentration of deuterium, in which the gas mixture ($H_2 + HD$) is dissolved in a solvent and the nondissolved gas is removed. He measured separation factors for different solvents (H_2O , NH_3 , SO_2 , CH_4 , H_2S , NO , CO_2 , CO , and A) and found his results compared fairly well with predicted values. Of greatest interest was the very high separation factor calculated for liquid neon (3.24), although he had no experimental data for comparison. He predicted that if this figure could be attained, D_2O could be produced for \$12.50/lb. By adsorption in liquid N_2 , if no cost for the nitrogen is assumed, D_2O could be produced for \$19.57/lb.

Ion exchange, in principle, looks attractive since hydrogen ions can be adsorbed and desorbed many times while passing through a short column, and exchange is rapid. It will be necessary to find an exchange reaction that has a sufficiently high separation factor.

The separation factors for ion exchange of isotopes are usually very low. Exchange of Li ions on Dowex 50 Resin were measured to be about 1.002.⁽¹⁴²⁾ Spedding et al., found an α of 1.025 for ^{15}N separation on ion exchange columns,⁽¹⁴³⁾ but this relatively high value was attributed to superimposition of two contributing effects: isotopic exchange on the resin and (especially) exchange between free ammonium ions and dissolved ammonia. They were able to concentrate ^{15}N from 0.36 to 44.8%. A modification especially valuable for isotopic concentration is the use of moving resin beds. Diffusion through suitable membrane structures also causes many equilibrium changes over a short length and might prove effective. Considerable progress has been achieved in membrane development recently.

Adsorption or ion exchange will probably never be a suitable method until some one develops a relatively inexpensive column with a very much higher capacity, extremely rapid sorption and desorption rates, and one that does not require excessive expenditure of energy to complete the cycle. An alternative, although less probable, is the development of a column that can efficiently adsorb deuterium selectively.

4. Diffusion

Gaseous, mass, and thermal diffusion and the ultracentrifuge have all been considered and generally discarded as processes for concentrating or separating deuterium. Benedict states that diffusion methods and the gas centrifuge give such low separation effects that they cannot be considered.⁽²⁸⁾ The separation factor for the gas centrifuge depends on differences in molecular weights, rather than ratios, and centrifugal procedures are much more effective for the heavy isotopes.

The principal difficulty with diffusion methods is the extremely low efficiency, 8×10^{-6} for gaseous diffusion to 7×10^{-8} for thermal diffusion. The power required for pumping or heating would be so great that cost of D_2O would be very much higher than the presently accepted price of \$28/lb.

These methods are used for concentrating isotopes when no other method is available and when the product is so valuable that these expensive procedures are warranted.

A separation nozzle, developed by Becker et al.,⁽¹⁴⁹⁾ as a possible procedure for separating uranium isotopes, has been suggested as a tool for deuterium separation.⁽¹⁵⁰⁾ Feed gas flows at very high velocities through a jet arrangement as shown in Figure 49 and is separated by a variable vane to produce the desired cut into light and heavy fractions. The separation factors are very low ($\alpha - 1 \approx 0.004$), and pumping costs would probably be excessive for such a system to be used in D_2O separation.

The Ranque-Hilsch vortex tube,^(151,152) Figure 50, which operates in a similar fashion, is used primarily to obtain cooling air,⁽¹⁵³⁾ but could also be adapted to separate isotopes.⁽¹⁵⁴⁾ The deuterium would be enriched in the central colder fraction and the feed gas depleted in deuterium would gravitate to the outer warmer stream. Again, efficiency would be low, and pumping costs would be high.

5. Electrolysis

Economic analyses seem to prove that electrolysis of water is not an economic process for initial concentration of deuterium, even when used as a dependent adjunct to some process such that the feed gas is essentially free.

The classical procedure, as used at Norsk Hydro and at Trail, was discussed previously. As an independent process where the D_2O must bear the total power cost, electrolysis is not competitive. If the process is dependent and the H_2 is merely borrowed, D_2O is assessed only a small part of the power costs (~4%). Even under these favorable circumstances, electrolysis is economical only where power is very cheap. Electrolysis is used by Sulzer for initial concentration (from 0.03 to 0.15% HD)⁽¹⁵⁵⁾ This is economical only because the H_2 is generated principally as feed for an NH_3 plant and because the plant operates only during that part of the year when electrical demand is low. The Nangal plant also uses electrolysis for primary concentration for similar reasons.

A seemingly attractive alternative is the use of electrolytic cells to carry out reversible electrolysis of water with a greatly reduced expenditure of energy. Barr and Drews⁽⁹⁾ discuss this possibility and conclude that even with optimistic assumptions, the process is not economical. The plant is so large that capital costs will be high (\$125/lb-year based on 1960 costs), and operating expense and electricity will bring total cost to about the same as for the GS process. Figure 51 is a possible direct electrolysis plant as visualized by Barr and Drews. Their analysis appears to

FIGURE 49. Cross Section of Separation Nozzle System⁽¹⁴⁹⁾

- (a) Longitudinal section
- (b) Cross section of nozzle
- K Annular gap for hot gas (variable)
- D Aperture for exit of cold gas
- T Tube
- t_i Inlet temperature
- t_h Hot outlet temperature, $t_h > t_i$
- t_c Cold outlet temperature, $t_c < t_i$

FIGURE 50. Ranque-Hilsch Vortex Tube⁽¹⁵³⁾

FIGURE 51. Simplified Schematic Flow Plan for Reversible Electrolysis of Water⁽⁹⁾

be rather cursory. It is possible that a thorough examination might reveal methods or materials to fabricate a plant at lower costs.

The principal expense in concentration of deuterium results from the fact that the large amount of water is selectively removed from the small amount of deuterium. Thus, it is necessary to electrolyze 6999 gal of H_2O to obtain 1 gal of D_2O . If it were possible to electrolyze only the 1 gal of D_2O from the 7000 gal of H_2O , or to achieve any sort of concentration by selectively removing the D_2O and leaving the large mass of depleted H_2O in the tank, D_2O could be produced very cheaply. Barr and Drews estimate such a scheme might easily reduce D_2O costs by a factor of two or more.

Maclaren^(9, 156) has suggested a possible method to electrolyze D_2O directly: superimposition of an alternating current on the direct current during electrolysis to selectively excite the deuterium ions. He suggests such an effect might be possible since hydrogen and deuterium have different masses and possibly might have sufficiently different resonant frequencies. If such an effect could be achieved such that the deuterium could be selectively released from the solution, initial concentration might be achieved at a very low cost. For example, such a method could be used as a single stage to provide feed (0.15% D_2O) to a GS, NH_3-H_2 , or distillation plant. Since this initial concentration accounts for about 60% of the total costs, great savings could be made.

This idea, however, has not been tested in the laboratory.

6. Other

G. Last⁽¹⁵⁷⁾ has suggested a modification of the adsorption process. One procedure for producing nickel consists of treating nickel sulfate with hydrogen at high temperatures and pressures.⁽¹⁵⁸⁾

If hydrogen reacts preferentially, the deuterium would concentrate in the gas stream. Some modification of this reaction might be possible where the feed gas passes over an oxide bed and becomes enriched through preferential adsorption. The limitations are the relatively small scale of production and the costs of regeneration of the bed.

Deuterium may also be concentrated by reversible reactions consisting of forming and decomposing solid hydrides:

Orbach and Oliver suggest formation of alkali metal hydrides to preferentially remove H_2 and leave the residual gas enriched in D_2 .⁽¹⁵⁹⁾ The feed gas is passed over the molten metal at 0.5 to 10 atm.

Preferential excitation of one isotope has also been suggested. A Belgian patent suggests halogen hydrides be submitted to monochromatic radiation to preferentially decompose the DX molecules.⁽¹⁶⁰⁾ Rozenberg states that deuterium may be separated from hydrogen by photochemical reaction with light sources, but yields are too low for this method to be used for large-scale production.⁽¹⁶¹⁾ Laser beams have also been suggested.

Shay⁽¹⁶²⁾ has patented a method using preferential wetting of a surfactant having a polyalkylene glycol hydrophilic group.

Enriched D_2O has been prepared by catalytic hydrogenation of CO at a temperature around 200 ° C.⁽¹⁶³⁾ The degree of enrichment depends on temperature, velocity of gas, and percent of conversion.

A magnetohydrodynamic effect was used by Ruskin et al., to concentrate heavy water.⁽¹⁶⁴⁾ Ordinary-water is forced through a tube at high velocity in a high magnetic field (10,000 G). The peripheral fraction, depleted in D_2O , is discarded, and the central portion, enriched in D_2O , is collected.

Since deuterium appears to be more inert, Schaurer and Heinzel⁽¹⁶⁵⁾ propose incomplete reaction of synthesis gas to concentrate deuterium. The $N_2 + 3H_2$ gases are reacted incompletely, the NH_3 is taken off and fresh gases added until the unreacted gases attain a concentration of at least 0.12% HD. The enriched gas can then serve as feed for additional stages or for some other process.

IV. CONCLUDING REMARKS AND SUMMARY

According to data in published literature, the present world capacity for producing D_2O is about 300 tons/year. When the new Canadian plants go into production, the capacity will be slightly more than 1000 tons/year. Additional proposed plants, if erected, will increase the total production by 20 to 40%, but even this amount is inadequate for projected needs based on the best knowledge available.

The cost of D_2O to be produced in the next few years, based on financing at 14%, is calculated to be \$16 to 20 (U. S. 1967 dollars)/lb. The actual cost cannot be stated with certainty until the D_2O is being produced in these new plants on a routine basis.

Research to develop improved methods for producing D_2O have proceeded along several lines.

By far the greatest effort has been expended to modify the procedures originally studied and shown to be competitive: GS process, H_2 distillation, NH_3 - H_2 chemical exchange, and H_2 - H_2O chemical exchange. The so-called improvements are almost all in equipment design with no really new fundamental ideas for improving the process itself. The new GS plants have larger towers, better heat exchange design, slightly different flow patterns, and more efficient plant layout; the process itself is almost exactly as it was and is at SRP and Dana. Similarly, the H_2 - H_2O chemical exchange is limited to the two types of catalysts used previously (Pt and Cr_2O_3 on carriers), and NH_3 -HD exchange is limited to KNH_2 catalyst.

Some new ideas have been introduced and some are being investigated, but so far the major effort has been a painstaking determination of the necessary constants such as exchange rates and solubility limits for established processes. Real imaginative research is conspicuously absent.

The probable reason for this state of affairs is twofold:

(1) Development of a new procedure will be very expensive and time consuming; a new process will cost several million dollars to develop, and a plant based on a new process will not produce D_2O until about 10 years after start of research. (2) The market for heavy water is not well-defined since it depends on so many unknowns, including supply of uranium, power needs for the next 50 years, time required to develop fast breeder reactors, acceptance of different types of reactors, and relative efficiencies of different reactors. In the U. S., almost all large nuclear reactors are PWR's or BWR's, with a few GCR's. No heavy water reactors are being built, and there are no firm plans to build HWR's. The market for PWR's and BWR's is well established.

The desirability of any reactor type is definitely tied in with cost of electricity produced, which in turn depends to a large extent on cost of the reactor. A large portion of HWR cost is the heavy water, amounting to many millions of dollars. Heavy water reactors would be more desirable, and more heavy water reactors would be sold, if heavy water were cheaper. However, no company wishes to expend a great deal of time and money to develop cheap D_2O until there is an established market for D_2O . Thus, the reasoning appears to end in a circle. On the one hand, the reactor manufacturers wish to wait until a plentiful supply of cheap D_2O is available; on the other hand, the companies capable of developing cheap D_2O will not proceed until a market for D_2O is apparent.

Canada, however, is producing HWR's for use at home and for export. It needs large amounts of D_2O for these reactors, and cheaper D_2O will make these reactors more competitive. It has contracted with two companies to build large D_2O plants and is investing in development of alternate procedures. However, since their need is imminent, the plants being built are based on the established GS procedure, and the alternate process being studied is the bithermal NH_3 -HD chemical exchange, which is a backup but not necessarily an improvement over the GS process.

France is also developing D_2O production processes, but their need is not so imminent. Their stated aim is to develop a process that will be more economical (than the GS process) in Europe where steam costs are higher than in the U. S. Such a process could be used in France or licensed in other countries.

India studied the relative merits of available processes to aid in the choice of a D_2O plant, but has no continuing research program.

Russia investigated several procedures and decided to develop the H_2 distillation process, apparently for domestic use.

Industrial concerns in other countries (Sulzer in Switzerland, Degussa in Germany, and John Brown in England) have studied processes for the commercial sale of D_2O or D_2O production equipment.

There has been little international cooperation or even a national program to develop D_2O processes on a long-term approach.

Some of the possibly meritorious ideas that should be evaluated are:

Distillation

- H_2O . A definitive evaluation should be made of the possibility of producing cheap D_2O by distillation of water with the use of very cheap (dump) steam, modern efficient packing, and integration of equipment. An effort should be made to investigate the lead suggested by Pogorski that high separation factors can be obtained in a ternary or perturbed system.

Chemical Exchange

- NH_3 -HD. Some effort should be made to find an effective catalyst that is less expensive and not so flammable or

explosive. Other needs are efficient economical catalyst recovery, and an economical first stage necessary for an independent process.

- H₂O-HD. The H₂O-HD exchange is a process of very high potential, but at present it is not competitive because no suitable catalyst has been developed. The catalyst must be relatively inexpensive to use, not corrosive, and must effect a rapid reaction rate. An expensive catalyst could be used if it could be economically recovered or if it were present as a stable bed and not removed by the liquid or gas.
- Other exchange processes. Some of the exchange systems listed by Barr and Drews should be evaluated. Amine-H₂ and other systems that provide adequate exchange rates at moderate temperatures and pressures might prove more economical than the GS and other processes now considered.

Electrolysis

Novel systems such as direct electrolysis of deuterium might be a profitable long-term study. Fuel cell designs might prove effective for final stages to concentrate D₂O from 0.1 to 99.8%. Conventional electrolysis might also be effective for initial concentration (to 0.1% D₂O) as feed for some other process.

Adsorption, Ion Exchange, or Diffusion

Work should be done to develop suitable adsorbent membrane, or ion exchanger. Suitable hydrogen containing compounds should be identified.

Finally, some effort should be devoted to new and novel approaches. Only in this way will substantial reductions in price of D₂O be possible.

Really cheap D_2O will result from use of new technology in a pertinent field such as electrolysis, distillation, cryogenics, or catalytic chemical exchange. Development of an unlimited source of cheap hydrogen as was mentioned earlier may be such a breakthrough. The NH_3-H_2 and especially the H_2O-H_2 exchange processes will be much more efficient with a feed of pure hydrogen and, even more important, the plants will not be limited in size. Hydrogen distillation will not be encumbered with purification problems. An intensive effort is required to examine all the newer technology and see how this new information can be utilized. New and novel approaches which formerly appeared infeasible may now be suitable methods for large-scale production.

APPENDIX

HEAVY WATER REQUIREMENTS FOR HEAVY WATER REACTORS

The HWR's now built or scheduled for completion during the next five years require 1.0 to 1.2 tons of D_2O per megawatt electrical (Table A.1). This requirement will probably be reduced as newer designs are developed, especially if the reactors are cooled by boiling light water. It is predicted that the ratio may be about 0.5. Conservatively, this lower ratio is adopted in this paper.

TABLE A.1. Heavy Water in Canadian Reactors

<u>Reactor</u>	<u>Date</u>	<u>Tons</u>	<u>Elect Power MW</u>	<u>Specific Inventory ton/MW</u>
NPD	1962	80	20	4
Douglas Point	1966	240 ^(a)	200	1.2
Pickering 1	1970	540 ^(a)	500	1.1
2	1971	540 ^(a)	500	1.1
3	1972	540 ^(a)	500	1.1
4	1973	540 ^(a)	500	1.1
CANDU-BLW	1971	240	250	1.0

(a) 23% in coolant system

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