Separation of Hydrogen Isotopes

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A symposium co-sponsored by the
Physical Chemistry Division of the
Chemical Institute of Canada and
the Canadian Society for Chemical
Engineering at the 2nd Joint
Conference of the Chemical Institute
of Canada and the American
Chemical Society, Montreal,
May 30–June 1, 1977.

ACS SYMPOSIUM SERIES **68**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1978

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.fw001

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.fw001

Library of Congress CIP Data

Main entry under title:
Separation of hydrogen isotopes.
(ACS symposium series; 68 ISSN 0097-6156)

Includes bibliographies and index.

1. Deuterium oxide—Congresses. 2. Hydrogen—Isotopes—Congresses. 3. Isotope separation—Congresses. 4. Heavy water reactors—Congresses.
I. Rae, Howard K., 1925- . II. Chemical Institute of Canada. Physical Chemistry Division. III. Canadian Society for Chemical Engineering. IV. Series: American Chemical Society. ACS symposium series; 68.

TK9350.S46 661'.08 78-760
ISBN 0-8412-0420-9 ASCMC8 68 1-184 1978

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In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.fw001

ACS Symposium Series

Robert F. Gould, *Editor*

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.fw001

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

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PREFACE

This volume describes process development and plant performance for the separation of deuterium from hydrogen, tritium from hydrogen, and tritium from deuterium. All of the important processes that are recognized today are included although not necessarily in equal detail or appropriate relative emphasis. Nonetheless, this volume forms a valuable, up-to-date report on the status of hydrogen isotope separation.

Obviously heavy water production is essential to a program of nuclear power production that is based on natural uranium-fueled and heavy water-moderated reactors. Canada and India have selected this route to nuclear power, and both are establishing an industrial heavy water production capability.

The Canadian design of a heavy water power reactor, the CANDU design, requires 0.85 Mg of heavy water per electrical MW of installed capacity. The heavy water is not consumed by reactor operation so that the demand for heavy water is set by the rate at which new nuclear power stations are built. A small make-up of less than 1% of the inventory per year is needed to replace losses by leakage.

With 4000 MW of nuclear–electric generating capacity in operation and with 15,000 MW committed for operation by 1988, Canada has a very substantial demand for heavy water. Several large production plants are in operation and more are being built. Thus, it is not surprising that one-half of the papers in this volume are from Canada; the chapters report on plant performance and on the development of alternative processes to the established water–hydrogen–sulfide exchange method.

Tritium is produced by neutron capture in deuterium and by uranium fission. Thus, heavy water in reactors contains a gradually increasing concentration of TDO, and aqueous wastes from any water-cooled reactor and from fuel reprocessing contain THO. Tritium recovery from these sources is desirable to minimize the release of tritium to the biosphere, and such tritium separation plants will become increasingly common. Tritium separation on a much larger scale will be necessary when fusion reactors are developed successfully.

Atomic Energy of Canada, Limited
Ontario, Canada
December, 1977

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In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

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Selecting Heavy Water Processes

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

Hundreds of methods have been proposed for the production of heavy water, but only a few show any real promise. This paper will discuss the important characteristics which define relative process attractiveness and will compare several chemical exchange and distillation processes. In this way it will show why the GS (Girdler-Sulfide) process has dominated heavy water production for 25 years. It will also review the current status of several promising alternatives.

A brief review of heavy water process development and heavy water production will set the background. Deuterium was first separated by the fractional evaporation of hydrogen in 1932 by Urey, Brickwedde and Murphy (1). Over the next few years water electrolysis, water distillation and hydrogen distillation were investigated as hydrogen-deuterium separation methods. During World War II in the USA, and to lesser extent in Germany, there was a very large effort to evaluate and develop methods for heavy water production (2,3). Two promising chemical exchange processes were defined—water-hydrogen and water-hydrogen-sulfide. The former was the basis of the first heavy water production at a reasonable cost from industrial scale plants. The latter eventually became known as the GS process, and the basis of all large heavy water plants.

Throughout the fifties and the sixties hundreds of methods were considered, dozens were investigated in the laboratory and in pilot plants, but only a handful were used in production (4). Major research and development to investigate heavy water processes (4) was done in nearly all the countries that built prototype heavy water power reactors: Canada, France, Germany, India, Italy, Sweden, Switzerland and United Kingdom.

Despite this large effort involving hundreds of man-years by chemists, physicists and engineers, no other method has reached the stage where it can challenge the GS process as the major source of heavy water.

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Heavy Water Plants

So far plant operating experience has been obtained with five processes, as shown in Table I.

Monothermal water-vapour-hydrogen exchange, with the enriched hydrogen reflux provided by electrolysis, was used at Trail in Canada (5) and in Norway (5); the latter plant is still in operation. An improved version of this process using exchange with liquid water is described by Hammerli (6) and referred to as combined electrolysis and chemical exchange (CECE). The original plant in Norway simply used electrolysis to produce heavy water. Water-hydrogen exchange units were being added to the plant in 1943 during the German occupation of Norway when it was destroyed by Allied raids; the plant was rebuilt and expanded after the war.

Water distillation was used as a production method briefly in three small plants during World War II (2).

In the USA in 1950 there was a need for a large heavy water production capacity and the GS process was chosen as the preferred method (7). Two 500 Mg/a plants were built. One third of the Savannah River plant is still operating after twenty-five years. The GS process was adopted in Canada in the mid-sixties to supply the CANDU* power reactor program. Current operating capacity in Canada is 1600 Mg/a in three plants and three more are being built (8). In India a 100 Mg/a GS plant is at an advanced stage of construction.

Five small hydrogen distillation plants have been operated. The plant in India, of 13 Mg/a capacity, continues in operation (9). The size of the Russian plant has not been reported; it also probably continues in operation.

A 25 Mg/a ammonia-hydrogen plant operated for several years in France (10). The first of three Indian ammonia-hydrogen plants, each about 65 Mg/a, (11,12) is being commissioned.

Heavy Water Production

The cumulative world production of heavy water to May 1977 is 11 Gg (excluding USSR and China). This is distributed by process as follows: GS - 93.2%, H_2O/H_2 exchange - 4.4%, H_2 Distillation - 1.3%, NH_3/H_2 exchange - 0.9% and H_2O Distillation - 0.2%. By country, 59% has been produced in the USA, 35% in Canada, 4% in Norway, 1% in India and 1% in France.

By about 1982 the Canadian heavy water production capacity will be 4000 Mg/a. This will consist of the three operating plants—Port Hawkesbury in Nova Scotia with a nominal design capacity of 400 Mg/a, Bruce A in Ontario of 800 Mg/a and Glace Bay in Nova Scotia of 400 Mg/a—and three plants now being built—

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*Canada Deuterium Uranium

Bruce B and D, each of 800 Mg/a nominal capacity, and La Prade in Quebec of 800 Mg/a. This capacity is expected to meet demands until about 1990 (8).

General Process Characteristics

Before considering the various individual processes and comparing their characteristics, it is important to look at the general nature of the deuterium-hydrogen separation problem which derives from the low deuterium content of all potential source materials. The consequences of this for any process can be readily seen in terms of its affect on the design of GS heavy water plants.

This very low value of the deuterium-to-hydrogen ratio in nature of about 150 ppm is the main factor responsible for the high cost of heavy water. It is necessary to process at least 8000 mols of feed per mol of product for all processes, and for the GS process the ratio of feed to product is nearly 40,000 to 1.

Reactor grade heavy water is 99.75 mol% D_2O. Thus, the overall concentration ratio from feed to product is about 3×10^6. This means that hundreds of separative elements in series are needed to go from natural water to reactor grade heavy water.

The combination of a very large feed flow and a very large number of separative elements means that heavy water plants are very large in relation to most other chemical plants. As a consequence heavy water is an extremely capital intensive product. Figure 1 shows the Glace Bay Heavy Water Plant. The first stage towers are about 7 m in diameter and 60 m high. Feed water goes to six of these towers in parallel at a total flow rate of about 40,000 m^3/d (10^7 US gallons/day). Total heat rejection by the plant is 300 thermal MW, mainly by cooling towers at the right of the photograph. The effluent water is cooled by spray modules in the effluent channel at the left of the photograph.

The combination of a dilute feed and a large overall concentration ratio means that cascading confers very important advantages. Figure 2 illustrates three cascade arrangements for a typical GS process design. In each case the product is 20% D_2O. In the two-stage arrangement the first stage gives a ten-fold enrichment. In the three-stage arrangement the first stage gives a four-fold enrichment while the second stage provides a further six-fold enrichment. The relative tower volumes show a 30% decrease for the two-stage case and a further 10% reduction for the three-stage case. The change in heavy water inventory is more dramatic. In the single stage case the inventory approaches the annual plant capacity. For two stages this is reduced by an order of magnitude and for three stages is reduced further by a factor of two. Adding more stages is not worthwhile since each stage adds extra equipment and increases plant complexity.

In all cases the first stage dominates plant costs. Thus, when comparing processes it is generally only this first stage

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

Table I

HEAVY WATER PRODUCTION PLANTS

Process	Country	Number of Plants: Shut Down	Number of Plants: Operating	Number of Plants: Being Built	First Plant	Operating Capacity 1977 Mg/a
H_2O/H_2	NOR.,* CAN	1	1		1934	30
H_2O Distn	USA	3			1944	-
GS	USA, CAN, IND	1	4	4	1952	1800
H_2 Distn	W. GER, RUS FR, SWIT, IND	3	2		1958	>13
NH_3/H_2	FR, IND	1		3	1968	-

* electrolysis only until 1948.

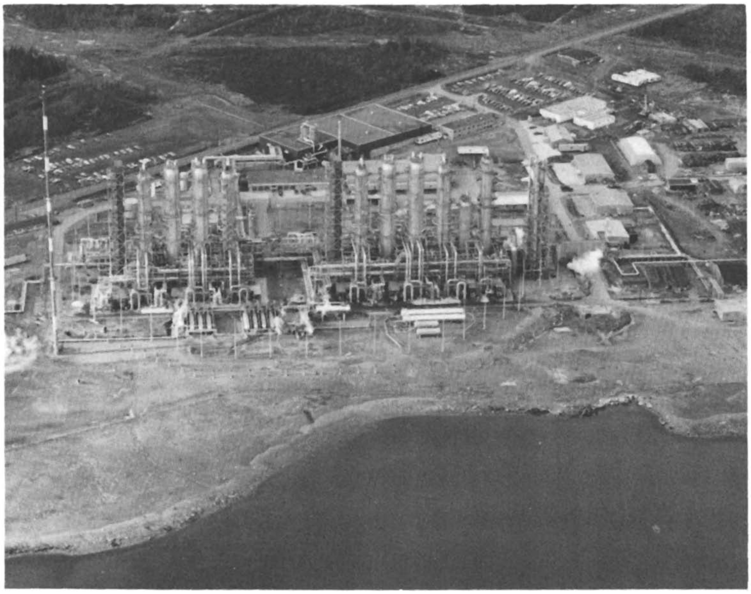

Figure 1. Glace Bay heavy water plant

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

that needs to be considered.

Figure 3 illustrates a three-stage GS process design showing the relative molar flow rates of water and hydrogen sulfide in each stage and the various interstage connections. The relative tower sizes are also illustrated. Because of the very large flows required in the first stage it is necessary to have several large towers in parallel; three are shown in this example. The product from the third GS stage is 20% D_2O. It is brought to reactor grade by water distillation which is a much simpler process operating at low pressure with a low potential for leakage. This final enrichment unit represents less than 5% of the total plant investment. Nearly all heavy water plants have been designed with different processes for primary enrichment and final enrichment (13).

Types of Processes

Table II is a partial list of the types of processes that have been considered for heavy water production.

Distillation is one of the simplest. However, tower volume is excessive for all potential working substances except hydrogen itself.

The most promising processes are based on chemical exchange.

Irreversible processes like diffusion have high energy costs and very large membrane or barrier areas are needed. Both electrolysis and gravitational processes, while offering fairly high separation factors, are very energy intensive and for this reason unattractive.

Adsorption processes are not particularly selective for deuterium and therefore require very large volumes of adsorbent. Biological processes have the same shortcomings as adsorption,

Table II

POSSIBLE HEAVY WATER PROCESSES

Process Type	Status
Distillation	Size Excessive Except H_2
Chemical Exchange	Most Promising
Diffusion	Barrier or Membrane Costs Excessive; High Energy
Electrolysis	Excessive Energy
Gravitational	Excessive Energy
Adsorption	High Adsorbent Volume
Biological	Excessive Volume
Crystallization	Impractical on Large Scale
Selective Photochemical	Promising if Selectivity Approaches 10^4

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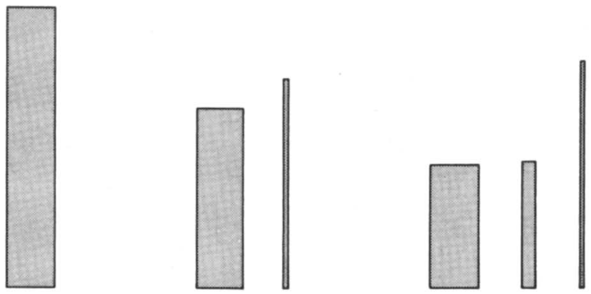

	SINGLE STAGE	TWO STAGES	THREE STAGES
RELATIVE TOWER VOLUME	1	0.7	0.6
RELATIVE PROCESS INVENTORY	1	0.12	0.05

Figure 2. GS process cascades

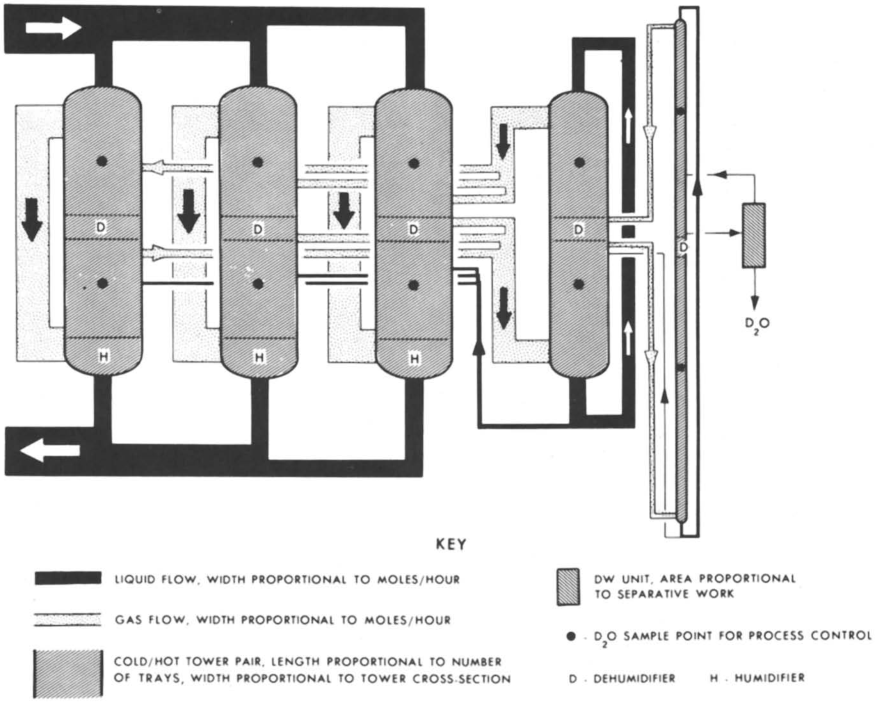

Figure 3. GS flowsheet

and hence require the production of excessive amounts of deuterium-depleted organisms.

Countercurrent crystalization systems (ice-water) can conceivably have very large numbers of separating elements in a reasonable volume and have a low energy requirement; however, a reasonable processing rate can only be achieved with an impractically small crystal size (14).

Selective photochemical processes are at too early a stage to assess properly. If success is to be achieved for deuterium-hydrogen separation, a very high selectivity is needed to offset the disadvantage of the low natural abundance of deuterium.

The remainder of the paper will review distillation and chemical exchange processes in more detail.

Separation Factor

One of the most important parameters in defining the attractiveness of a process is the separation factor. It is defined as

$$\alpha = (D/H)_A/(D/H)_B$$

where A and B are enriched and depleted streams from a separating device, are two phases in physical equilibrium, or are two compounds in chemical equilibrium.

The separation factor is frequently the first parameter to be determined in studying a new heavy water process. Values range from unity (no separation) to about 30 (low temperature electrolysis of ammonia).

Distillation

Table III compares four distillation processes based on hydrogen, methane, ammonia and water. In each case optimum conditions have been selected. For water the pressure is higher than is used for final enrichment. This is because the process, as optimized for primary enrichment, is based on vapour recompression to conserve energy. The low separation factors for the

Table III

DISTILLATION PROCESSES

	Temperature k	Pressure kPa	Separation Factor
Hydrogen	24	250	1.5
Methane	112	100	1.0035
Ammonia	239	100	1.036
Water	378	120	1.024

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three substances other than hydrogen are an overwhelming disadvantage. This can be seen by comparing tower volumes. The relative tower volume is proportional to $TP^{-1}(\alpha-1)^{-2}m^{-1}$ for a given gas velocity and HETP (height equivalent to a theoretical plate) where T is absolute temperature, P is pressure, α is separation factor and m is the number of hydrogen atoms per molecule. Clearly $(\alpha-1)^{-2}$ dominates this expression. Figure 4 shows this relative tower volume as a function of pressure. There is a three to four orders of magnitude difference in tower volume between the compounds of hydrogen and molecular hydrogen itself. The capital cost associated with the former as distillation working substance would be far too high for these to be attractive heavy water production processes. However, as already indicated, water distillation is used extensively for final enrichment from a D/H ratio of about 0.1. Hydrogen distillation, on the other hand, is a potentially attractive process. As will be discussed later, it is close to being competitive with the GS process.

Chemical Exchange

The GS process is the archetype of chemical exchange processes. Deuterium is transferred from a water molecule to a hydrogen sulfide molecule and visa-versa:

$$H_2O + HDS \rightleftharpoons HDO + H_2S.$$

The separation factor is roughly equal to the equilibrium constant for this reaction. At 303 K α = 2.33 and at 403 K it is 1.82. This difference is the basis of the bithermal concentration process to be described later.

The large flows and large energy input have already been discussed qualitatively. For the GS process the feed rate per kg D_2O is 35 Mg and the energy required per kg D_2O is 25 GJ of thermal energy and 700 kWh of electrical energy.

The three other chemical exchange processes discussed in this paper are water-hydrogen, ammonia-hydrogen and amine-hydrogen:

$$\begin{aligned} H_2O + HD &\rightleftharpoons HDO + H_2, \\ NH_3 + HD &\rightleftharpoons NH_2D + H_2, \\ CH_3NH_2 + HD &\rightleftharpoons CH_3NHD + H_2. \end{aligned}$$

In each case the gas is hydrogen and the other component is the liquid.

Figure 5 illustrates the simplest chemical exchange flowsheet - that for monothermal exchange as used in Norway or at Trail. The liquid feed is enriched in deuterium as it flows down the tower and encounters progressively richer gas. At the bottom of the tower the liquid is totally converted to the gas,

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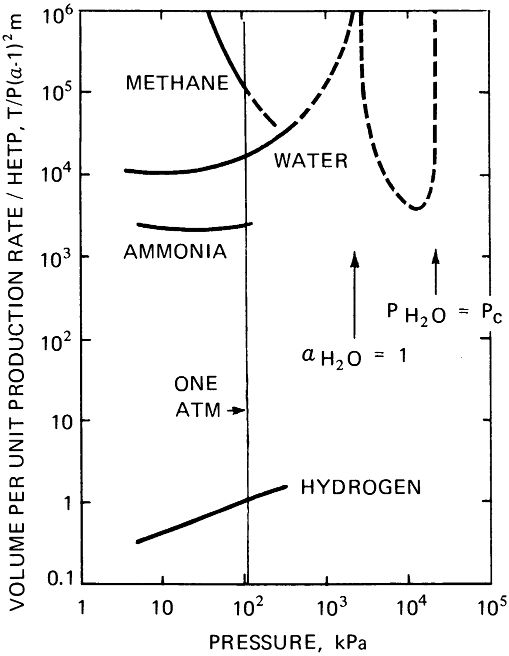

Figure 4. Relative tower volume for distillation

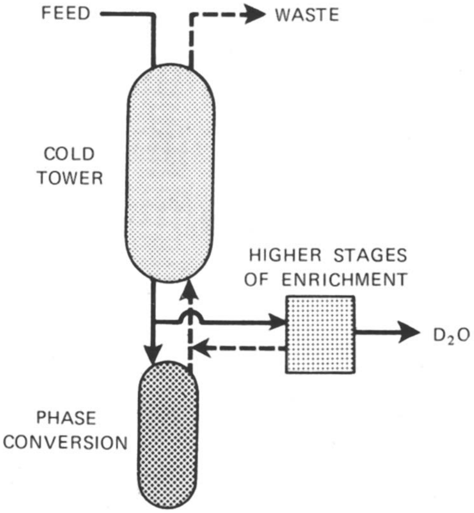

Figure 5. Simple monothermal process

except for that fraction which forms the feed to higher stages in the cascade. This phase converter is analogous to a reboiler in distillation. Phase conversion is expensive in most exchange systems. However, water electrolysis used for commercial hydrogen production can be a special case. Then heavy water recovery becomes a byproduct operation. Other hydrogen production techniques can function in a similar manner (15).

Ammonia-hydrogen exchange is most readily adapted to monothermal operation because the heat of formation from hydrogen and nitrogen is relatively low. In this case ammonia synthesis gas is the deuterium source, so the feed is a gas. The ammonia exchange liquid is not only cracked in the phase converter at the bottom of the exchange column as in Figure 5, but is also synthesized for reflux at the top of the column - in this form the monothermal flowsheet is completely analogous to a distillation process. Such a monothermal ammonia-hydrogen exchange process was first used at Mazingarbe in France and is the basis of two plants in India (11).

Practical monothermal processes are unfortunately rare because phase conversion is generally too complex or too costly. Instead, the bithermal arrangement is used as illustrated in Figure 6 for the GS process. The phase converter of Figure 5 is replaced by a hot tower. In this illustration, and in several of the GS plants, the hot and cold towers are combined in a single vessel: they are then referred to as hot and cold tower sections. In the GS process the water is enriched in deuterium in the cold section and is depleted in the hot section. The water contacts the same gas at the top of the cold section as at the bottom of the hot section, and the flows are controlled so gas and water tend to approach equilibrium with each other at these two locations. Therefore, the deuterium-to-hydrogen ratio in the depleted effluent water approaches a value equal to α_h/α_c ($\approx$0.8 for the GS process) of that in the feed. The countercurrent gas and water flows, if appropriately controlled at close to the correct flow ratio, cause a net transport of deuterium up the hot section and down the.cold section to provide enriched gas and water at the centre of the tower. Here a small enriched stream is fed forward to another tower working in a higher concentration range (a higher stage) and is matched by a partially depleted returning stream. The net transport of deuterium to the higher stage is controlled to equal the extraction rate from the feed water. The connection between the first stage and the higher stage can be gas as in Figure 6, or water or both.

The hot tower of the bithermal process can be thought of as analogous to an imperfect reboiler, and so provides gas to the cold tower at a considerably lower deuterium concentration than is achieved by the phase converter of the monothermal process. As a consequence, not only does the hot tower and its associated heating and cooling equipment of the bithermal process replace the phase converter of the monothermal process, but the

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bithermal process requires a much larger cold tower.

The monothermal and bithermal process arrangements are compared in Figure 7 in the form of McCabe-Thiele diagrams. The equilibrium lines have slopes of $1/\alpha$. The operating line for the monothermal case has a slope of unity, equal to the liquid-to-gas flow ratio (L/G). The large divergence between the operating and equilibrium lines allows a substantial enrichment (e.g. 5 times the feed concentration) to be reached with only a few theoretical trays. The difference in deuterium concentration between the feed (F) and the waste (W), i.e. the recovery from the feed, can be large; as a fraction it approaches $(\alpha-1)/\alpha$. For the bithermal case L/G, the slope of the operating lines, must be between $1/\alpha_c$ and $1/\alpha_h$. Consequently, both hot and cold columns are severely pinched and many theoretical trays are required for the same five-fold enrichment. The recovery, as already noted, is small; less than $(\alpha_c-\alpha_h)/\alpha_c$. Thus, the penalty for circumventing the need for phase conversion is a large increase in flows and an even larger increase in column volume. Nonetheless, bithermal is generally the more attractive arrangement to select because feasible reactions for a monothermal process are rare and require large energy inputs.

Although the simple flowsheets discussed so far have limited recoveries set by the above relationships, it is possible to add stripping sections to the process and achieve high recoveries approaching unity in the limit. This means adding more column volume as shown in Figure 8, for a gas-fed bithermal process. This is the arrangement of the amine-hydrogen process which has been studied extensively by Atomic Energy of Canada Limited (16). To strip the gas to a low deuterium content requires a liquid sufficiently lean in deuterium. This is produced by recycling some lean gas to the hot tower and lengthening the hot tower correspondingly. In the simple case without stripping, the gas feed would enter the bottom of the hot tower and not require a gas recycle. Another version of a gas-fed bithermal flowsheet with stripping is described by Nitschke (12).

Figure 9 describes the separation factor as a function of temperature for the four systems being considered. The larger absolute values for the hydrogen-based systems are evident, as are the possibilities of much larger values of α_c/α_h. The two non-aqueous systems can reach very low temperatures with a consequent large increase in separation factor. In this respect the amine system (17) is particularly attractive. Relative to the GS system, the much larger separation factors for the hydrogen-based systems mean that recoveries are higher, flows per unit product lower and fewer theoretical trays are required. All these advantages could lead to substantially smaller tower volume for the hydrogen-based processes, but this can only be assessed after rates of exchange are considered which relate actual trays to theoretical trays.

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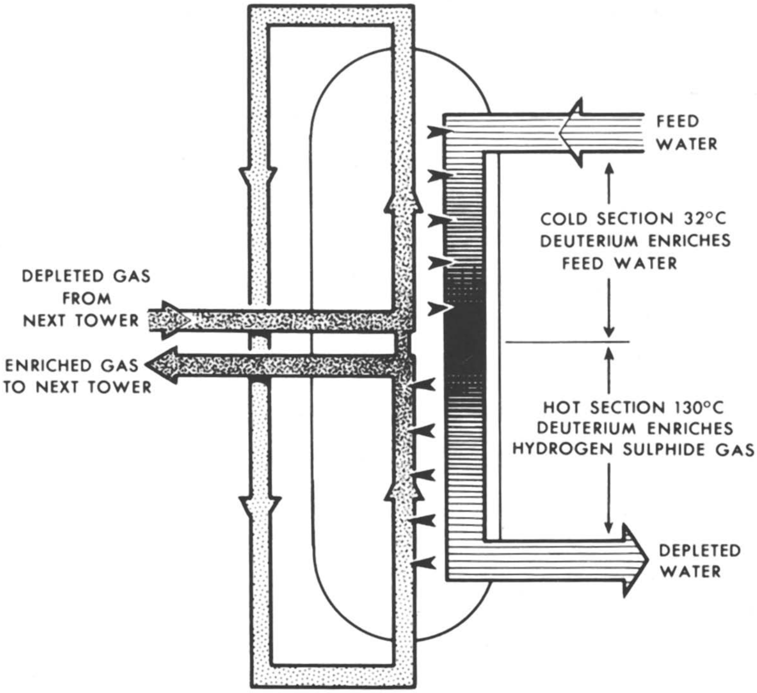

Figure 6. Exchange tower with gas feed forward

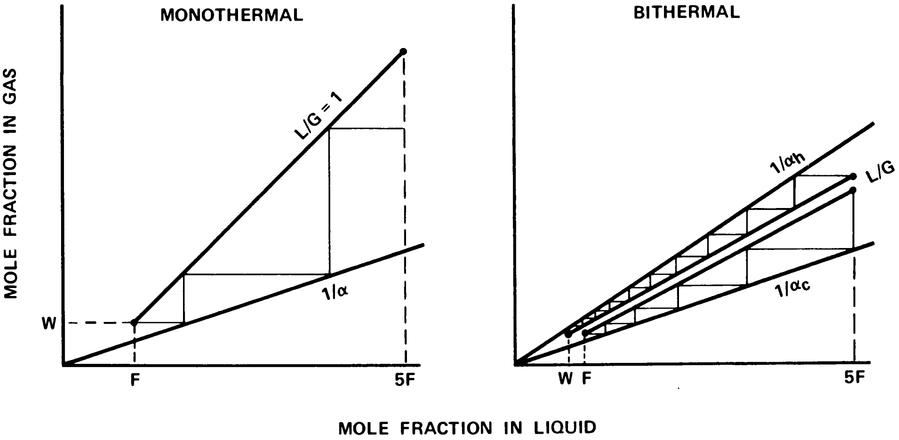

Figure 7. McCabe–Thiele diagrams

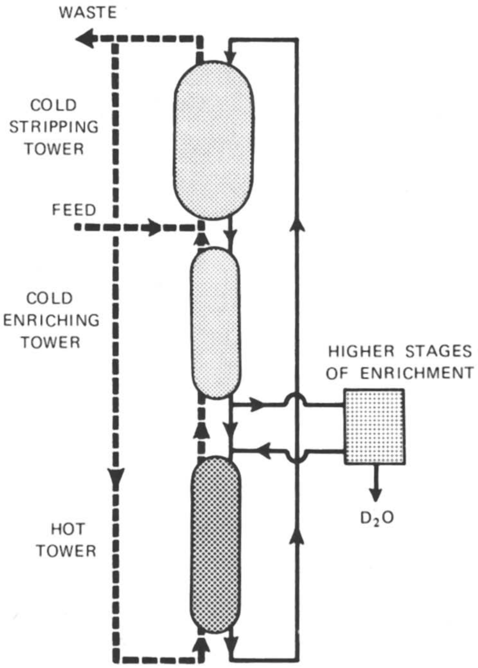

Figure 8. Gas-fed bithermal process with stripping

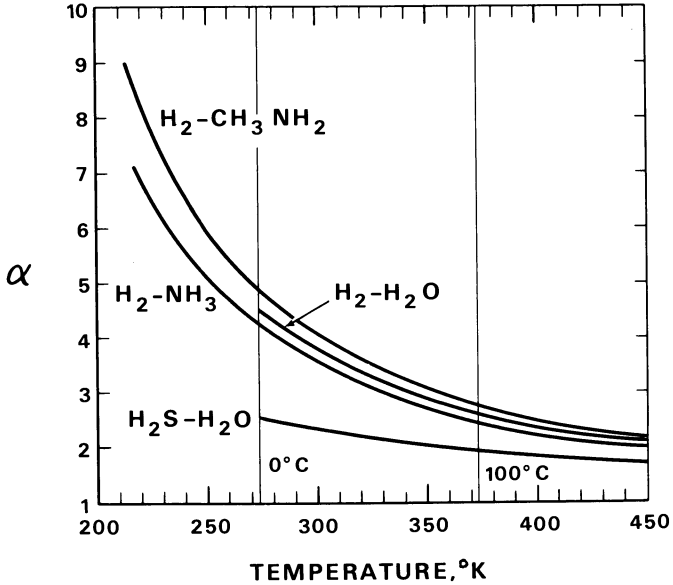

Figure 9. Liquid–gas separation factors

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Because exchange rates are generally fast at hot tower conditions for all four processes being considered, the important mass transfer and kinetic limitations occur in the cold tower. These will now be discussed in some detail.

The first step in comparing rates of deuterium exchange is to define practical process conditions for each system, and this is done in Table IV. Because of the low solubility of hydrogen, given as the reciprocal of Henry's Law constant in the Table, the hydrogen-based processes operate at high pressure. The temperature ranges are primarily dictated by vapour pressure for the upper value and by a minimum practical exchange rate for the lower value. The amine process is restricted in hot tower temperature by thermal stability of the catalyst (16). The GS process is restricted in cold tower temperature by the formation of a solid hydrate. Each of the hydrogen-based processes requires a catalyst - homogeneous for the non-aqueous ones and heterogeneous for water-hydrogen. Even so the values of the kinetic rate constants which can be achieved are low (18, 19). The value given in Table IV for water-hydrogen is for the catalyst as a colloidal slurry (20); higher effective rates can be achieved with a fixed-bed catalyst as will be discussed later.

For the purposes of comparison exchange rates are evaluated here for gas-liquid contacting on a sieve tray, even though this is not the most practical cold tower contacting equipment for all four processes. As illustrated schematically in Figure 10, the gas flows up the tower through a multitude of holes in each tray. The liquid flows across each tray, over a weir and down to the next tray; the gas pressure drop across a tray holds the liquid on the tray. Thus, there is continuous, multi-contact, countercurrent operation. The gas-liquid mixing on each tray generates a large interfacial area between them in the form of bubble and droplet surfaces. The gas and liquid then must separate before each phase passes to its subsequent tray.

Table IV

CHEMICAL EXCHANGE PROCESSES

	GS	Amine	NH_3/H_2	H_2O/H_2
Pressure MPa	2	7	7	10
Temperature K	303	220	230	300
	400	315	330	440
Catalyst	-	CH_3NHK	NH_2K	Pt/C
Rate Constant* s^{-1}	5000	130	15	1
Gas Solubility* mol/(m^3.MPa)	830	24	10	8

*at cold tower temperature and a practical value of catalyst concentration.

In simple terms the tower volume is given by:

$$\text{Volume} = \text{GRTN}/(\text{PK}_G\text{a})$$

where G is the gas flow in mols/s, R is the gas law constant (MPa.m^3/(mol.K)), T is the temperature in K, N is the number of theoretical trays, P is the pressure in MPa, K_G is the overall mass transfer coefficient in m/s and a is the interfacial area per unit volume (m^2/m^3). The overall mass transfer coefficient can be related to the gas phase mass transfer coefficient, k_G, and the liquid phase mass transfer coefficient, k_L, by:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L RT}$$

where H is the Henry's Law constant (MPa.m^3/mol).

For a soluble gas like hydrogen sulfide the value of H is small (Table IV) and the gas phase resistance is important and possibly controlling. For hydrogen H is larger by two orders of magnitude and k_G is also increased; thus, only the liquid phase resistance need be considered. The value of k_L depends on both mass transfer and chemical reaction so that the kinetic rate constant, k_r, enters into its determination.

It is beyond the scope of this paper to treat the evaluation of k_L in any detail. Following the exposition of Astarita (21), Figure 11 shows how k_L, the mass transfer coefficient for the liquid phase for combined absorption and chemical reaction, is related to k_L^o, the liquid phase coefficient for physical absorption without reaction, as a function of k_r. In expressing this function the ratio of k_r/s is used where s is the fractional rate of surface renewal (s^{-1}). A typical value of s for a sieve tray is 50 s^{-1}. If D is the diffusivity of the dissolved gas (m^2/s), then $k_L^o = (Ds)^{0.5}$. The parameter in this figure, $\varepsilon s^{0.5}/aD^{0.5}$, allows for the effect of the volume fraction of liquid contained in the total unit volume, ε, which is important in the slow reaction regime.

In the slow reaction regime in Figure 11, the exchange reaction occurs in the bulk liquid. k_L is less than k_L^o and equals $\varepsilon k_r/a$. In the case of the ejector contactor (15) where a is very large and s is likely also increased relative to a sieve tray, the low value of $\varepsilon s^{0.5}/aD^{0.5}$ could bring both the water-hydrogen and the ammonia-hydrogen systems into the slow reaction regime.

When $k_L \approx k_L^o$ the exchange rate is controlled primarily by physical absorption. This is a transition region or the diffusion regime where $k_r < s$. The reaction occurs primarily in the bulk liquid, but sufficiently rapidly that physical absorption is the rate controlling step. Both the slurry-catalyzed water-hydrogen system and the ammonia-hydrogen system are in this region for contacting on a sieve tray.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

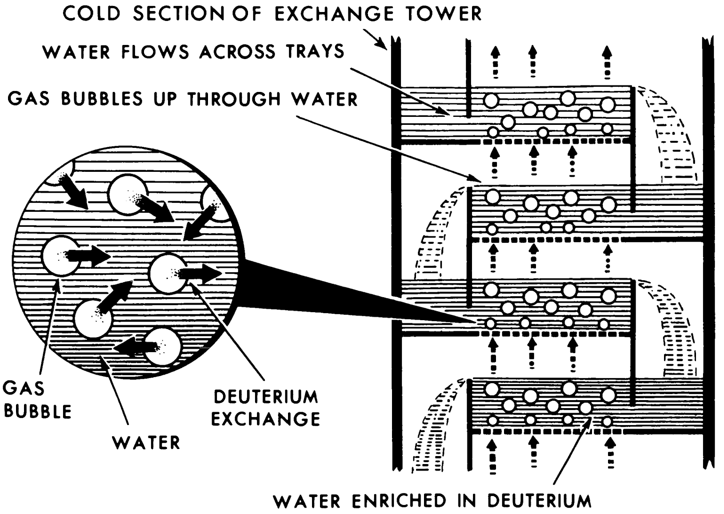

Figure 10. Sieve tray operation

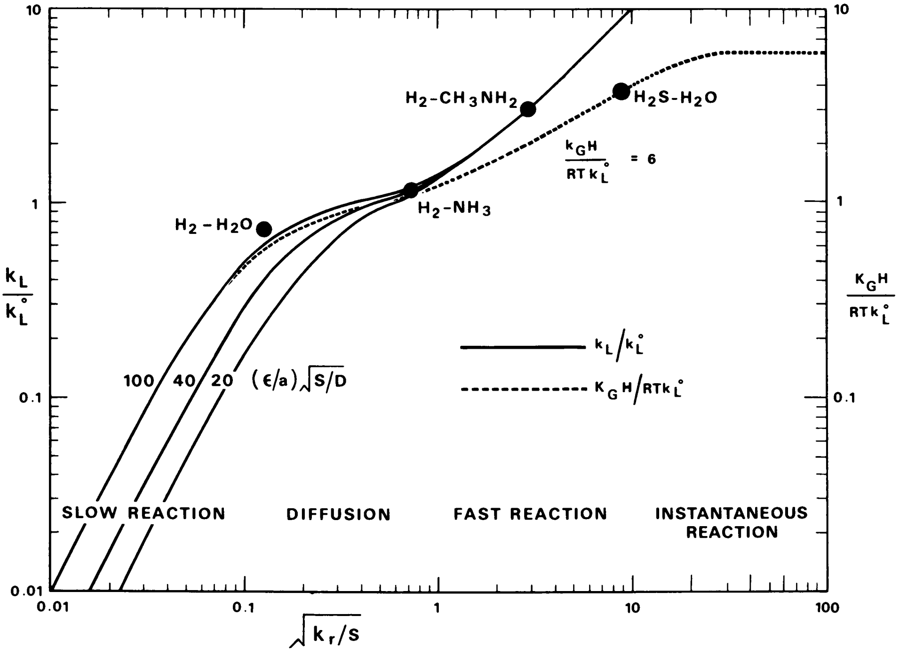

Figure 11. Cold tower mass transfer coefficients

The fast reaction regime in Figure 11 begins when $k_L > k_L^o$, and chemical reaction enhances the mass transfer rate. Once k_r/s exceeds about 3, then k_L is equal to $(k_rD)^{0.5}$. Here the reaction zone is limited to fresh elements of liquid brought to the interfacial surface by turbulent eddies; diffusion and reaction occur simultaneously at the surface while the bulk liquid is always at equilibrium. The amine-hydrogen process is clearly in this regime.

For any given contactor system the fast reaction regime ends once the gas phase mass transfer rate begins to control; this is the instantaneous reaction regime. As shown in Figure 11 the GS process is almost in this regime. The value of k_r for this system given in Table IV is only approximate; no reliable measurement has been made. However, 5000 s^{-1} probably is a lower limit. As discussed above the low value of H for the H_2O-H_2S system means the gas phase resistance must be considered even at modest values for k_r. Pilot plant data for GS sieve tray efficiency are consistent with k_GH/RTk_L^o equal to 6. The dotted line in Figure 11 represents K_GH/RTk_L^o when $k_GH/RTk_L^o = 6$ for various values of k_r and hence k_L.

Using the data in Table IV and Figure 11, the overall volumetic mass transfer coefficients, K_Ga, and the tower volumes have been estimated as shown in Table V assuming $a \approx 300\ m^{-1}$ for H_2O-H_2S and H_2O-H_2, and $a \approx 600\ m^{-1}$ for NH_3-H_2 and CH_3NH_2-H_2. For the processes based on hydrogen the low values of K_Ga are compensated for by the fewer number of theoretical trays, the higher pressure and the lower gas flow rate. Thus, for the amine process the tower volume is less than for the GS process. However, the higher pressure for the former results in a vessel weight which is similar to that for the GS process. K_Ga can be enhanced by using mechanical energy to increase the interfacial area very considerably, as in the ejector contactor (15), and so to reduce tower volume significantly at the expense of complex and costly internals.

The overall exchange rate is of course dependent on catalyst concentration and on the form of catalyst used. For the water-hydrogen process the values of K_Ga given in Table V are for a hydrophobic platinum catalyst supported on the surface of a packing in a trickle-bed reactor (22). This new catalyst developed by Atomic Energy of Canada Limited provides a higher volumetric mass transfer rate than the slurry catalyst referred to earlier. The bithermal process arrangement requires a high pressure (10 MPa) so that K_Ga is low and the tower volume is large. For the monothermal CECE arrangement the pressure is lower (1.5 MPa) and K_Ga is an order of magnitude higher giving a somewhat larger value for PK_Ga; the much smaller tower volume results mainly from the reduction in N and G. The same advantage for the monothermal flowsheet can also be seen for the ammonia-hydrogen system.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

Turning now to consider hot tower volumes, there is no longer a problem of low exchange rates. For the GS process the rates in the cold and hot towers are roughly similar, both controlled by mass transfer in the gas phase. For the hydrogen-based processes the rates of exchange are much faster in the hot tower than in the cold tower. Thus, in principle the hot tower volumes for these processes could be smaller than for the GS process. However, in practice the bithermal design in these cases is optimized to concentrate separative work in the hot tower and so limit demands on the cold tower; as a result both tend to have about the same volume. The values of N used in Table V reflect this optimizing process, and so the relative cold tower volumes are representative of the relative total tower volumes for the bithermal flowsheets.

Transfer Processes

A special category of chemical exchange reaction is high temperature processes which transfer deuterium from a source material available as large single streams, such as water or methane, to hydrogen. Thus, the very large scale possible with these source materials can be combined with the inherent advantages of using a hydrogen-based process which can concentrate deuterium more efficiently. Hydrogen itself is an abundant source (world production equivalent to 30,000 Mg D_2O/a but it is derived from a vast number of individual units, with a typical large unit being equivalent to only 70 Mg D_2O/a.

The steam-hydrogen process illustrated in Figure 12 links a water feed to the amine-hydrogen process. Water is evaporated into depleted hydrogen and the mixture is heated to 870 K where the exchange reaction occurs over a nickel oxide catalyst to transfer deuterium from the steam to the hydrogen. The steam is condensed and the hydrogen returned to the bithermal amine-hydrogen unit. Two steam-hydrogen equilibrations in series are required, and even so the deuterium content of the replenished hydrogen is significantly below natural. Flows are large and energy requirements are high; the steam-hydrogen transfer process by itself is equivalent in cost per kg of heavy water extracted to more than half the cost of the heavy water produced by the GS process. Although some improvements in this transfer process may be possible, it will be difficult to achieve a competitive combination with amine-hydrogen or other hydrogen-based process.

A similar transfer process which can be used to extract deuterium from methane (23) has been studied at the Gulf Research and Development Company. Depleted hydrogen is mixed with methane feed and the exchange reaction is carried out over a catalyst at about 1000 K. The two components are separated by liquefying the methane. The replenished hydrogen feeds a distillation unit which separates the deuterium. This process combination is illustrated in Figure 13. Again two equilibrations

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Table V

RELATIVE COLD TOWER VOLUMES

	Gas Flow kmol/mol D_2O	Theoretical Trays[1]	K_Ga s^{-1}	Relative Volume[2]
H_2O - H_2S	74	27	0.9	1
CH_3NH_2 - H_2	24[3]	10	0.04	0.6
NH_3-H_2				
monothermal	14	5	0.008	0.9
bithermal	31[3]	10	0.008	4
H_2O - H_2				
CECE	9	4	0.08[4]	0.3
bithermal	50	8	0.008[4]	5

[1] For a 4-fold enrichment.

[2] Volume = GNT/PK_Ga; see Table IV for P and T except for CECE which has $P = 1.5$ MPa.

[3] Weighted average for stripping and enriching columns (see Figure 8).

[4] For the fixed-bed hydrophobic platinum catalyst.

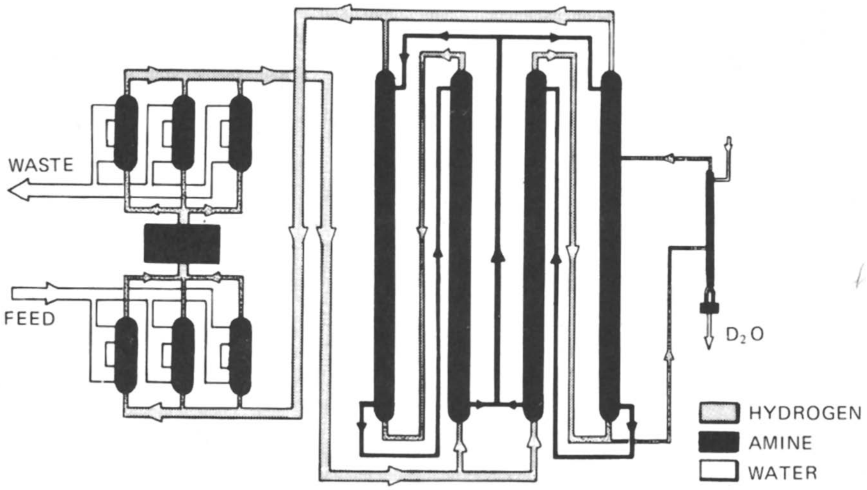

Figure 12. Steam–H_2–amine process

with countercurrent flow of hydrogen and methane between them are needed. Energy consumption is high, most of it for refrigeration. The methane-hydrogen part of the process is probably similar in cost to steam-hydrogen transfer.

It should be noted that selective photochemical processes based on the use of lasers will require a similar transfer step to link the separation process to an abundant feed. Depending on the molecules involved, high temperature may not be needed to achieve a separation factor near unity for the transfer reaction, but unusually low pressures may be a requirement. Certainly, this can be a costly operation because of the large volume of material to be handled and the necessity to recover the recirculating deuterium carrier from the waste stream with a high efficiency .

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Process Comparison

While the separation factor is a key property for ranking the economic attractiveness of processes, energy consumption is almost of equal importance. A convenient chart to illustrate this is shown in Figure 14. An expanded scale of log(α-1) is used for the separation factor. Electrical or mechanical energy is converted to equivalent thermal energy using 40% efficiency and added to the actual thermal energy requirement to give total equivalent thermal energy in GJ/kg. The GS process requires 30 GJ/kg which is equivalent to about 5 barrels of oil per kilogram.

The energy consumption for a process is difficult to define without a detailed design. It depends on the degree of energy recovery which in turn depends on such factors as the ingenuity of the designer, the relative cost of energy and capital equipment, and how the plant is to be financed. Total energy if often under-estimated in preliminary process evaluations because of the simplifying assumptions that are usually made.

Processes in the uneconomic region of Figure 14 have too low a separation factor (water crystallization), too high an energy consumption (hydrogen diffusion) or both (water distillation). Electrolysis ranks highest in separation factor and highest in energy consumption unless it is undertaken for hydrogen production. In that case about one third of the deuterium contained in the feed water can be recovered as a hydrogen stream enriched to three times natural at practically zero cost (9).

The Gulf process (23) is described in Figure 13; while its energy consumption is high, it has many inherent advantages which are likely to permit an attractively low capital cost. However, not only is its energy consumption about twice that of the GS process, but this energy is primarily mechanical and therefore expensive. Under especially favourable circumstances the Gulf process might become competitive with GS.

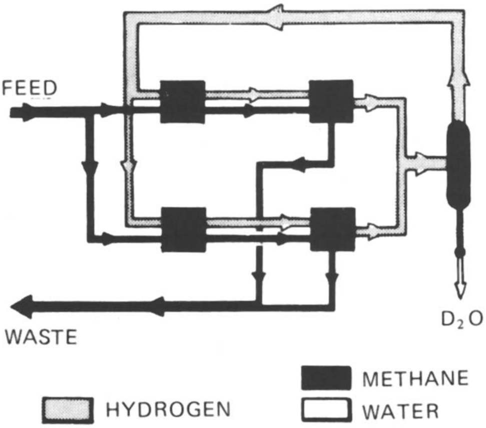

Figure 13. C_4–H_2 *process*

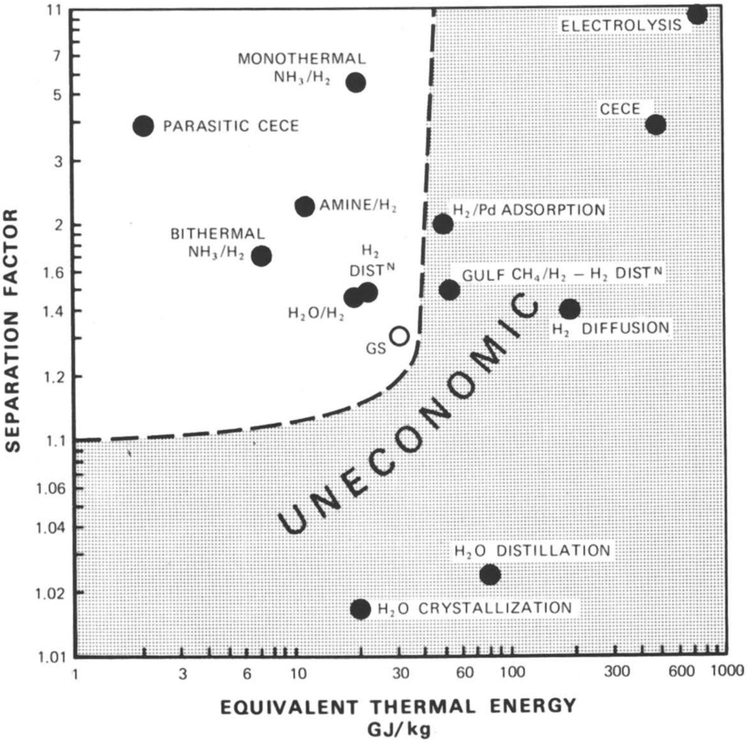

Figure 14

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

The CECE process is shown twice - at the high energy consumption for the case where there is no market for the electrolytic hydrogen and at the low energy consumption where the heavy water is a by-product of the hydrogen production. The latter is a particularly favourable situation.

The value of α used in Figure 14 for the separation factor of the bithermal exchange processes is α_c/α_h in order to characterize each of them by a single value.

The GS process has a lower separation factor and a higher energy consumption than six other processes in Figure 14. It even has the distinctly undesirable feature of using hydrogen sulfide which is corrosive, smelly and toxic. Yet the GS process dominates heavy water production and is still the preferred method of production. Why? Table VI compares it with two of its potential competitors:

- the GS process uses an abundant feed and therefore enjoys the advantage of a large scale; hydrogen-fed plants are limited to less than 100 Mg/a capacity and the hydrogen-based processes are expensive to link to water or methane,
- while the GS process energy consumption is higher than the other two, it is not excessive,
- the GS process enjoys fast mass transfer rates, but so does hydrogen distillation,
- the temperature which controls GS process energy input is moderate, whereas both hydrogen distillation and amine-hydrogen require expensive refrigeration,
- the GS process pressure is not high enough to incur a large cost penalty,
- while the GS process separation factor is not as high as for the other processes, it is reasonable.

The major reason for the success of the GS process is the scale effect.

Table VI

PROCESS COMPARISON

	GS	Amine	Hydrogen Distillation
Feed	H_2O	H_2	H_2
Energy GJ/kg D_2O	30	11	22
Mass Transfer	Fast	Slow	Fast
Temperature* K	400	220	24
Pressure MPa	2	7	0.25
Separation Factor	1.3	2.2	1.5

*Controlling major energy input

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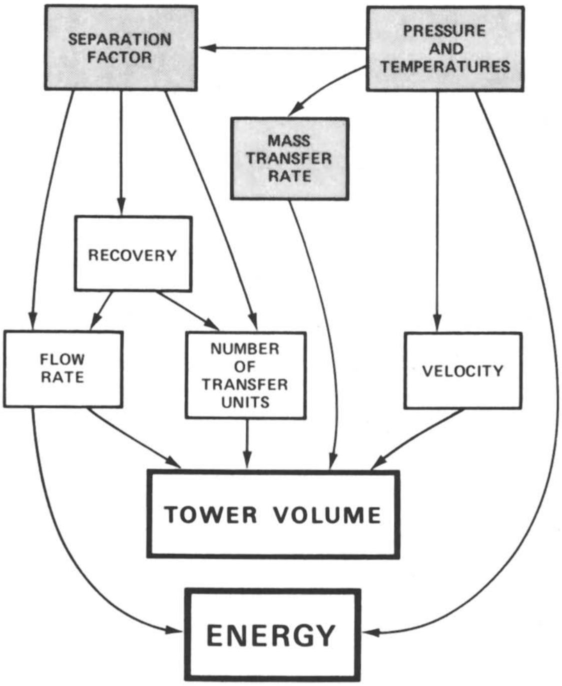

Figure 15. Key factors in process evaluation

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

The key factors in process evaluation are outlined in Figure 15. The inherent process conditions and properties of pressure, temperature, mass transfer rate and separation factor are all important. Pressure and temperature can be varied to optimize the conditions, but usually only a relatively narrow range is practical. These conditions set the values of α and K_Ga. Knowing α it is possible to select the recovery, the flow rate, G, and the number of transfer units or theoretical trays, N. The pressure and temperature set the allowable velocity, V. Then G, N, K_Ga and V combine to define tower volume. The major parameters determining energy consumption are flow and temperature, but as already noted the detailed process flowsheet is important here.

Summary

The GS process is the only large-scale independent process with a direct water feed and this is largely responsible for its pre-eminent position in heavy water production.

Water-hydrogen exchange is only attractive in combination with electrolytic hydrogen production - the combined electrolysis and catalytic exchange (CECE) process.

Three hydrogen-based processes, amine-hydrogen, ammonia-hydrogen and hydrogen distillation, are all close to being competitive with the GS process. Of these, amine-hydrogen is likely to be the cheapest. Hydrogen distillation linked to natural gas as the deuterium source, while distinctly energy intensive, may be a near competitor under some circumstances.

Hydrogen is a potentially abundant heavy water source, but individual plants are small. However, hydrogen-based heavy water plants are being built and more will be committed. Nonetheless, the GS process will continue as the dominant one for another 10 or 20 years.

Nomenclature

a - interfacial area per unit volume of mixed phases, m^{-1}
D - diffusivity of dissolved gas, m^2/s
(D/H) - atom ratio of deuterium to hydrogen
G - gas flow rate, mol/s
H - Henry's Law constant, $MPa.m^3/kmol$
k_G - gas phase mass transfer coefficient, m/s
K_G - overall mass transfer coefficient based on gas phase concentrations, m/s
k_L - liquid phase mass transfer coefficient, m/s
k_L^o - liquid phase mass transfer coefficient for physical absorption, m/s
k_r - psuedo first order rate constant for conversion of monodeuterated dissolved gas to monodeuterated solvent, s^{-1}
L - liquid flow rate, mol/s

m - number of hydrogen atoms in the molecule
N - number of theoretical trays
P - pressure, MPa
R - gas law constant = 8.2×10^{-3} m^3.MPa/(kmol.K)
s - fractional rate of surface renewal, s^{-1}
T - temperature, K
V - gas velocity based on the active area of the tray, i.e. tower cross sectional area minus total downcomer area, m/s
α - deuterium separation factor
ε - volume fraction of liquid on a tray

Subscripts: c - cold tower; h - hot tower

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RECEIVED December 16, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch001

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Bruce Heavy Water Plant Performance

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch002

To satisfy the Canadian demand for heavy water which is used as a moderator and heat transport medium in CANDU reactors, Atomic Energy of Canada Limited contracted the Lummus Company of Canada Limited in 1969 to design and construct Bruce Heavy Water Plant 'A' at the Bruce Nuclear Power Development.

The 9.5 square kilometer (2300 acres) site had previously been purchased by Ontario Hydro for the Douglas Point Nuclear Generating Station. It is located in the County of Bruce on the eastern shore of Lake Huron, midway between the towns of Kincardine and Port Elgin, approximately 240 kilometers (150 miles) northwest of Toronto.

Ontario Hydro was responsible for commissioning and operating the plant which has a design capacity of 96.6 kg/h of 99.75% purity heavy water (D_2O).

Commissioning of Plant 'A' commenced in 1971 and proceeded without any major difficulty through 1972 and 1973. On 28 June, 1973, Ontario Hydro purchased the plant from AECL and declared the plant in-service. Design production capacity was reached in April, 1974 after eleven months of operation. Production rates and capacity factors have steadily been increased such that the official capacity was increased to 100.6 kg/h in 1976.

As a result of the early operating success of BHWP A, Ontario Hydro announced the construction of three additional and essentially identical heavy water plants at Bruce (BHWP B, C and D). A cutback in the Nuclear Generation construction program in 1976 resulted in one of these, BHWP C, being cancelled and the schedule for another, BHWP D, being deferred by two years.

Bruce Heavy Water Plant uses the proven Dual Temperature Hydrogen Sulphide - Water Exchange Process to separate deuterium. This process has been in use on a commercial scale in North America for 25 years.

Following a brief description of the production process, BHWP A performance from in-service to the end of 1976 is described in terms of the following key performance criteria: Employee Safety, Care of the Environment, Reliability and Manpower Development. Finally, commissioning progress to date of BHWP B is described.

Production Process

Water is pumped from Lake Huron (see "Figure 1") with a deuterium isotopic content of 148 mg/kg. It is filtered to remove solids and preheated to 29°C. The pH is lowered to 3.8 - 4.2 by the addition of sulphuric acid to decompose carbonates, the water is degassed of oxygen and carbon dioxide, and then the pH is raised to 6.0 - 6.5 by the addition of caustic to avoid corrosion to carbon steel processing equipment. This treated water is then fed to the Enriching Units.

Each of the heavy water plants consists of two identical enriching units and one finishing unit. Each Enriching Unit can be divided broadly into three sections: the absorption and desorption section, the extraction section and the enriching section.

The absorption and desorption section serves two functions: removal of H_2S from the depleted water before it is returned to the lake, and removal of H_2S in the purge gas before it is flared. As the feed water passes through this section, it is partially saturated with H_2S.

In the extraction section (see "Figure 2") water passes counter-current to a recirculating stream of hydrogen sulphide (H_2S) gas in three large sieve tray towers operating in parallel which are the first stage. By making use of a two temperature exchange reaction (see "Figure 3") between hydrogen sulphide (H_2S) and water - at 30°C deuterium is concentrated in the liquid phase and at 130°C deuterium is concentrated in the gas phase. The three first stage towers (see "Figure 2") each have two distinct process temperature sections - the top being a cold section and the bottom being a hot section. Deuterium is carried forward to the second stage only in the gas phase while anything not extracted from the water is returned to the lake from the first stage after it has been stripped of H_2S and cooled. If H_2S in the effluent is not within the

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch002

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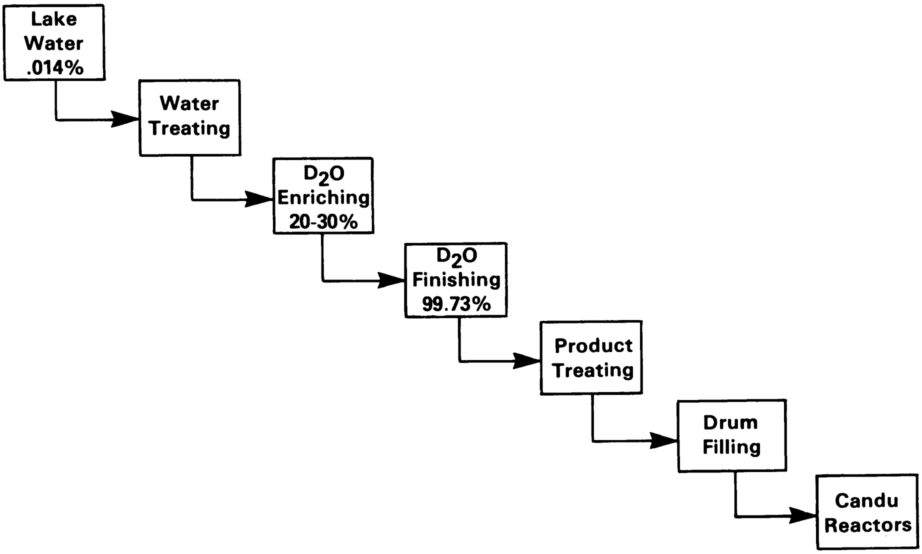

Figure 1. BHWP-A D_2O production

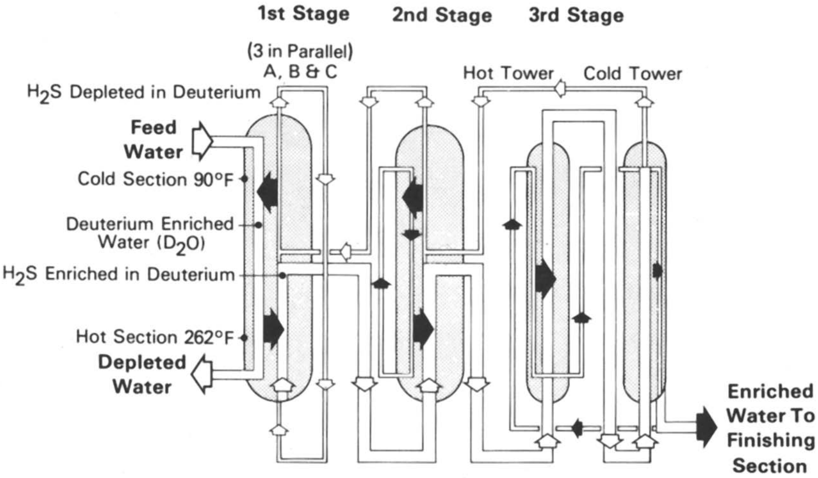

Figure 2. Enriching section

$$H_2O\ (\ell) + PDS\ (g) \underset{130°C}{\overset{30°C}{\rightleftharpoons}} PDO\ (\ell) + H_2S\ (g)$$

Figure 3. GS process

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch002

regulatory limits it is diverted to aerated lagoons where the gas is removed and the water is sent to the lake.

One part in 7000 coming out of the lake is deuterium. But it is only economical to remove about 20% or one part in 35000.

The second and third stages only enrich or concentrate the deuterium which has been extracted. The second stage is a single tower whose operation is similar to the first stage towers. However, there is no heating section at the bottom of the hot tower as the gas is already hot coming forward from the first stage. To maintain liquid circulation in the second stage, water is pumped from the bottom of the hot tower, through a cooler to the top of the cold tower. The third stage consists of two separate towers - one cold tower, the other a hot tower. Third stage operation also differs from the previous two. Enriched liquid from the bottom of the cold tower is taken forward for further processing. The H_2S in this enriching unit liquid product is stripped out and returned to the third stage gas loop.

Enriched water at 20 - 30% D_2O concentration from both enriching units is fed to the finishing unit. The finishing unit is a three stage, four tower steam vacuum distillation system that concentrates the product from the enriching units into the final reactor grade heavy water. All finishing unit towers contain sieve trays.

The heavy water is then treated in either of two potassium permanganate batch kettles to oxidize organic impurities. The product is either drummed or shipped in bulk to CANDU reactors.

Translated into reality, the process units are shown in the aerial view of BHWP (see "Figure 4"). BHWP A water intake is shared with the Douglas Point Nuclear Generating Station. The figure shows the building housing the sand filters, the degassing towers, the main switch yard, the steam supply from Douglas Point Nuclear Generating Station and the Bruce Steam Plant, the H_2S storage bullets, the flare (145 m or 475 feet above grade), the lagoons, the absorption and desorption section consisting of an Absorber tower, Purge tower and an Effluent Stripper tower, the three first stage towers, the second stage tower, the third stage and the four tower, three stage Finishing Unit. The figure also shows the bank of heat exchangers across the front of each unit, used to achieve the two process temperatures and optimize steam utilization.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch002

Employee Safety

One major disadvantage of the Dual Temperature Hydrogen Sulphide - Water Exchange Process is the toxicity of the H_2S gas and the potential safety hazards it poses. The greatest danger from the inhalation of hydrogen sulphide is from its acute effects; it is not cumulative in action. Exposure to moderate concentrations causes headaches, dizziness, nausea and vomiting in that order. Continued exposure may cause loss of consciousness, respiratory failure and death if the gas concentration is high enough. Hydrogen Sulphide is also flammable and in certain mixtures with air it can be explosive.

From the outset, Ontario Hydro operating staff established rigorous safety policies and procedures for all aspects of commissioning and operating Plant A, with special emphasis on the handling of H_2S and equipment containing it.

Safety performance at Bruce Heavy Water Plant is presented in terms of "H_2S Incidents" (see "Figure 5") or the number of employees temporarily affected by the toxicological properties of hydrogen sulphide, number of lost time accidents and lost time accident frequency (see "Figure 6").

"H_2S Incidents" are defined as "sub-acute" or "acute". Briefly, a "sub-acute" incident is one in which a person exposed to Hydrogen Sulphide shows signs of being affected but does not require resuscitation or assistance to exit from the area affected by H_2S, while an "acute" incident is one in which a person overcome by Hydrogen Sulphide requires resuscitation and/or assistance to exit from the area affected by Hydrogen Sulphide.

Only one H_2S Incident has resulted in a lost time accident (in 1975) when the affects of H_2S caused an employee to fall and bruise his ribs.

In the two year period from May 1972 to May 1974, which covered the bulk of commissioning, there was not a single lost time accident. The two lost time accidents in 1976 were both back injuries caused by improper lifting techniques.

Factors contributing to BHWP safe work performance (see "Figure 7") have been grouped under the broad headings of Management Policies, Safety Training, General Training, Procedures, Employee Relations, Plant Integrity, Personal Protective Equipment and Safety Equipment. All are important to a successful safety program.

At no time during the history of Bruce Heavy Water

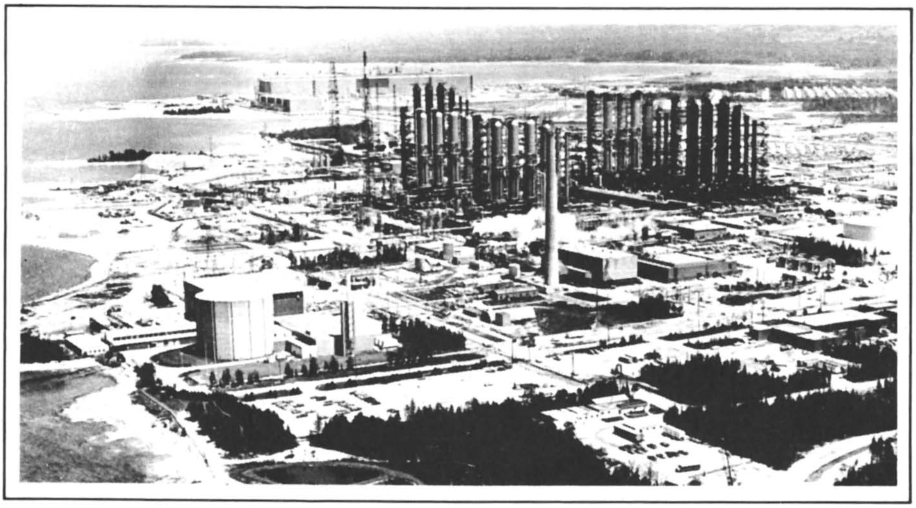

Figure 4. Aerial view of BHWP

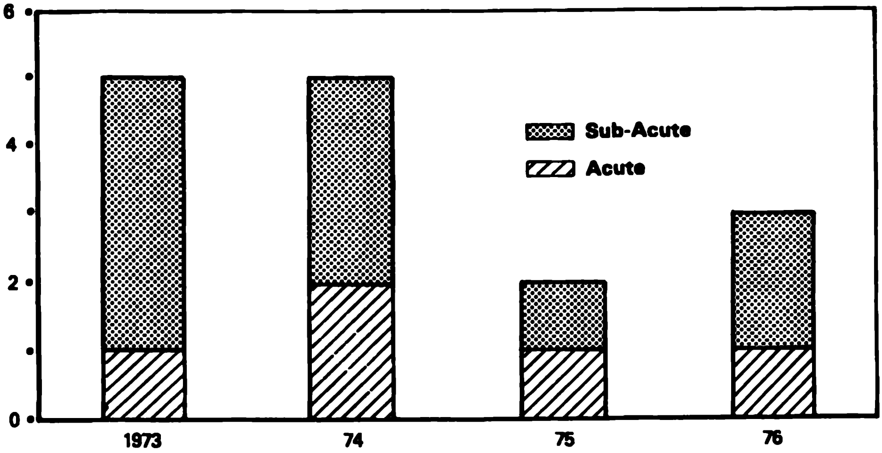

Figure 5. BHWP—History of H_2S incidents

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch002

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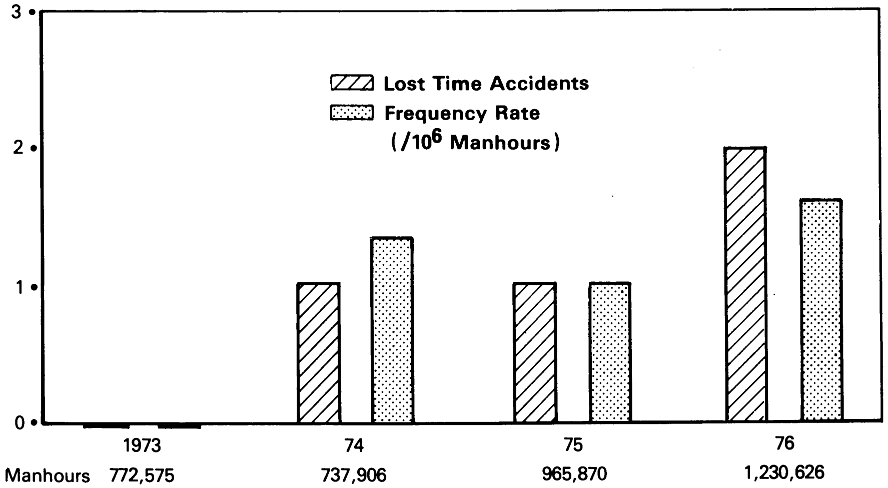

Figure 6. BHWP—Safety performance

1. **Management Policies**
   - number 1 priority
   - work environment
   - training
   - procedural approach
   - plant modification control
   - equipment maintenance
   - event reporting.
2. **Safety Training**
   - new employee orientation
   - emergency procedures
   - buddy training
   - rescue training
   - protection training - fire, chemical, electrical, etc.
   - Work Protection Code
   - tank car repairs
   - vessel entry
   - first aid
   - regular meetings.
3. **General Training**
   - science fundamentals
   - equipment/systems principles
   - plant systems
   - field skills.
4. **Procedures**
   - plant access control
   - the buddy system
   - work on H_2S systems
   - control of work
   - equipment inspections.
5. **Employee Relations**
   - Medicals
   - Personal Hygiene
   - communications.
6. **Plant Integrity**
   - isolating circuits and devices
   - equipment design
   - emergency power, steam, water and air
   - equipment inspections.
7. **Personal Protective Equipment**
   - conventional
   - breathing equipment
   - rescue stations.
8. **Safety Equipment**
   - fire fighting
   - H_2S detectors and monitors
   - gas detectors
   - rescue vehicle
   - survey vehicles
   - first aid room.

Figure 7. Factors contributing to safe work performance

Plant has its operation presented a risk to the health and safety of the public.

Care of the Environment

Bruce Heavy Water Plant has two major environmental considerations - H_2S emissions to atmosphere and H_2S emissions to water. On the first of these, Hydrogen Sulphide is an odourous material. If concentrations reach more than 200 $\mu g/m^3$ (micrograms per metre cubed) H_2S can be smelled by most people and is considered by virtually all as an unacceptable odour. The plant is situated in a rural and summer resort area. Complaints of odour started to be received shortly after H_2S was introduced into the units in 1973. By year end, a total of 56 complaints were registered (see "Figure 8"). A task force was formed to rectify this unsatisfactory situation. Several actions were taken: efforts were directed toward reducing the amount of H_2S released; steps were taken to insure a combustible mixture of stack gas at all times; drain water to be stripped of H_2S was minimized; releases of steam or nitrogen and other inerts to the flare were accompanied by increased propane flows to the flare. In 1974, three odour reports came in, in 1975 four odour reports were received and in 1976 there were two. Relations with the public are no longer a problem as far as H_2S odours are concerned.

An H_2S recovery system to minimize H_2S and propane usage is being built as part of the plant expansion. As a result, H_2S releases to the flare will be further reduced.

On the second environmental consideration, H_2S emissions to water, all water streams containing H_2S must be stripped of it before the water is returned to the lake. "Figure 8" shows the number of times the regulatory limit for hydrogen sulphide in water was exceeded by year. Unstable flows in the towers were quite frequent in 1973. This instability caused the effluent stripper operating conditions to fluctuate deterring its effectiveness. Physical changes to tower tray weirs and the addition of antifoam to the process water steadied operating conditions and therefore improved the effectiveness of the stripper. Replacement of unreliable instrumentation and better process control during startups and shutdowns have improved performance. A continuous H_2S-in-water monitor which has proven reliable with quick response was installed on the stripper outlet. This monitor plus other effluent stripper process parameters of

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feed temperature, level and pressure have all been interlocked to automatically divert effluent to the lagoons if a preset concentration of H_2S is exceeded or the measured variables exceed defined limits.

Reliability

The reliability of BHWP A has generally been good for a plant of its size with minimal redundancy in its operating equipment. "Figure 9" shows downtime experience to date. Planned unit turn-arounds have been reduced from 10 weeks in 1973 to 4 weeks in 1975. An outage planned for September, 1976 was advanced to take advantage of an unplanned outage in July.

Another factor of reliability is production rate. "Figure 10" shows instantaneous production rates in kilograms per hour that the plant was operating, i.e. shutdown periods have been excluded. The original Design Capacity was 48.3 kg/h for each enriching unit. Following start up in 1973, tray flooding problems caused by foaminess of the process and a deficiency in tray design were experienced. Correction of these problems by the addition of antifoam to the feedwater and modification of the trays resulted in dramatic improvements in production rates.

Production rates have continued to improve, resulting in a re-rating of the plant capacity in 1976 to 100.6 kg/h.

Capacity Factors (based on Design Capacity for 1973 to 1975 and based on Demonstrated Capacity for 1976) and annual production are shown in "Figure 11". These do not include about 99 Mg that were "enriched" to 20% isotopic purity during 1974/1975/1976, of which 31 Mg were "finished" to reactor grade elsewhere in 1975 and 42 Mg were "finished" elsewhere in 1976. If these "finished" quantities were completely credited to BHWP A, the apparent Capacity Factors in 1975 and 1976 would be 71.7% and 90.9% respectively.

Manpower Development

The purpose of training is to ensure that each position in the plant is filled by a person with appropriate knowledge and skills so that the plant is operated safely, effectively and efficiently. Training is therefore a part of the plant's performance objectives.

Formal training is provided by lectured courses and demonstrated skills in the classroom and the field. For each job, the level and proficiency which must be

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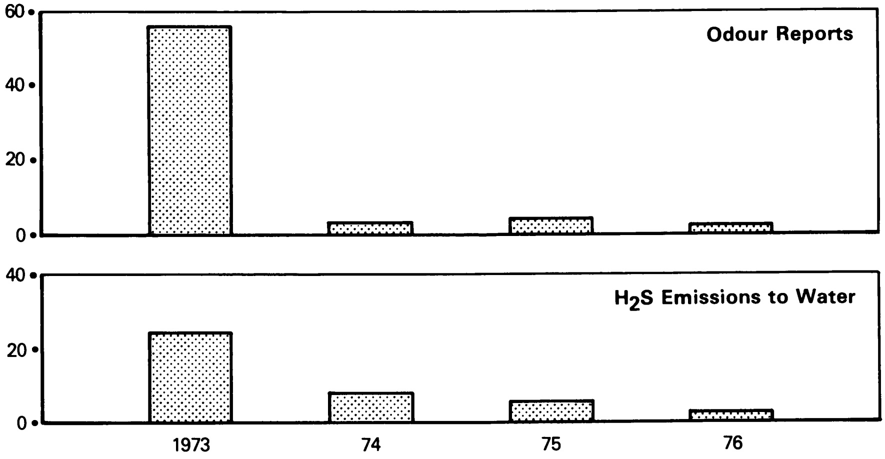

Figure 8. Environmental performance to date

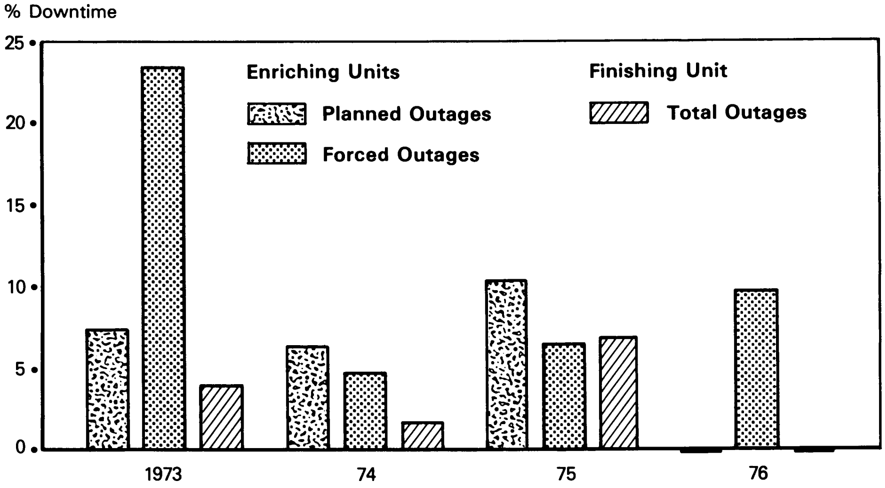

Figure 9. BHWP—Reliability

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attained are specified in each of the following: Management, Science Fundamentals, Equipment and System Principles, Field Skills, Specific Plant Systems, AECB Operating License, Protection Training.

Training is provided by the Nuclear Training Department of Ontario Hydro at Rolphton, by the Manpower Development Department of Ontario Hydro at Orangeville, by the Bruce Training Centre at the site and by the BHWP Training Section.

BHWP Training Section is staffed by eight Training Technicians, two engineers and a Training Officer.

BHWP operates a five shift system instead of the traditional four, so that operators, maintainers and control technicians on shift spend ten to fourteen percent of their time in training. In 1975 there were 6,822 man courses given and in 1976 there were 11,400 man courses given at BHWP.

Commissioning Progress Report - BHWP B

Assembling a commissioning team of engineers, operators, maintainers and control technicians for Plant B began in 1975. A nucleus of personnel with operating experience in Plant A is being augmented with new employees. The commissioning group is preparing commissioning estimates and procedures, and inspecting and witnessing equipment tests as the plant is being built. This group is commissioning and operating the various plant systems as they are turned over from construction.

The air compressor system for Plant B and the utilities for Finishing Unit F2 were turned over from construction and commissioned in the last quarter of 1976.

The last turnover of the Finishing Unit process system was on 6 January, 1977. Pre-startup checks of equipment and instrumentation were completed by 18 February, 1977. Operation of F-2 on demineralized water followed and this program was completed by the end of April. Equipment inspections following this run and minor deficiency corrections were completed by 10 May, 1977 and startup on intermediate product from Plant A commenced. First reactor grade product from F2 was produced on 23 May, 1977.

The plan (see "Figure 12") shows last turnover of Enriching Unit E4 equipment for commissioning 1 May, 1978. Enriching Unit E3 last turnover is scheduled for 15 December, 1978. This plan also shows Plant D Finishing Unit F4 last turnover for commissioning at the end of September, 1979 with Enriching Units 7 and

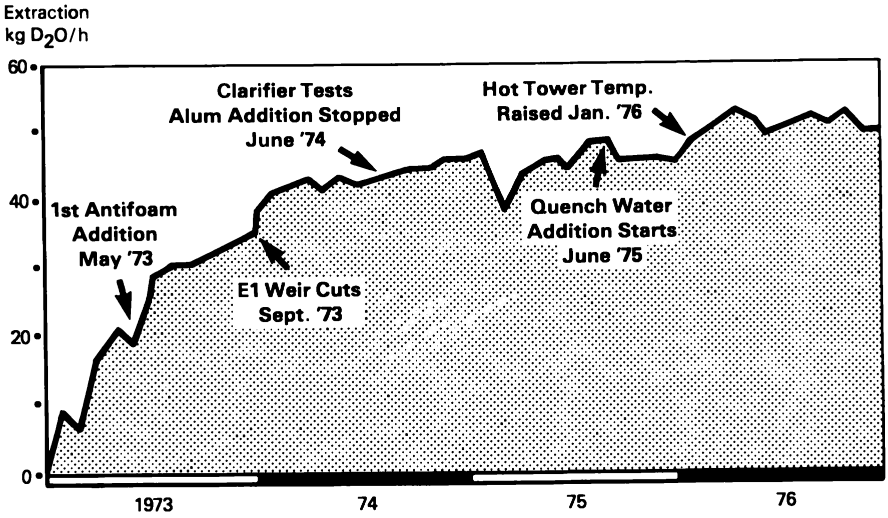

Figure 10. Enriching unit extraction (kg D_2O/h)

	Capacitor Factor %	Production Megagrams
1973 (6 mo.)	57	249
1974	76	640
1975	68	574
1976	86	758
	74	2221

Figure 11. BHWP-A

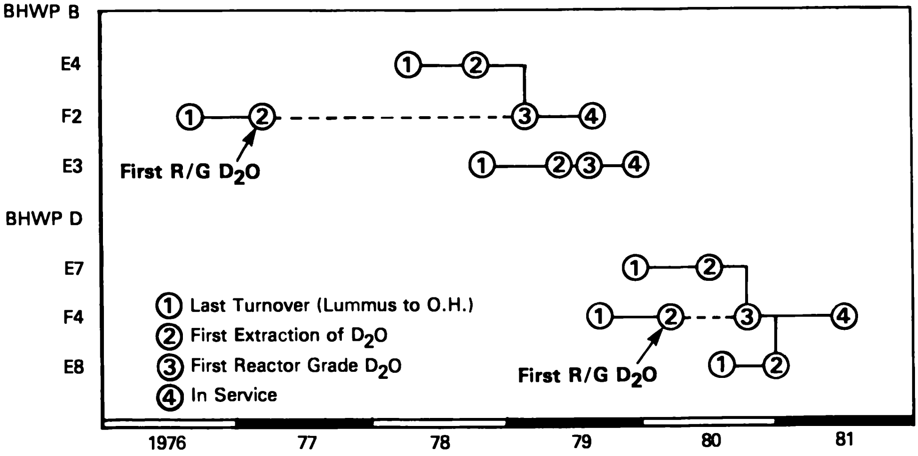

Figure 12. Commissioning milestones

8 to follow in 1980.

Conclusion

The co-operation of AECL and Ontario Hydro has brought success to Bruce Heavy Water Plant to date. Comparable results are expected in the future.

RECEIVED September 12, 1977

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Hydrogen-Amine Process for Heavy Water Production

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch003

Ammonia-hydrogen or amine-hydrogen exchange is one of the three major chemical systems considered useful for deuterium enrichment processes. The other two being the water-hydrogen sulfide system (GS process) presently being used to produce the major fraction of the world's heavy water supply and the hydrogen-water system which is currently under active development. Heavy water plants based on ammonia-hydrogen exchange have operated in France and are being commissioned in India. The usefulness of amines in place of ammonia was shown by Bar-Eli and Klein (1) in 1962. This work showed amines, particularly methylamine had faster exchange rates than the comparable ammonia-based system.

At Chalk River, after work with the ammonia-hydrogen system showed a water-fed plant did not offer any advantage over the GS process, development was started on the amine-hydrogen system. A parallel development program for the amine process was also initiated by the Commissariat a L'Énergie Atomique in France and details of the exchange reaction work were reported by Rochard and Ravoire (2). The amine chosen was methylamine (MA). The advantages of methylamine over ammonia are faster deuterium exchange rates, higher hydrogen solubility and a low vapour pressure. The choice of methylamine over other amines was discussed in detail by Bancroft and Rae (3). The original catalyst was the potassium salt of methylamine, potassium methylamide (PMA), because of its favourable exchange rate coupled with reasonable cost. Subsequent work forced a modification of the catalyst and the reasons for this will be discussed.

The development of the amine process at CRNL proceeded in three major areas: contactor development, process chemistry and process design. Development of efficient gas-liquid contactors was required to provide high mass transfer rates per unit volume in the cold towers (-50°C) where the exchange reaction rate is relatively slow. This program evolved through a series of pilot plant contactors ranging in size from 5 to 15 cm diameter at low pressure in glass to a 25 cm stainless steel contactor that operated at 2 MPa (300 psi) for both cold tower and hot tower testing. Further information on contactor development and process design was obtained in cooperation with Sulzer Bros., Switzerland who had independently constructed a pilot plant using a full scale contactor operating at full process pressure (4).

Extensive process design work and economic evaluations were done at CRNL and under contract with industrial engineering firms.

The very extensive chemistry program consisted of determining the physical and chemical properties of the system, developing handling and analytical techniques, determining the reactivity of the system with potential impurities, examining factors which affect the deuterium exchange rate, looking for better catalysts to improve the exchange rate and studying the stability of the catalyst solution at process conditions. This program was very much of a pioneering one because of the scarcity of information on solutions of alkali metal alkylamide in amines in the literature. It was necessary to first develop suitable laboratory techniques to handle such a reactive system safely and in the absence of atmospheric contaminants to obtain meaningful quantitative data. The absence of previously published information on related systems meant that little guidance was available for prediction of the chemical behaviour and all aspects of the work had to be experimentally determined. Development of a complete range of analytical methods was a major component of the program. With this lack of background information, unforeseen results were often observed. A prime example in this work was the discovery that hydrogen at process pressure is a reactive species; not only in the deuterium exchange reaction but also chemically. This is not so in the comparable ammonia system and was totally unexpected. It was this discovery that necessitated the development of a new catalyst to make the process viable. Because the process operates at high pressure (6-13 MPa, dictated by the host ammonia plant) to obtain effective mass transfer rates, much of the chemistry had to be done at conditions which simulated the process. This added the complication of having to develop special experimental techniques.

This work illustrates the importance of chemistry studies in process development. Although deuterium exchange is the central feature of a heavy water process, successful development requires detailed knowledge of all aspects of process chemistry. In many cases these are largely unknown beforehand.

The chemistry work was done by a number of groups at CRNL and through contracts with the University of Alberta, Trent University, Raylo Chemicals Ltd. in Alberta and Chemical Projects Ltd. in Toronto. A more detailed review of this chemical work forms the major portion of this paper.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch003

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Process Chemistry

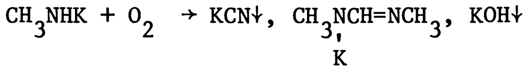
The process liquid, methylamine, must contain a dissolved catalyst to provide an acceptable deuterium exchange rate. This catalyst is prepared by dissolving potassium metal in the methylamine. The potassium slowly dissolves to give a blue solution typical of alkali metals in ammonia or amines.

$$K + CH_3NH_2 \rightarrow \overset{\text{Blue}}{K^+, K^-, e^-_{solv}} \rightarrow \overset{\text{Yellow}}{KNHCH_3 + \tfrac{1}{2}H_2}$$

In amines with potassium Fletcher et al (5,6) at CRNL have shown this colour to be due to an equilibrium between potassium anions and solvated election ion pairs. The blue coloured solution slowly decomposes to give the yellow potassium methylamide solution and hydrogen.

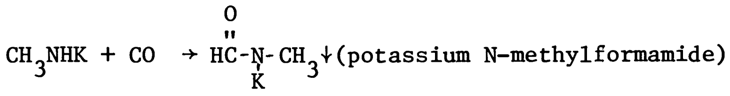
Alkali metal alkylamides dissolved in amines are strong bases and are very reactive chemically. They react vigorously with air and water so that special techniques are required when handling and studying these systems. Some of the more important reactions with impurities encountered in the process are listed below.

$$CH_3NHK + H_2O \rightarrow CH_3NH_2 + KOH\downarrow$$

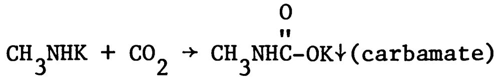


$$CH_3NHK + O_2 \rightarrow KCN\downarrow,\ CH_3\underset{K}{N}CH{=}NCH_3,\ KOH\downarrow$$

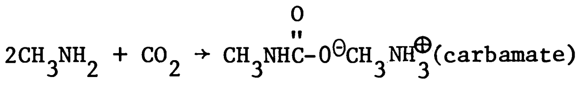
Potassium
Dimethylformamidide



$$CH_3NHK + CO \rightarrow H\overset{O}{\overset{\|}{C}}\text{-}\underset{K}{N}\text{-}CH_3\downarrow\text{(potassium N-methylformamide)}$$



$$CH_3NHK + CO_2 \rightarrow CH_3NH\overset{O}{\overset{\|}{C}}\text{-}OK\downarrow\text{(carbamate)}$$



$$2CH_3NH_2 + CO_2 \rightarrow CH_3NH\overset{O}{\overset{\|}{C}}\text{-}O^{\ominus}CH_3NH_3^{\oplus}\text{(carbamate)}$$

$$CH_3NHK + NH_3 \rightarrow CH_3NH_2 + KNH_2\downarrow$$

All of these reactions have been studied in varying degrees of detail to determine the identity of the products and the effect they have on the process. The major consequence of these reactions is destruction of catalyst thus reducing the exchange rate, and producing insoluble solids that may cause deposition and blockage of equipment. It is therefore a requirement that these impurities be maintained at an acceptably low level in the process to avoid these problems.

An area of process chemistry that was extensively studied both at Chalk River and by Sanford, Prescott and Lemieux at Raylo Chemicals, Edmonton was the thermal stability of the PMA-MA system. Thermal decomposition occurs to yield three major products: hydrogen, potassium dimethylformamidide (PDMFA) and ammonia,

$$2CH_3NH_2 + CH_3NHK \rightarrow 2H_2 + CH_3N{=}CHNKCH_3 + NH_3.$$

The rate of this reaction has been determined over the range of process conditions. As a result the optimum hot tower temperature originally set at 70°C (3) based on preliminary decomposition data was reduced to 40°C. The decomposition reaction has two process effects; it results in a loss of catalyst that requires make-up and it produces ammonia and PDMFA both of which must be removed. The ammonia must be removed because of its reaction with PMA forming potassium amide which has a limited solubility (0.06 mmoles/g). Removal of PDMFA is of less importance but it will eventually build up to a concentration that exceeds its solubility (3.3 mmoles/g @ -40°C) and will precipitate.

In the study of ways to reduce the decomposition rate an unexpected side reaction was discovered. Since hydrogen was a product of the decomposition, one of the postulated first steps was dehydrogenation of the PMA to a methylenimine,

$$CH_3NHK \rightleftarrows CH_2{=}NK + H_2.$$

If this postulated intermediate step was reversible then a high hydrogen partial pressure might inhibit the decomposition. Since the process operates most effectively at high hydrogen pressure it was essential to investigate the decomposition reaction over the full pressure range. High hydrogen pressure did reduce the decomposition rate but the results were very erratic and the experiments were plagued by the irreproducible appearance and disappearance of white precipitates. Workers at Raylo Chemicals showed the hydrogen was reacting with the PMA-MA solution to give potassium hydride which was insoluble.

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

The apparent reduction in thermal decomposition rate was due to removal of PMA from solution. This reaction to form KH does not occur in the ammonia system and was not expected in methylamine. A reaction between KNH_2 and hydrogen does occur in ammonia at very high hydrogen pressure, but gives the solvated electron (the blue solution) rather than a hydride precipitate (7,8).

The gas liquid contactor work at Chalk River was done at 2 MPa and missed the hydride reaction. A low pressure contactor was used because the mass transfer coefficient was liquid phase controlled and could be reliably extrapolated to higher pressures. It was only through the chemistry study the reactivity of hydrogen with potassium methylamide came to light.

The hydride reaction had major process implications. Because of the low KH solubility the net reaction at process hydrogen pressures was to the right so that the major portion of the catalyst was taken out of solution as the hydride. This is shown in Figure 1. There is little temperature effect on the reaction, which occurs to give a similar shape of solubility versus pressure from -30°C to +50°C. The effect of the low maximum catalyst solubility in solutions at process pressure was to reduce the cold tower exchange efficiency to about half that measured at 2 MPa.

After discovery of the hydride reaction an extensive program was initiated to find a method of inhibiting the reaction. A very large number of chemical additives and alternative systems were investigated. Work at Chalk River showed the analogous reaction occurred with sodium methylamide in methylamine and with sodium and potassium dimethylamide in dimethylamine. It did not occur with lithium methylamide or with cesium methylamide, but lithium methylamide is a very poor catalyst for deuterium exchange and cesium is expensive. It was found, however, that when lithium was added to PMA in methylamine the reaction with hydrogen did not occur, at least in the range of hydrogen partial pressures of interest to the heavy water process. This is shown in Figure 2 where PLMA represents equimolar potassium-lithium methylamide. This discovery solved one of the major process problems but required the answer to many questions such as the effect of added lithium on the exchange reaction, the reactions with impurities, the thermal decomposition reaction, and the optimum lithium concentration.

Exchange rates were studied in the laboratory at Chalk River using a small rapidly stirred exchange cell where the transfer of deuterium from hydrogen to methylamine was monitored with an on-line mass spectrometer. Large-scale exchange work was done in the 25 cm pilot plant contactor. Kinetic exchange data using a single-sphere absorber was also obtained by Professor F.D. Otto at the University of Alberta. Initial work showed the PLMA exchange catalyst gave equal or somewhat higher rate constants and tray efficiencies than PMA. However, subsequent more detailed work has shown the exchange rate constant is dependent on the amount of lithium added and decreases with increasing lithium concentration. This is shown in Figure 3.

The temperature coefficient of the exchange reaction was found to be the same for both the PMA and PLMA systems with an activation energy of 28 kjoules/mole, the same as was found earlier by Rochard for the PMA system (2).

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch003

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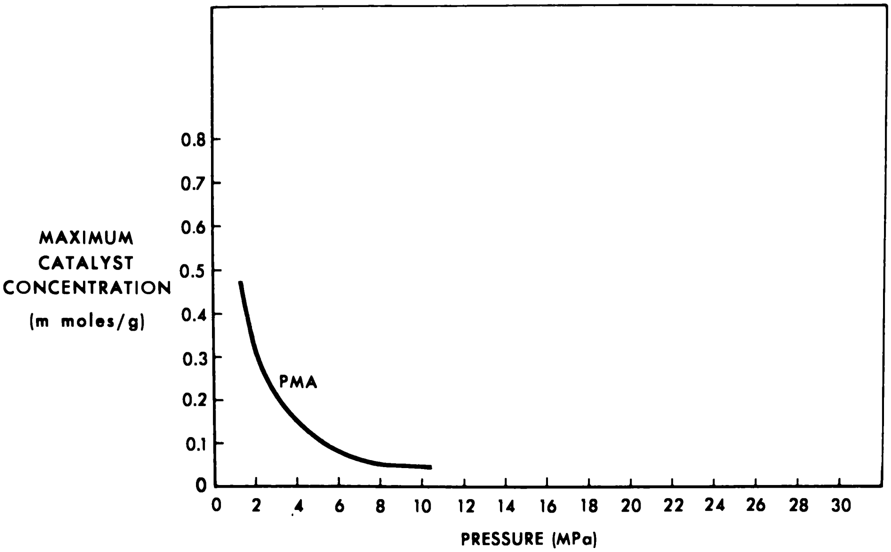

Figure 1. Effect of hydrogen on PMA solutions at 296°K

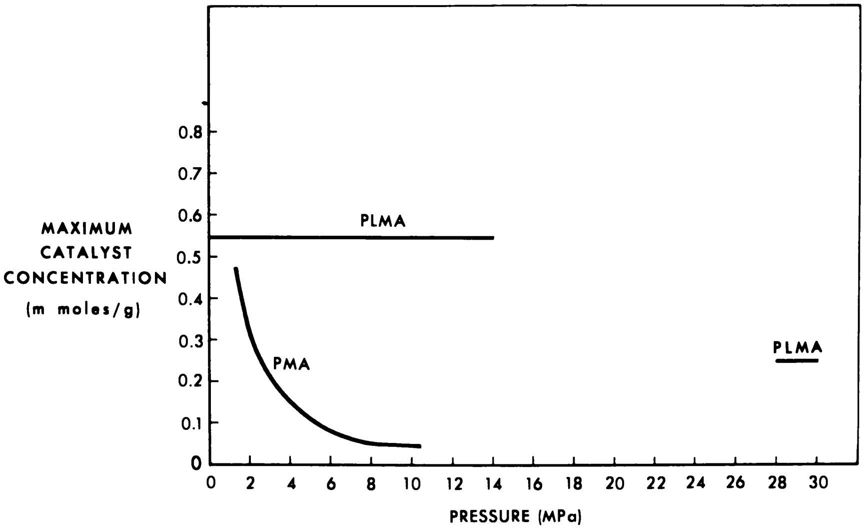

Figure 2. Effect of hydrogen on PMA and PLMA catalyst solutions at 296°K

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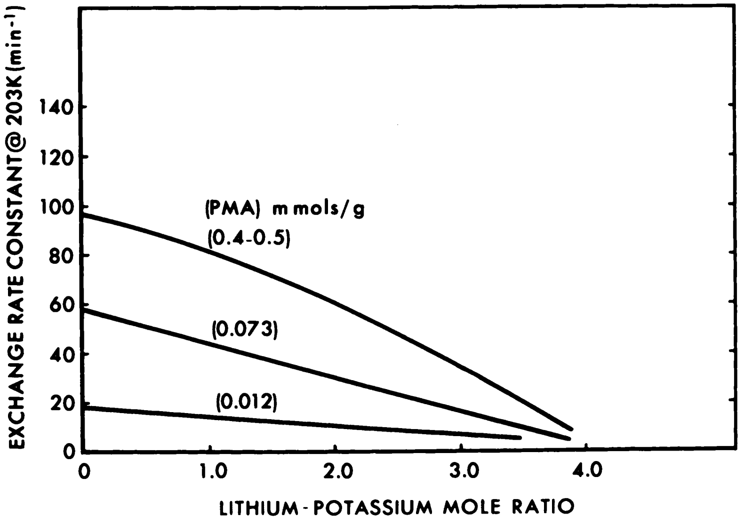

Figure 3. Effect of lithium–potassium mole ratio on exchange rate. Stirred exchange cell at 203°K.

A second exchange reaction that occurs in both the PMA and PLMA system is deuterium exchange between the amino- and methyl- groups of methylamine. This reaction was studied in detail by Halliday and Bindner (9) at CRNL and is more than 1000 times slower than the amino-group-molecular hydrogen exchange. While it does result in a slow buildup of deuterium in the methyl group of the process liquid, it does not constitute a process problem.

The solubility-temperature relationship of PLMA (Figure 4) is opposite to that of either PMA or LMA (lithium methylamide), showing a somewhat lower solubility at the low temperature and a much higher solubility at high temperatures. The solubility is also markedly dependent on the lithium concentration as shown in Figure 5. As the amount of lithium increases the total solubility increases rapidly. In fact systems with high lithium ratios yielded clear solutions with a salt content close to 30% by weight.

The effect of added lithium on the thermal stability of the solution is shown in Figure 6. The solution is more stable in the presence of lithium with the half-life for an equimolar potassium-lithium solution being higher (100 days) at 40°C than a PMA solution (25 days). In the heavy water process where the solution is circulating between cold and hot towers the time spent at 40°C is only a fraction of actual time in the process so that the practical half-life of the solution is greater than the 100 days measured in the laboratory. The products of decomposition are the same as from PMA with the addition of lithium dimethylformamidide. The ammonia formed reacts indiscriminately with lithium and potassium salts to precipitate $LiNH_2$ and KNH_2. In addition, it was found that the amide salts co-precipitated methylamide along with them thus further removing active catalyst from the solution. For this reason the purification system must maintain the ammonia at a concentration below 0.06 mmole/g which corresponds to the amide solubility. Sanford at Raylo has demonstrated a simple purification method based on distillation of a side stream to remove ammonia and convert amides back to methylamides.

$$MNH_2 + CH_3NH_2 \rightarrow CH_3NHM + NH_3\uparrow$$

From the fundamental point of view the question arises of how lithium modifies the properties of the solution. Lithium methylamide by itself in methylamine solution is a very poor catalyst with an exchange rate less than 1% of that of PMA. The work reported in this paper suggests that potassium and lithium methylamide exist in solution as a complex rather than a simple mixture of the two salts in solution. Such a complex in equilibrium with the two methylamides is shown below.

$$K_2Li_2(NHCH_3)_4 \rightleftharpoons 2KNHCH_3 + 2LiNHCH_2$$

Evidence for such a complex in solution is summarized in Figure 7. The totally opposite solubility-temperature relationship

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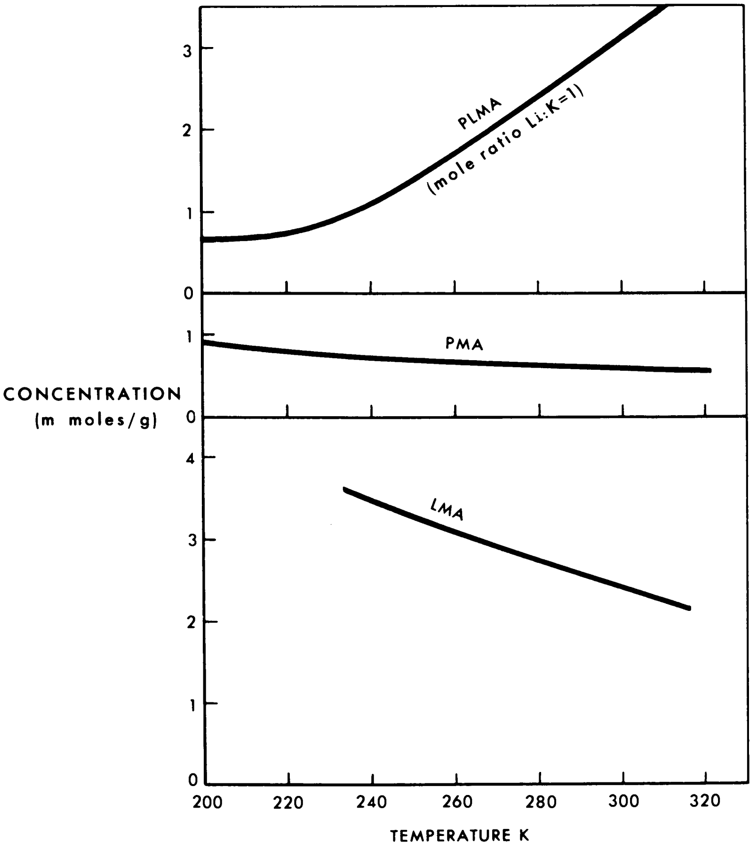

Figure 4. Solubility of methylamides

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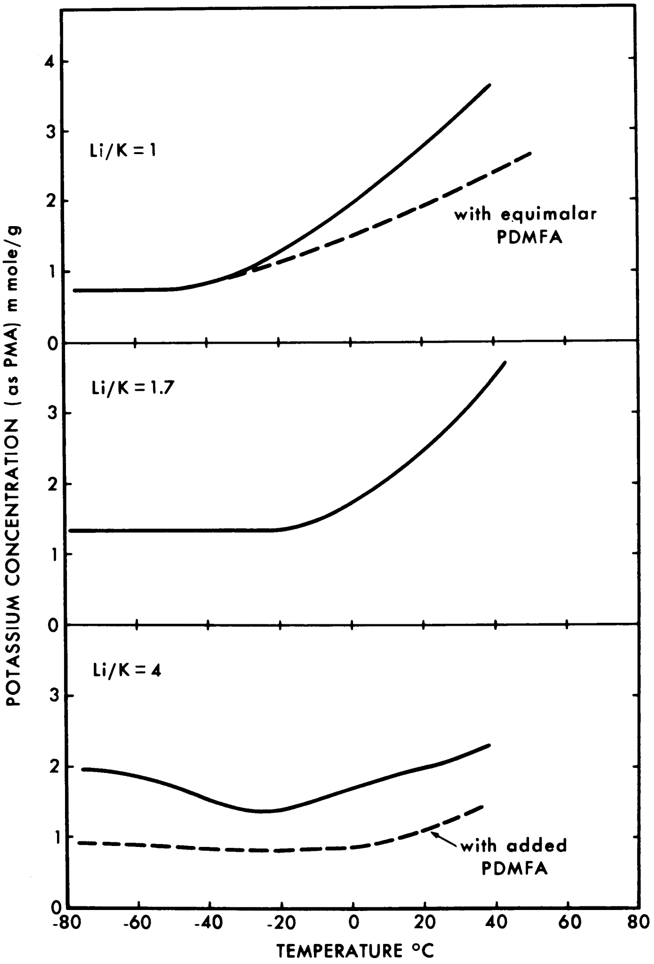

Figure 5. Solubility of potassium–lithium methylamide in methylamine

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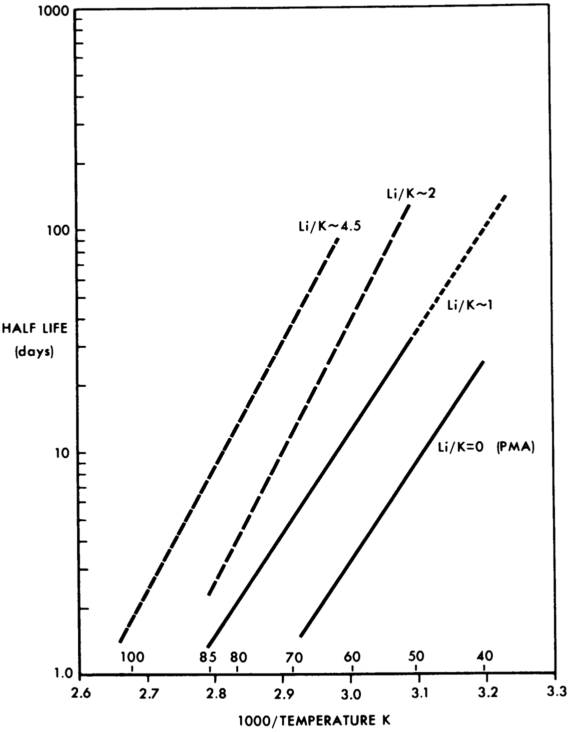

Figure 6. Effect of temperature on thermolysis rate of methylamide solutions

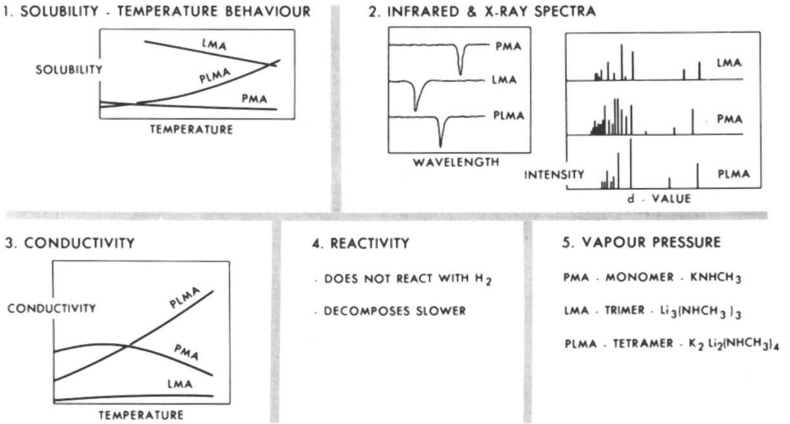

Figure 7. Evidence that PLMA is a complex

indicates a complex rather than a mixture. The IR and X-ray spectra obtained in Günthard's laboratory in the Swiss Federal Institute of Technology under contract to Sulzer shows unique spectra for PLMA rather than a sum of all the lines from PMA and LMA. Conductivity data obtained at CRNL shows a different temperature behaviour for PLMA than for PMA or LMA. The reactivity is different than PMA and the vapour pressure data obtained by Sanford at Raylo Chemicals indicates a different species in solution than either of the two component salts. All of these observations are consistent with a complex rather than a simple mixture.

Conclusion

It has been demonstrated that potassium-lithium methylamide is a superior catalyst for the amine-hydrogen heavy water process. It does not react with hydrogen, and it has a favourable deuterium exchange rate, good solubility and an acceptable thermal decomposition rate. A patent has been granted for this new catalyst (10).

The amine-hydrogen process is rich in chemistry, much of it previously unknown. The practical aspects of the chemistry which directly affect the process, i.e., the preparation of catalyst, thereactivity of the catalyst solution with process ingredients and process impurities, the deuterium exchange properties, the thermal stability have been thoroughly investigated. The process chemistry studies provide a firm basis for the process, however there is still many fundamental aspects of chemistry of the system which could be a fertile area for further basic research.

As a result of the success achieved in the three areas of development, that of gas-liquid contactors, process chemistry and process design, the amine-hydrogen heavy water process his reached the position where the next stage is commitment of a prototype plant, and thus is now being pursued.

Acknowledgements

We acknowledge the contributions of Dr. H.K. Rae and A.R. Bancroft who directed the process development program and for their review of this manuscript. We also acknowledge Drs. J.F. Prescott and E.C. Sanford at Raylo Chemicals and R.E. Johnson and R.P. Denault of the Chemical Engineering Branch, CRNL for their major contribution to the experimental work and to Dr. J.P. Mislan and co-workers of the General Chemistry Branch, CRNL, who did much of the analytical methods development.

Abstract

The hydrogen-amine process for heavy water production employs a deuterium isotope exchange reaction between hydrogen and methylamine containing a dissolved alkali metal methylamide catalyst.

This system is chemically very reactive and a detailed understanding of all aspects of the process chemistry was required. This understanding was made more difficult by the lack of information in the literature on this or similar systems. The majority of the work was of a pioneering nature. For example, a hitherto unknown side reaction of hydrogen at process pressure with the original exchange catalyst was discovered. The successful development of a new catalyst restored the viability of the process so that commercial application is now feasible and is being pursued.

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Received September 7, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch003

4

AECL-Sulzer Amine Process for Heavy Water

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch004

The purpose of this paper is to outline the design of the AECL - Sulzer amine process for heavy water, to demonstrate why the process is attractive compared to existing processes and to summarise the steps which have been taken to prepare the process for commercial exploitation.

Work on process development was started independently by Atomic Energy of Canada and by Sulzer Brothers. AECL were evaluating alternatives to the established GS separation process and conducted experiments to compare exchange rates for ammonia-hydrogen and amine-hydrogen. Sulzer were interested in the amine-hydrogen process as a successor to the series of hydrogen fed heavy water plants with which they had been involved. This involvement had started in 1956 with the construction of a plant using liquefaction and distillation of electrolytic hydrogen at Ems in Switzerland (1) and has continued with the construction of three plants using the monothermal ammonia-hydrogen process. The prototype plant was built at Mazingarbe (2,3,4) in France in 1967 and was followed by two plants supplied to India by the GELPRA consortium (5,6). The first of these plants, at Baroda, is currently being started up and the second, at Tuticorin, is in the final stage of construction. The other ammonia-hydrogen plant at Talcher (6), also in India, uses a final enrichment system designed and supplied by Sulzer and is also in the latter stages of construction. Similar final enrichment systems using vacuum distillation of water have been supplied by Sulzer for a majority of the Canadian GS heavy water plants (7).

In 1973 Sulzer and AECL agreed to exchange information on amine process development. A heavy water process was designed using a flowsheet development from Sulzer's experience with the five ammonia plant based heavy water plants mentioned above together with the AECL owned catalyst developed at Chalk River Nuclear laboratories. Advantages over existing processes were apparent and sufficient for Sulzer to commit themselves to develop the process to a stage at which a turnkey plant could be built with known costs and guaranteed performance.

The stimulus behind this development was the recognition that the process can produce heavy water using considerably less equipment and less energy than existing processes. There are two principal reasons for this. The first depends on the deuterium exchange properties of methylamine and hydrogen and can best be illustrated by comparing this chemical exchange pair with the two other exchange pairs commonly used in industrial heavy water plants: hydrogen sulphide-water and ammonia-hydrogen (8,9). The second factor is tied up with the use of hydrogen, in the form of ammonia synthesis gas, as deuterium feedstock. This will be demonstrated by discussing the way in which the heavy water plant is coupled with the synthesis gas production system of the ammonia plant.

Bithermal Enrichment using Amine-Hydrogen Exchange

Most of the deuterium separation in the amine-hydrogen process is achieved using the bithermal (dual temperature) enrichment technique (10). This technique is also used in the GS plants and in the ammonia-hydrogen plant being built at Talcher (6).

The technique makes use of a temperature dependent deuterium exchange reaction between a liquid and a gas. In the amine-hydrogen process deuterium is exchanged between the amino group of liquid monomethylamine and gaseous hydrogen according to the reaction:

$$HD + CH_3NH_2 \rightleftharpoons H_2 + CH_3NHD$$

A simple gas fed bithermal enrichment loop is shown in Figure 1. Feed gas is successively passed through hot and cold exchange towers in countercurrent to a closed loop of liquid. In the hot tower the equilibrium for the above reaction is to the left, therefore deuterium passes from the liquid to the gas. In the cold tower the equilibrium shifts to the right so that deuterium passes from the gas to the liquid. The gas leaving the hot tower is enriched in deuterium and a portion of it is used as feed for a higher enrichment stage. This gas returns depleted and joins the main stream of gas which is deuterium stripped in the cold

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tower.

The separation power of such a bithermal loop depends on the difference in the exchange equilibria in the hot and cold towers. The separation factor, α, is defined as the ratio of D/D+H in liquid to D/D+H in the gas. Efficient deuterium extraction and enrichment is achieved with a low value of the separation factor in the hot tower (α_H) and a high value in the cold tower (α_C).

The simplest standard of comparison for bithermal enrichment processes is the maximum recovery available using a single enrichment loop with an infinite number of theoretical plates in hot and cold towers, given by the term $1-\alpha h/\alpha c$. This value is a rough indication of the amount of product heavy water separated by plants processing the same molar quantity of feedstock, be it water or hydrogen. For the same production rate therefore, the feedstock quantity to be processed is roughly proportional to the reciprocal of this number.

The separation factors that can be realised in a bithermal loop depend upon the properties of the exchange partners. Figure 2 shows the variation in the separation factor, α, as a function of temperature for the following exchange reactions:

1 $HDO + H_2S \rightleftarrows H_2O + HDS$

2 $HD + NH_3 \rightleftarrows H_2 + NH_2D$

3 $HD + CH_3NH_2 \rightleftarrows H_2 + CH_3NHD$

The curves are only shown for the temperature range in which an industrial heavy water process can operate well. For the GS process the hot tower operates at 130 °C to limit the amount of water vapour in the gas phase. Cold tower temperature is limited by the formation of a solid hydrate at 28 °C. For the ammonia-hydrogen process a hot tower temperature around 60 °C limits the ammonia vapour concentration in the gas phase. Cold tower temperature is limited to about -25 °C by the poor kinetics of the exchange at low temperatures. Amine-hydrogen hot tower temperature is limited to +40 °C to minimise the rate of catalyst decomposition. The cold tower can operate at -50 °C however, because of the far superior kinetics of the chemical exchange reaction, compared with ammonia-hydrogen exchange. However, the use of special gas-liquid contactors is necessary to take full advantages of the amine-hydrogen exchange kinetics at -50 °C.

Listed below are the hot and cold tower operating

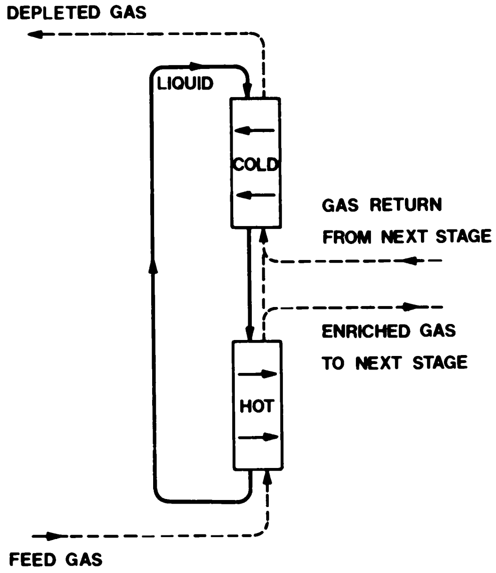

Figure 1. Gas-fed bithermal enrichment stage

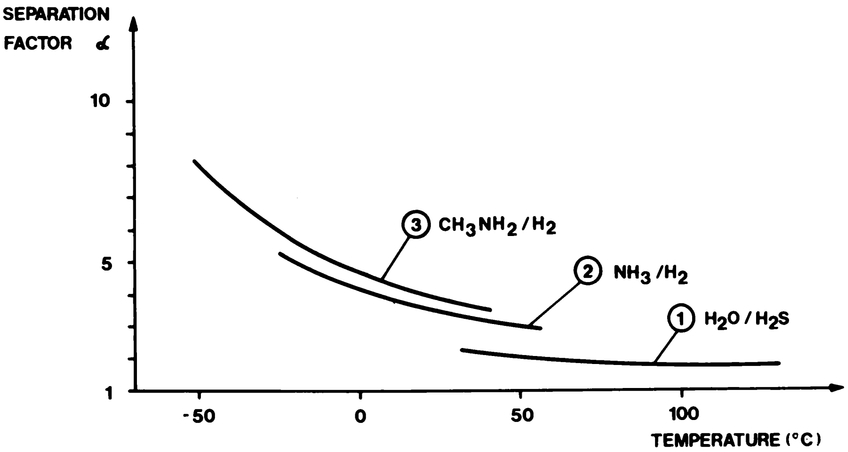

Figure 2. Deuterium exchange equilibria for bithermal enrichment processes

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch004

conditions, separation factors and maximum possible yield for the three systems.

System	H_2S/H_2O	NH_3/H_2	CH_3NH_2/H_2
cold tower operating temperature (°C)	+30	-25	-50
cold tower separation factor	2.22	5.3	7.9
hot tower operating temperature (°C)	+130	+60	+40
hot tower separation factor	1.76	2.9	3.6
maximum possible yield	0.21	0.45	0.55

This simple comparison indicates that for the same deuterium extraction the ammonia-hydrogen system only needs to process about half as much feedstock as the GS system and the amine-hydrogen system only about 40 % as much.

A more realistic comparison is to look at the performance of the systems with a finite number of theoretical stages in the exchange towers. Attainment of the high separation factor in the cold towers of the hydrogen based processes is necessary to achieve a high yield. This can only be achieved by operating at low cold tower temperatures where the slow isotopic exchange requires the use of special contacting devices to achieve reasonable tray efficiencies. Each of these special contactors requires more tower volume than a sieve tray which gives a reasonable tray efficiency in the GS cold towers. Consequently, for the same outlay in equipment, less theoretical stages will be available in the cold towers of the hydrogen based processes.

Figure 3 compares the performance of the three bithermal systems using a finite number of transfer stages in the hot and cold exchange columns. GS performance has been computed for hot and cold towers each with fifty sieve trays using tray efficiencies reported in the literature (11). The performance of the amine-hydrogen and ammonia hydrogen system has been computed for hot towers with fifty sieve trays and cold towers with five special cold contactors. Stage efficiencies are based on Sulzer and AECL pilot tests. The cold towers with five cold contactors roughly correspond in tower height to the fifty sieve trays used in the GS cold tower considered here. Hence the comparison is for enrichment loops with roughly similar equipment costs, but operating with different exchange fluids.

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The performance of these systems cannot accurately be compared using the single variable of deuterium recovery since this is dependent on the enrichment produced. Figure 3 shows the enrichment/yield characteristics for the three systems. At an enrichment factor of 1 (no enrichment) the yields are the maximum theoretical values of $1-\alpha_h/\alpha_c$. As the enrichment factor increases the yield is reduced. This effect is more marked for the hydrogen based processes because less contacting stages are available in the cold tower. This is the penalty for the comparatively poor exchange kinetics of the hydrogen based processes at low temperatures.

An enrichment factor of about four corresponds to operating conditions in the GS plants (11) and in the amine-hydrogen process. At this point the yield for the ammonia-hydrogen loop is no more than that for the GS loop. The yield from the amine-hydrogen loop is however twice as great, i.e. unit product from the amine-hydrogen loop requires only half the amount of feedstock of the other two processes.

The amount of fluid requiring processing is a key parameter in determining the cost of a process. Heavy water is expensive because huge quantities of feedstock require processing to produce a relatively small amount of product. A process built from a cascade of high yield enrichment loops is likely to be cheaper. Not only tower volumes but equipment and energy costs for purification, humidification and de-humidfication are all proportional to the amount of gas and liquid requiring processing in the enrichment loops.

The processing costs per mole of circulating gas are difficult to compare for the amine-hydrogen and GS processes as the problems are of a different nature. Problems of corrosion and the toxic properties of hydrogen sulphide add to the costs of the GS process. In the amine process costs arise from the use of low temperature refrigeration and low temperature steels. Comparison between ammonia-hydrogen and amine-hydrogen is easier. These processes operate at similar pressures and use similar equipment. The amine process operates at a lower temperature so refrigeration is more expensive. On the other hand less refrigeration is required per mole of hydrogen circulated because the vapour pressure of amine is only half that of ammonia. Therefore less refrigeration is required for dehumidifying the circulating gas. Processing costs per mole of gas circulated are unlikely to be significantly different.

The above comparison using the deuterium exchange properties of the three systems shows that an amine-hydrogen bithermal loop need only be half the size of

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an ammonia-hydrogen loop of equivalent performance. This is one of the key reasons for the economy of the amine-hydrogen process and it has provided the stimulus for Sulzer to shift development from the ammonia-hydrogen to the amine-hydrogen process.

Special Cold Contactors

The achievement of high isotopic exchange efficiencies at low temperature was the first goal of the amine-hydrogen process development program. Early tests made by AECL show a sieve tray efficiency of only 0.7 % at -50 °C (12). Subsequent development work has produced contactors with efficiencies ranging up to 70 % at this temperature. Success in this key area led to a more general development effort which has brought the process to its current mature state.

Deuterium exchange between methylamine and hydrogen occurs via the catalyst dissolved in the liquid phase. In principle the rate of isotopic exchange is dependent on both the intrinsic chemical kinetics of the exchange reaction and the rate of diffusional mass transfer of reactants and products. Because of the low solubility of hydrogen in amine and the high activity of the catalyst, even at the low cold tower temperature of -50 °C, the reaction is in the fast regime (11). This means that simultaneous mass transfer and chemical reaction occur only in fresh elements of liquid brought near the gas-liquid interface.

Increases in exchange rate have been produced by increasing both the gas-liquid interfacial area and the rate of surface renewal by producing a turbulent gas liquid mixture. Exchange efficiencies in the specially developed contactors are also higher than for the sieve tray because of greater residence time, i.e. the contactors contain more liquid in which exchange is occurring. Figure 4 shows two suitable low temperature contactors. The cocurrent bed contactor is basically a deep sieve tray which is filled with a knitted mesh packing to reduce bubble coalescence. The flow pattern is mainly concurrent because of the high overflow weir. This contactor has been developed by Chalk River Nuclear Laboratories (11,13).

The ejector contactor, shown schematically in Figure 4, was developed by Sulzer originally for use in the monothermal ammonia heavy water process (14,4). In each stage gas is expanded through nozzles and liquid is sucked into the high velocity gas stream giving a very intimate gas/liquid mixture. The mixture passes up a reaction tube and is then separated in a centri-

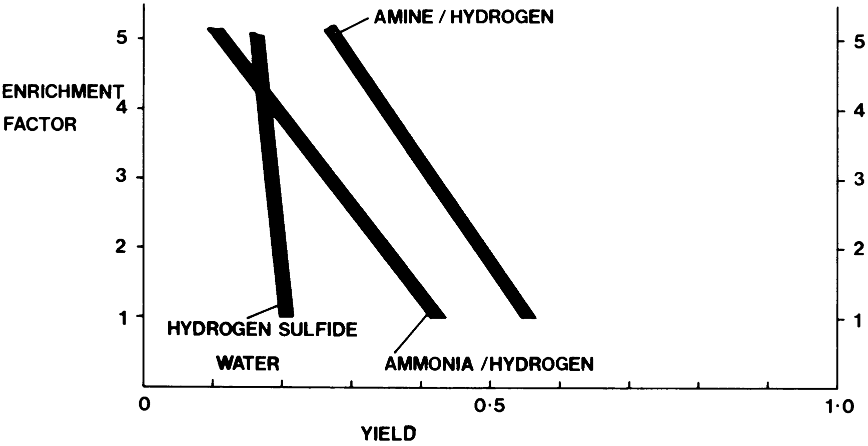

Figure 3. Comparison of bithermal enrichment fluids

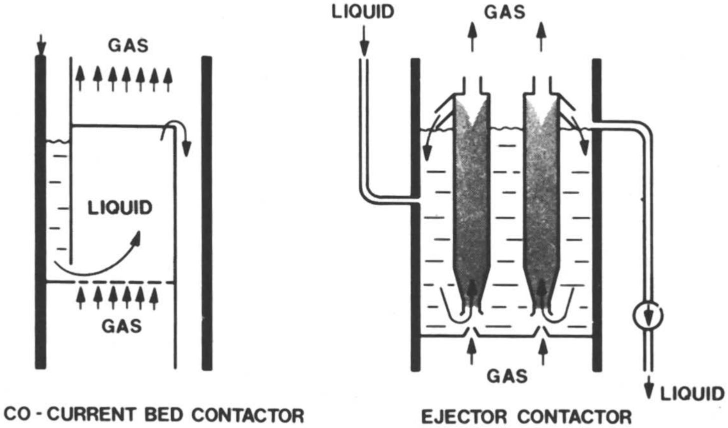

Figure 4. Cold-contacting devices

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fugal separator, gas passing on to the next stage and liquid being recycled to the ejectors. The liquid throughput in the tower is pumped from stage to stage to overcome the pressure difference caused by the pressure drop in the ejector driving nozzle.

The design features and performance of the special contactors on amine-hydrogen exchange at -50 °C are contrasted with those of a normal sieve tray below:

contactor type property	sieve tray	packed bed	ejector
flow pattern	cross current	co-current	recycle co-current
gas phase superficial residence time, τ, (s)	1	6.7	7.6
specific energy dissipation (watts/liter)	1	1	10
stage efficiency (%)	0.7	22	70
ratio of mass transfer rates	1	5.7	23
interfacial area (m^2/m^3)	250	1300	6000

The packed bed contactor developed by AECL performs better than the sieve tray for two reasons. Firstly the packed bed is deeper so the gas phase residence time is higher. Secondly the rate of mass transfer in the mixture is higher. This is attributable to the high voidage packing increasing gas-liquid interfacial area by preventing bubble coalescence. It is also probable that the upper regions of the sieve tray were operating in the spray regime where liquid phase turbulence would be relatively poor. The specific energy dissipation is defined as the gas phase pressure drop multiplied by the gas flowrate and divided by the reaction mixture volume. Both the sieve tray and the packed bed are designed to keep the pressure drop across the sieve plate low so as to reduce liquid backup in the downcomers and reduce tray spacing. This results in the specific energy dissipation being low and similar for both devices.

The ejector shows more than a threefold improvement in efficiency compared to the packed bed. The residence times for the two devices are similar. The better performance is attributable to the higher rate of energy dissipation in the ejector producing a much more intimate gas-liquid mixture. The higher energy input is caused by the pressure drop in the gas nozzles of the ejector which requires the use of pumps for passing liquid stagewise down the tower. The reduction in tower volume by a factor of over three when using the ejector more than makes up for the cost of these pumps. Energy costs in the form of increased gas stream pressure drop are small. In fact the ejector contactors use less energy than the sieve trays for a given mass transfer duty. Though the rate of energy dissipation per unit reaction volume for the ejector is higher than for the sieve tray, a tower using ejectors will require only 75 % of the energy in the form of pressure drop compared with a sieve tray tower of equal performance.

There are other advantages in using the ejector contactor. Multiple units consisting of nozzles, ejectors, reaction tubes and separators are installed in parallel inside each stage of the cold tower. Pilot testing of one full size unit eliminates the necessity for and avoids the risks of scale-up. Another advantage is that gas and liquid are mixed and separated using inertial forces. These are large compared to the normal interfacial forces acting in a two phase mixture. Variations in the foaminess of the process liquids caused by a concentration of impurities are less likely to affect the hydraulic performance of the ejectors.

The use of these special contactors is to a large extent responsible for the potential of the amine process. Because of the strong temperature dependence of the exchange efficiency, their use effectively lowers the optimum cold tower temperature allowing the process the economies of high deuterium recovery mentioned earlier.

Link-Up with the Ammonia Plant

Ammonia plant synthesis gas has been used as feedstock for a number of heavy water plants (6,15). The gas is stripped of deuterium in the heavy water plant and returned to the synthesis loop of the ammonia plant. One advantage of using synthesis gas is that the gas is relatively pure. The main contaminant, nitrogen, is inert and does not interfere with the heavy water process. The main disadvantage of using synthesis gas as a deuterium source is that the size of the heavy water plant is limited by the size of the ammonia plant to which it is connected. Synthesis gas

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from a one thousand ton per day ammonia plant can only yield about 65 tons per year of heavy water. This limits the scale economies possible for the heavy water plant.

Connection of the amine-hydrogen process to the ammonia plant has been designed so that a pre-enrichment in deuterium occurs before the synthesis gas reaches the heavy water plant, so reducing the enrichment necessary in the heavy water plant itself. This is the second reason why the amine-hydrogen process is able to produce heavy water cheaply.

In an operating ammonia plant the hydrogen in the synthesis gas has a deuterium concentration well below the average value of that of the hydrogen in the feedstock, which is normally around 130 ppm. The synthesis gas is depleted in deuterium by the large excess of steam required in the reformers where the synthesis gas is produced. At the high temperatures required the steam and product hydrogen reach isotopic equilibrium; the equilibrium producing a deuterium enrichment in the steam and a depletion in the hydrogen gas. When the unreacted steam is condensed out of the gas and dumped the deuterium content is lost. The distribution of deuterium in the main process streams of an ammonia plant is shown in Figure 5.

Most ammonia plants which have been coupled with heavy water plants have been modified to avoid this deuterium depletion in the synthesis gas. Two methods have been used, both effectively recycling deuterium from the enriched process condensate back into the reformer steam supply. Figure 6 shows one of these methods. The steam destined for the reformers is passed through a column in countercurrent to the process condensate and strips out the enriched water. The other method is to use the enriched condensate, after suitable treatment, as feedwater for the boiler which generates reformer steam.

A flowsheet has been used for the amine-hydrogen process which goes one step further; instead of restoring the deuterium content in the synthesis gas to its natural level it increases it still further. This pre-enrichment reduces substantially the number of bithermal enrichment stages required in the rest of the plant. Figure 7 shows in principle how this is done. Some of the deuterium extracted from the synthesis gas stream is transferred via a series of isotopic exchange columns to the reformer steam feed together with the deuterium from the enriched process condensate. In the first transfer column, the top one in the figure, deuterium is transferred into catalyst

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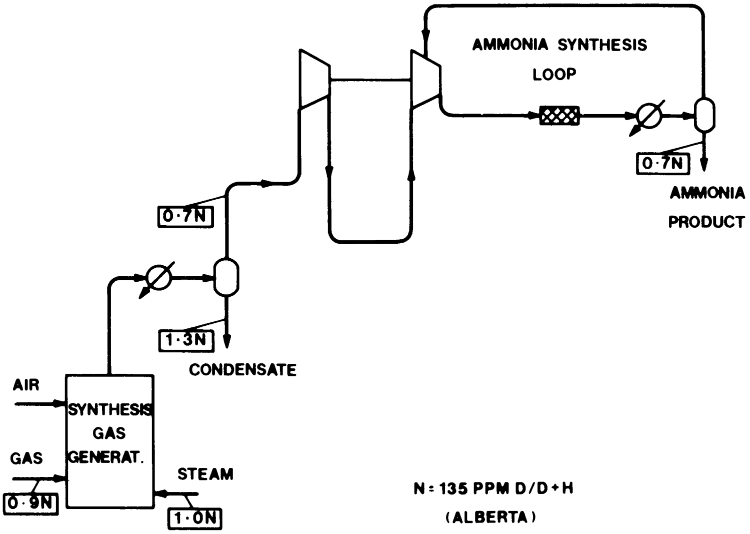

Figure 5. Deuterium concentrations in an ammonia plant

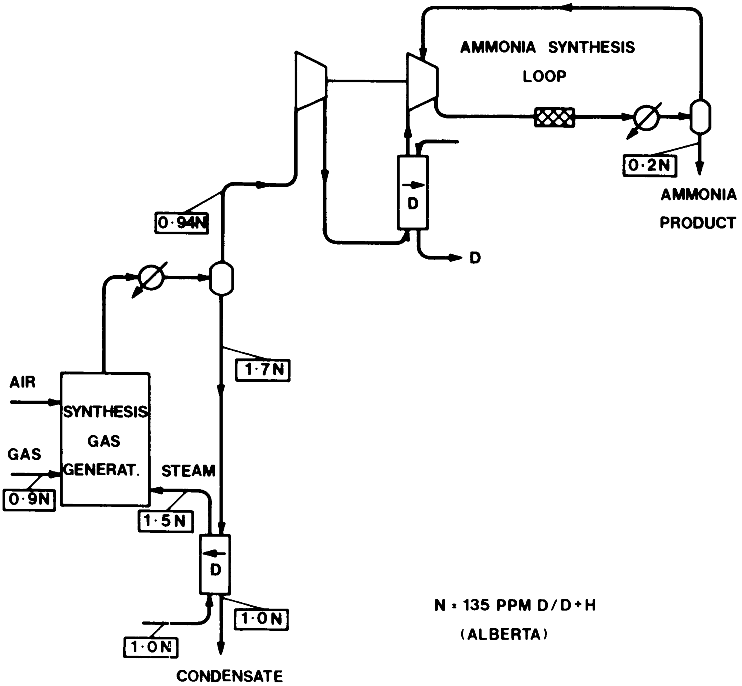

Figure 6. Concentrations with deuterium recycle from condensate

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laden liquid methylamine. In the next column the deuterium enriched amine is transferred into an amine vapor stream. In the third column deuterium is transferred from amine vapor to water which is passed, together with the enriched process condensate, into the condensate stripping column. This enriches the reformer steam which in turn enriches the synthesis gas produced in the reformer.

Deuterium transfer from the hydrogen in the synthesis gas back to the reformer steam is possible because the separation factor between water and hydrogen is greater than 1. If water and hydrogen of equal deuterium concentration are brought into isotopic equilibrium then deuterium will pass from the hydrogen to the water. The deuterium in the hydrogen is, in effect, more available. If hydrogen is produced from this water by removing oxygen, then it will also be enriched and can serve to enrich more water by isotopic exchange. This is the monothermal or decomposition enrichment technique which has been used with water and hydrogen in the heavy water plants at Trail and Rjukan and with ammonia and hydrogen in the plants at Mazingarbe, Baroda and Tuticorin (5). The disadvantage of the process is the cost of the decomposition step; electrolysis of water or thermal cracking of ammonia (15). However, in the amine-hydrogen process the decomposition step occurs in the reformers of the ammonia plant. Where synthesis gas is used as a deuterium source the ammonia plant is normally modified to recycle deuterium from the process condensate to the reformer steam. The extra cost of recycling deuterium from the synthesis gas to the reformer steam is small.

Detailed design of the link-up depends on the design of the ammonia plant. Kellogg Canada have collaborated with Sulzer in this area and the design package for the 65 tons per year heavy water plant is specifically tailored to the Kellogg ammonia plant design.

The degree of pre-enrichment possible using such a system is limited by the leaks of steam, water and synthesis gas occurring in the ammonia plant reformers. However, sufficient pre-enrichment can be achieved to more than halve the amount of equipment used in the subsequent bithermal amine-hydrogen enrichment section of the heavy water plant.

Deuterium Enrichment System

Figure 8 shows schematically the isotopic enrichment scheme used in the process. A cascade of two amine-hydrogen bithermal enrichment loops is used

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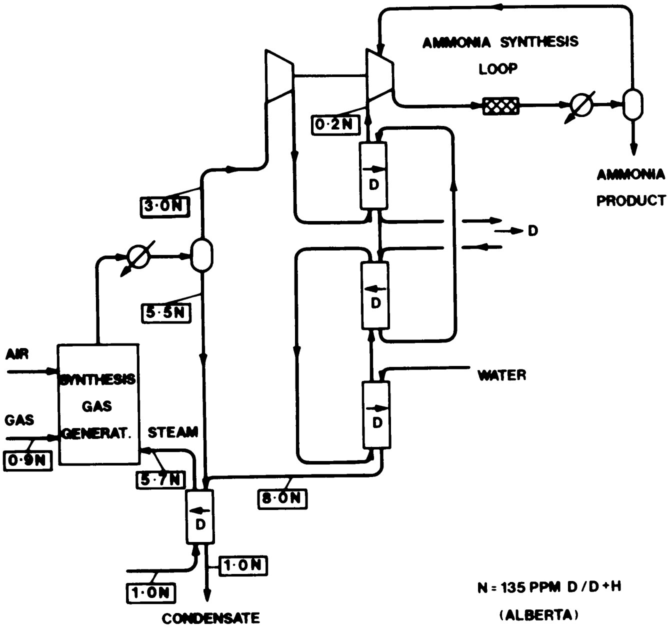

Figure 7. Concentrations with deuterium recycle from condensate and synthesis gas

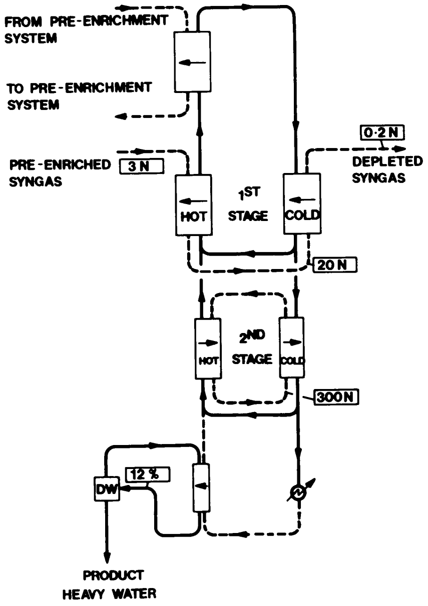

Figure 8. Isotopic enrichment scheme

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

coupled with final enrichment by water distillation. This scheme is used to reduce losses of deuterium enriched substances and to minimize the deuterium inventory of the plant.

Pre-enriched synthesis gas from the ammonia plant is treated to remove water and carbon oxides and then fed through the main bithermal enrichment loop. Depleted amine from the hot tower is further stripped by the pre-enrichment deuterium transfer column before being fed to the first stage cold column. The first stage enriches gas to about 20 times natural concentration. Enriched liquid is bled from between the cold and hot columns and fed to the second bithermal enrichment stage.

The second stage enriches gas to about 300 times natural concentration giving a deuterium concentration in methylamine of about fourteen percent. Condensed amine vapor from the second stage dehumidifier is contacted with water in a transfer column. This enriched water is then distilled under vacuum to give the heavy water product of 99.8 % deuterium concentration.

Process Status

The amine-hydrogen process for heavy water outlined here has been developed over the past ten years, starting with bench tests of amine-hydrogen deuterium exchange by Atomic Energy of Canada Limited (16) and culminating in the generation by Sulzer of a complete design package for a 65 tons per year plant linked to an ammonia plant in Alberta.

Laboratory work has centred around improving the low temperature kinetics of the amine-hydrogen exchange reaction. Three full scale ejector contactors have been piloted and successive modifications have improved exchange efficiency by a factor of four. All other unit processes not used in industrial heavy water plant have been piloted either by AECL or by Sulzer.

AECL have developed the homogeneous catalyst used to promote exchange and have measured rates of catalyst decomposition (17). Sulzer have piloted processes to remove these decomposition products from the plant inventory.

Process design has progressed from the general outline of the process given above to detailed heat, mass and isotopic balances for the complete process. Design is based on equipment performance determined during pilot tests or on manufacturers' quoted guarantees for standard equipment items. The sensitivity of the process to equipment malfunction or operating

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errors has been assessed by computer modelling and suitable design margins incorporated. In general the process is much less sensitive to such disturbances than other bithermal heavy water processes because of the big difference in hot and cold tower separation factors (11).

Engineering design has been pursued simultaneously with the above activities. Equipment items have been specified and bids received from selected vendors. Preliminary design of civil work has been concluded by local companies. A safety report has been prepared as a guide to site selection. The plant capital cost has been calculated based on bids for equipment and engineering.

Conclusion

Amine-hydrogen process development was triggered by process considerations indicating considerable advantages over established production processes (16). Successful development, including laboratory and pilot work, has in turn stimulated the generation by Sulzer of a complete design package for a 65 ton/yr heavy water plant attached to a Kellogg ammonia plant in Western Canada. Estimates of heavy water production cost from this plant are based on a solid foundation and favour the exploitation of the process in the near future.

Abstract

A heavy water process based on isotopic exchange between hydrogen and methylamine and methylamine and water has been developed by Sulzer and Atomic Energy of Canada. Deuterium source is the synthesis gas stream of an ammonia plant. Deuterium enrichment is achieved by bithermal amine-hydrogen exchange, however, preliminary enrichment is made to occur in the reformers of the ammonia plant by using the steam reforming process as the decomposition step of a monothermal enrichment stage. This feature, coupled with the high value of the separation factor achievable with hydrogen-amine exchange, allows a high deuterium yield without the use of hydrogen recycle in the extraction stage. Design work has been based on pilot tests of the key process steps using industrial contacting equipment.

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RECEIVED September 6, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch004

Heavy Water Production by Isotopic Exchange between Hydrogen and Methylamine

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch005

Isotopic exchange between water and hydrogen sulphide was the first chemical process used on a large scale for the production of heavy water, and is still employed in the big Canadian plants.

Isotopic exchange between liquid ammonia and hydrogen, discovered by Wilmarth and Dayton(1) which offers a much higher separation factor than the former process, has been studied in French CEA laboratory, since 1956, and developed using available sources of hydrogen in the ammonia industry.

However, to extract deuterium from hydrogen, especially from NH_3 synthesis gases, Bar-Eli and Klein (2) then J. Ravoire and E. Rochard (3 and 4)studied the exchange between hydrogen and a primary or secondary amine, catalysed by an alkaline derivative of the amine used. Kinetic measurements showed that the exchange is much faster than that between hydrogen and ammonia, the separation factors being similar (7 at -60° C and 3.5 at +30° C). The hydrogen-monomethylamine system (MMA) can thus be used for productions of the same order as those of the NH_3-H_2 exchange process, as shown by detailed studies on a laboratory, pilot unit and plant project scale.

Laboratory Studies

It is easy to imagine the use of the amine-H_2 exchange in a dual-temperature process, turning to account the variation in the separation factor α with temperature. Once the α values were determined the points to be studied were as follows:

1. Exchange Kinetics. The exchange is catalysed by alkaline methylamides, the most efficient being CH_3NHK; the chemical rate is much faster than in the case of ammonia under the same temperature and catalyst concentration conditions.

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2. Solubility of Hydrogen. Hydrogen is more soluble in monomethylamine (MMA) than in ammonia (2.5 times at -50° C). This helps to speed up the exchange rate.

3. Thermal Stability of the Catalyst. Potassium methylamide is stable at low temperatures, but in solution at high temperature it is thermolysed and converted to a potassium salt of N,N'-dimethylformamidine, soluble in MMA. By long duration tests in pilot units, the stability was proved satisfactory under present working conditions.

4. Solubility of the Catalyst. Its solubility decreases as the temperature rises. In the presence of hydrogen the concentration of potassium methylamide is limited by the formation of potassium hydride:

$$CH_3NHK + H_2 \rightleftarrows CH_3NH_2 + HK.$$

The methylamide concentration at equilibrium is inversely proportional to the hydrogen pressure and is about 0.1 mol/kg amine for a hydrogen pressure of 50 bars. The equilibrium depends little on temperature; it is set up slowly and the hydride formation rate is bound up with the nature of the container walls.

5. Adjuvant Effect of Trimethylamine (TMA). It was discovered that a non-catalytic additive to the catalyst can speed up the exchange rate; thus, a multiplication factor of 1.7 was obtained by addition of about 7% (molar) of TMA to the MMA.

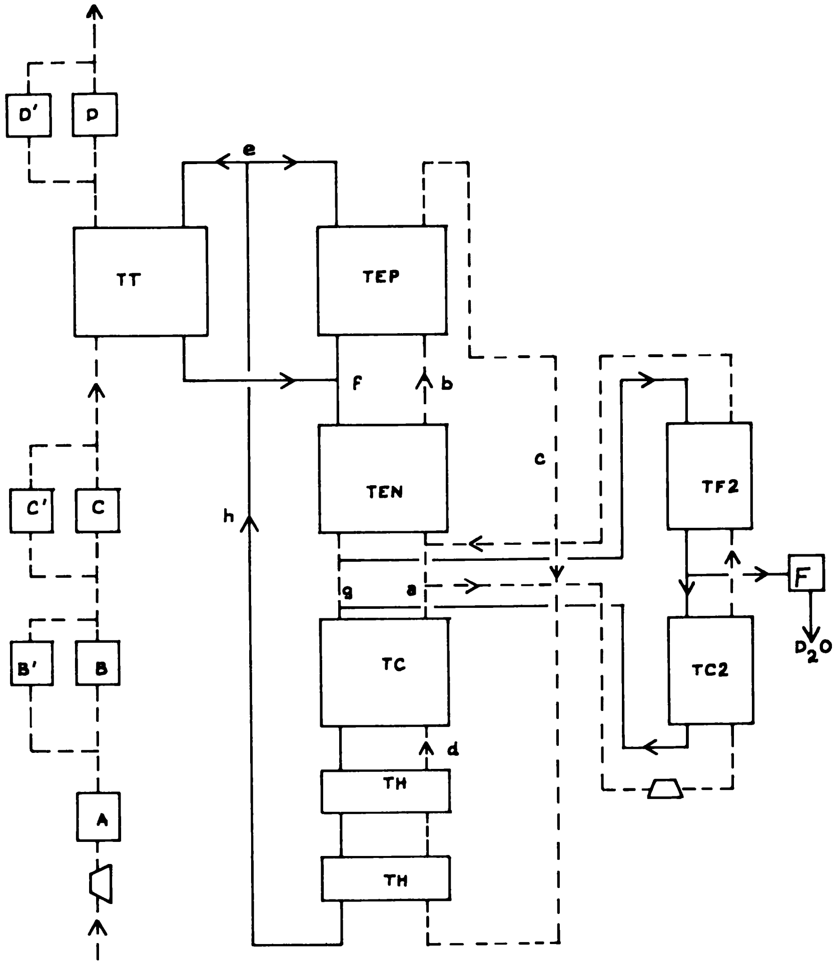
Pilot Plant Tests

The chief problem was to find a highly efficient contact system. Finely perforated plates, with suitable heights of liquid, are satisfactory since a 60 cm spacing is enough for the plates to function well.

Preliminary Draft of a Factory (in collaboration with la Société Chimique des Charbonnages)

1. Description of the Process. The results presented here concern research on the preliminary draft of a 60 T per year heavy water plant attached to a 1000 T per day ammonium sythesis unit; the exchange takes place by a dual temperature process, as mentioned above, to avoid any chemical transformation of the amine. As shown on Figure 1, the synthesis mixture (N_2 + $3H_2$), freed of oxygenated impurities by hydrogenation (A), dehydration (B) and finally by washing in the tower (C), transfers its deuterium to a current of MMA in a low-temperature TT tower (the only tower to contain a nitrogen-hydrogen mixture, enabling

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch005



A	methanation
BB'	dehydration
CC'	purification
TT	transfer tower
DD'	deamination
TEP	stripping tower (1st stage)
TEN	enrichment tower (1st stage)
TC	hot tower (1st stage)
TH	humidification tower (1st stage)
TF2	cold tower (2nd stage)
TC2	hot tower (2nd stage)
r	compressor(2nd stage)
F	finishing plant
abcd	hydrogen loop (1st stage)
efgh	liquid loop (1st stage)

Figure 1. Heavy water production unit

pure hydrogen to be used in the rest of the system). After recuperation of the methylamine the gas is sent to the ammonia synthesis unit. The liquid is fed through a series of hot and cold towers in which it accumulates deuterium against the counter-flow of a hydrogen loop. The process involves two enrichment stages before a finishing plant which can be either a hydrogen rectification or a water rectification after exchange between the water and the amine.

2. Determination of Working Conditions. The pressure and temperature conditions were determined on the basis of physico-chemical factors such as thermal stability of the catalyst, solubility in the presence of hydrogen, factors relative to association with ammonia systhesis such as the available pressure of feed-gas, and economic considerations. The choice of the pressure is the result of many compromises; the pressure must be low enough to allow a reasonable catalyst concentration, so as to obtain good plate efficiencies and the use of more conventional material than in high pressure ammonia synthesis; on the other hand it must be fairly high in order to avoid undue gas recompression and to maintain the low MMA vapour pressure which affects the energy consumption (amine saturation of the gas and condensation of this amine between the hot and cold towers). The higher temperature chosen is low enough to retain satisfactory behaviour of the catalyst. In choosing the cold temperature it was necessary to decide between lower flows at lower temperature on the one hand and less favourable kinetics, higher cooling costs and more elaborate steels on the other. After a detailed economic study a cold temperature of -50° C was adopted.

3. Economy of the Process. Table I shows the main specifications of the unit: dimensions of the isotopic exchange towers, distribution of investments according to the different items, and principal consumptions. Where investments are concerned the two main items of expense are the heat transfer equipment (cooling station + exchangers + insulation) and the exchange towers equipped with their plates. The capital cost for this process represents $460 per kg of heavy water per year. The pressure below that of the synthesis can involve an increase of gas recompression costs and of certain cooling costs. In spite of all these factors the energy expenses are lower than those of other processes, H_2S - H_2O for example, under the economic conditions published for the Port Hawkesbury and Bruce sites (5) (where 60% of the energy is recovered). The consumptions for our process are 0.7 T steam (60 psi)/kg D_2O and 700 kWh/kg against 11 T steam (330 psi)/kg D_2O and 550 kWh/kg.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch005

TABLE I

Main specifications of the heavy water production plant
(production: 58,5 T/year)

Feeding rate: 1000 T/day $N_2 + 3H_2$ Deuterium content of the hydrogen: 130 ppm

Loop gas flow-rate/supply gas flow-rate (H_2) = 1,4

Enrichment: 1000 (25 for the 1st stage)

Tower dimension			Diameter (m)	height (m)
	1st stage:	transfer tower	2,35	75
		stripping tower	2,44	73,8
		enrichment tower	2,44	51
		hot tower	2,94	55,5
	2nd tower	cold tower	1,22	2 x 49,8
		hot tower	1,47	28

Distribution of investments (%)

piping + valves	11,98%
electricity + control	7,18%
compressors + pumps	4,44%
building, engineering	5,59%
H_2 preparation tanks + catalyst preparation	10,00%
2nd stage	11,30%
dehydration + deamination	13,60%
cooling station + exchanger + insulation	18,46%
towers + plates	17,34%

Principal Consumptions

Electricity :	5893 kWh
of which :	2292 : 1st stage compressors
	2245 : cooling station
Steam :	6 tons/hour
Coolant water:	1164 m^3/hour

Conclusion

The exchange rates in the H_2-MMA system are extremely fast in view of the activity of the catalyst and the solubility of hydrogen. The development of a sufficiently stable and soluble catalyst means that the construction of heavy water plants is feasible under financially competitive conditions. The production of appreciable quantities of heavy water from the hydrogen used for synthesis of ammonia is now possible in many countries. If the use of hydrogen in the future as an energy vector is developed, the MMA-hydrogen process will profit from the scale effect in the building of units, and the low prices of thermal and electrical supplies available at the proximity of hydrogen chemical-nuclear generators.

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RECEIVED October 17, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch005

6

UHDE Process for the Recovery of Heavy Water from Synthesis Gas

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Heavy water, or deuterium oxide, has been used up to now, on an industrial scale, only as a moderator in nuclear reactors. Due to the good utilization of neutrons in heavy water reactors, natural uranium can be used as fuel. At the end of the fifties, when the feasibility of the various types of reactors was examined, the heavy water reactor was found to have very good prospects. Heavy water reactors are of particular interest to countries which have uranium deposits, but do not have their own uranium enrichment plants. Canada has consistently centred the development of the nuclear energy generation on heavy water and has assumed a leading role in this field (1). Also, in India, Argentina and Pakistan heavy water reactors are used as nuclear power plants.

Deuterium can also be used as fuel for fusion reactors. Intensive research is being made into the development of these reactors, but there are still several fundamental physical and technical problems to be solved. There are forecasts that some time in the future, the fusion reactor will supersede the fission reactor in energy production. However, it is difficult to predict when this will happen.

The heavy water requirement of a heavy water reactor is 0.7 t D_2O/MW; in other words, a 600 MW fission reactor requires approximately 400 t D_2O as an initial charge. Losses of one to two percent per year of the initial charge can be expected, i.e. the make-up requirement is 4 - 8 t D_2O per year. In the case of fusion reactors, the annual heavy water requirement for a typical 2000 MW fusion reactor would be no more than a few t D_2O.

There are two fundamental concepts to separate the deuterium isotope: one involving the physical characteristics of hydrogen and water and the other, the chemical isotope exchange characteristics which offer some favourable factors for commercial plant design. Under this category three systems have been applied for commercial application: hydrogen sulfide system, hydrogen-water exchange, and the hydrogen-ammonia exchange.

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The H_2O/H_2S process uses water as a feedstock and is used for industrial heavy water plants in the U.S.A. and in Canada. The feasible size of a plant is at a production of more than 200 t per year.

In contrast to this, the H_2/H_2O and H_2/NH_3 systems are based on hydrogen. When using hydrogen the production capacity is limited by the amount of hydrogen available. This limitation was often considered as a principal disadvantage. This argument is not valid any more, as the capacity of industrial hydrogen production plants, for example ammonia synthesis, has increased in recent years by a factor of 5 - 10. A 1500 t per day NH_3 synthesis plant is capable of producing more than 100 t per year D_2O at a yield of 80%.

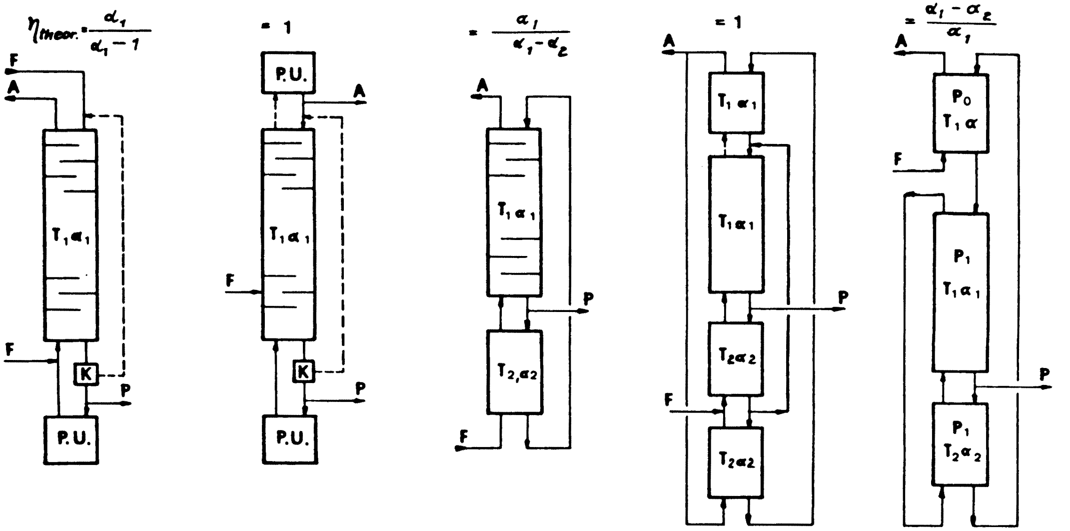
Principles of Isotope Separation

The attainable elementary separation factor is small in chemical isotope exchange. The necessary multiplication of the elementary separation factor by counter current of the liquid and the gaseous phase can be achieved by various schemes (2). The principal schemes are shown in Figure 1. Schemes a and b comprise only one column, which is coupled to a so-called phase conversion unit. In a rectification process phase conversion is achieved in a relatively simple way, by means of, respectively, the reboiler and the overhead condenser. For chemical systems such phase conversion involves a more complicated step-in a water/hydrogen system, for instance, a water electrolysis. In an ammonia/hydrogen system, phase conversion would be effected by the synthesis of the ammonia or the cracking of ammonia to hydrogen and nitrogen. This involves considerable problems from the design and operation point of view, as the catalyst must be separated and fed back to the top of the enrichment column.

Ammonia cracking means a relatively high additional investment and energy consumption, as the energy released during synthesis is obtained at a different level from the energy which is required for ammonia cracking.

When using the hot-cold principle, the phase-conversion is replaced by a hot column (Figure 1 c). Due to negative dependence of the equilibrium constant, the direction of the isotope transport is reserved. Hot-cold processes are also called bithermal or dual temperature exchange processes. The maximum yield which is theoretically possible is shown in the first line of the diagram. For the bithermal system, the yield is limited by the given separation factors at the operating temperature of the hot and cold column. The yield can be increased by adding a stripping system. Such a stripping system is a reverse hot-cold system, i.e. a cold column is followed by a hot column (Figure 1 d). For this purpose it is necessary to circulate an additional gas and liquid stream through the system.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006



a: with phase-conversion
F = Feed
P = Product

b: double phase conversion.
A = depleted stream
P.U. = phase-conversion

c: Hot-cold system
K = catalyst separation

d: Hot-cold system with. Stripping system

e: Hot-cold system with Transfer column

$T_1\alpha_1$ = Conditions of cold columns
$T_2\alpha_2$ = Conditions of hot columns

Figure 1. Principal schemes for chemical isotope exchange

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

In the bithermal system the temperature of the hot column is limited for process and economic reasons - the partial pressure of the liquid phase in the hot column should be small in relation to the total pressure; high pressure of about 300 kg/cm^2 is therefore requested in the system. Therefore, if the feed material, hydrogen, is only available at a relatively low pressure (100 - 200 kg/cm^2), one can add a transfer column which operates at a low temperature upstream of the enrichment system (Figure 1 e). The enrichment system itself is then coupled to the transfer column only via the liquid phase. A transfer column also gives additional advantages which will be shown later. The UHDE process is a combination of a stripping system with a transfer column (Figure 2).

Feasibility studies of the system have clearly shown that due to the improved recovery, the increase in capacity more than compensates for the extra cost of the stripping system. The economic optimum is approximately 80% yield.

Like the water/hydrogen system, the ammonia/hydrogen system also requires a catalyst for the deuterium exchange. Potassium amide (KNH_2) is a catalyst suitable for this purpose. This catalyst has the special advantage that it is homogeneously dissolved in ammonia. A number of other catalysts and catalyst groups have been tested, but up to now it is the only catalyst used in the commercial application.

Design of Heavy Water Plant

The plant as shown on the simplified flow diagram (Figure 3) consists of five essential sections, the gas purification section with transfer column, the first stage with stripping system, the second and third stage and lastly, the final concentration section comprising the exchange column and the water distillation section.

Another important plant section not shown on the flow diagrams is the refrigeration unit. The refrigeration compressor with two different temperature levels is driven by a steam turbine of the extraction condensing type. Back-pressure steam is used for heating and saturating the gas or liquid streams. Depending on the cooling water conditions the turbine can also be operated without the condensing part.

Purification System. The synthesis gas passes through a gas purification section in which all oxygen-bearing gas components such as H_2O, CO_2, CO and O_2 are removed (6). All these substances react with the potassium amide, forming substances which are insoluble in liquid ammonia. This would result not only in a reduction of the catalyst efficiency, but also introduces the risk of clogging in the column.

Water and carbon dioxide are removed in a first stage by liquid ammonia scrubbing. The ammonia is taken from the ammonia

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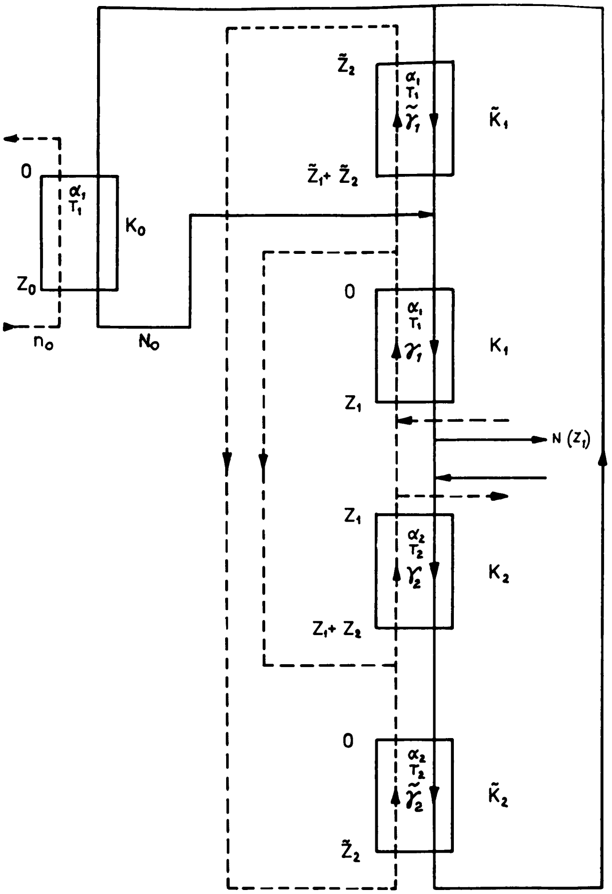

Figure 2. Transfer–stripping–enrichment system

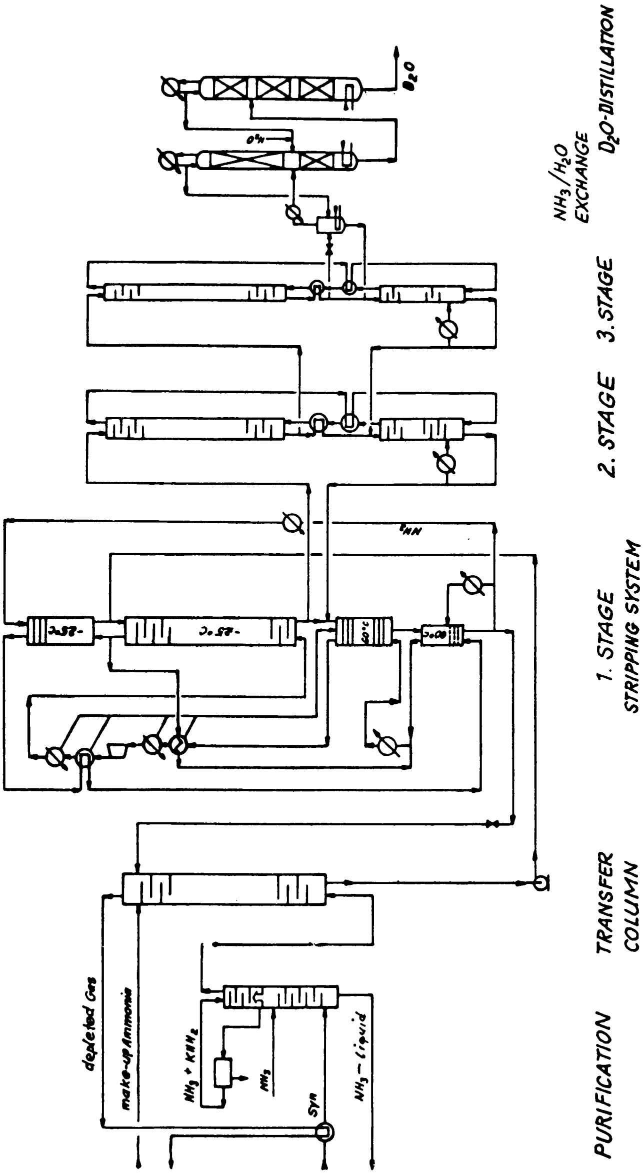

Figure 3. Simplified flow scheme of the D_2O plant

synthesis unit and returned to it after passing the purification unit.

Carbon monoxide and also oxygen, if the latter is present in the gas, are removed by scrubbing with potassium amide solution. A special design of the trays eliminates the risk of clogging. The reaction products formed in this stage are removed outside the column and the potassium amide solution is fed to the top again.

Transfer Column. The gas then passes through the transfer column where the deuterium is transferred to the ammonia and the syngas is returned to the ammonia synthesis unit. In washing trays at the top of the transfer column entrained potassium amide is removed. The enriched ammonia leaving the bottom of the transfer column is pressurized to the pressure of the downstream first stage.

First Stage and Stripping System. The first stage consists of the bithermal section proper and the stripping system. The operation of the individual sections of the first stage might best be explained with the aid of the McCabe-Thiele diagrams (Figure 4). Here, N(O) is the concentration of the liquid ammonia fed from the bottom of the transfer column to the top of the cold column of the enrichment system.

In the cold column, deuterium is transferred from the gas to the liquid; in other words, we are going up the working line. At the bottom of the cold column, deuterium-bearing hydrogen is removed and transferred to the next stage and a corresponding stream is returned; however, with a lower deuterium concentration. The concentration changes from N(z) to N'(z) and we follow the working line of the hot column as far as to the bottom of the hot column. Here the gas stream is split. On the McCabe-Thiele diagram, this means a change in the slope of the working line. In the hot stripping column deuterium continues to be transferred to the gas and the lowest deuterium concentration $N(\tilde{Z}_2)$ is finally reached at the bottom of the hot stripping column. Prior to entering the cold stripping column, the ammonia, which is being returned to the top of the transfer column, is removed. This alters the slope of the working line again and in the cold stripping column we come back to the feeding point. This diagram also shows that the slope of the working line is limited by the slope of the two equilibrium lines at the temperature of the hot and cold column. When designing the plant, the slope of the working lines must be determined in such a way that only a minimum of trays is required. As the tray efficiency in the hot and cold columns is different, this minimum refers to the number of actual trays; in other words, the column volume of the system is to be minimized.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

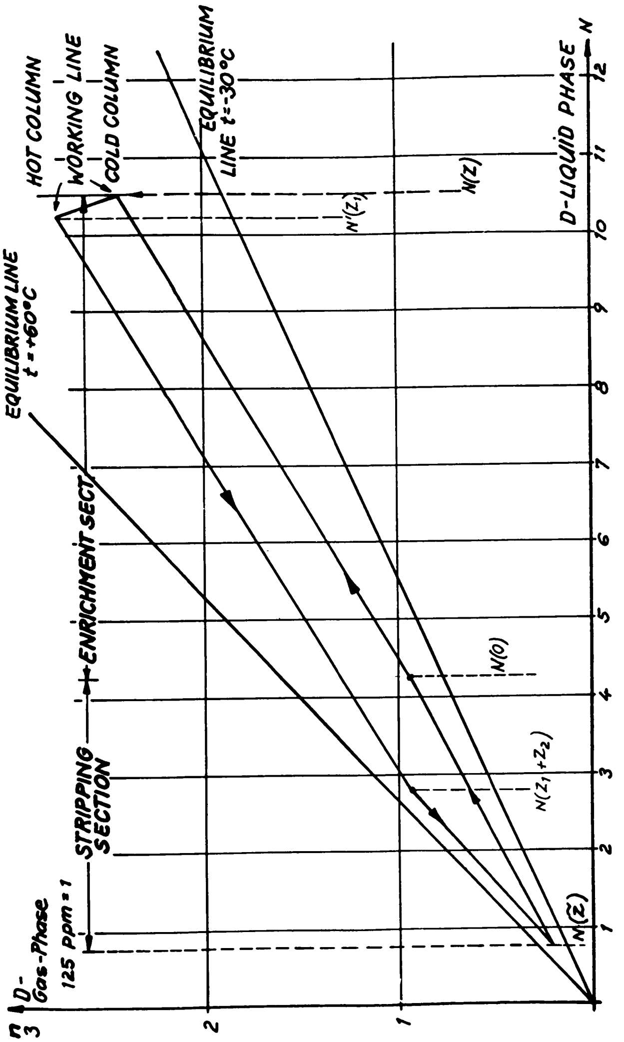

Figure 4. McCabe–Thiele diagram of the first stage

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

In the first stage there are two superimposed gas cycles. However, only one circulating compressor is sufficient as the different pressure drops in both cycles can be used for controlling the gas rates. When being transferred from the hot column to the cold column and vice versa, the gas and liquid streams are heated and cooled respectively. It is obvious that this must be done in a way to conserve the heat in order to reduce the energy consumption.

Figure 5 shows the enthalpy/temperature diagram for synthesis gas which is saturated with ammonia and the arrangement of the heat exchanges for cooling the synthesis gas from the hot column. Downstream of a direct heat exchanger, which is arranged inside the hot column, the heat is transferred to liquid ammonia at a relatively high temperature which then transfers this heat to the gas for saturation. The gas then flows through a water cooler and then through a gas/gas exchanger. The remaining gap to come down to the temperature of the cold column is provided by the refrigeration plant and transferred from the gas in two heat exchangers, connected in series. These operate at different temperatures in order to reduce the energy consumption for the refrigeration compressor. Altogether, almost 70% of the heat released during cooling is utilized.

The arrangement of the heat exchangers and the determination of the working range is not arbitrary, but is determined by the energy costs and the capital investment for heat exchangers, taking into account the special conditions at the site.

This problem of optimization was resolved simultaneously with the problem of minimizing the column volume by setting up appropriate computer programs. This work was done in a very close cooperation with the Institute for Nuclear Technology at Karlsruhe University (4). The cooperation is not confined to this subject but also to solving other problems, in particular the performance of pilot plant tests which supplied the results on which the design of the process is based (3),(5).

Second and Third Stage. The arrangement of the second and third stage is analogue to the first stage. In each stage the deuterium content is increased by a factor around 9. Ammonia which has been enriched to 15-20% deuterium can then be taken out between the hot and cold column of the third and last stage. Since the streams are smaller, i.e. inversely proportional to the enrichment factor, the heat recovery system between hot and cold column is made simpler.

Final Concentration. After careful examination Uhde decided for a water distillation as final concentration. Water distillation is a well-proven process and can be operated under normal pressure and temperature.

For this, it is necessary to transfer the deuterium from the ammonia to water. The enriched ammonia which had been

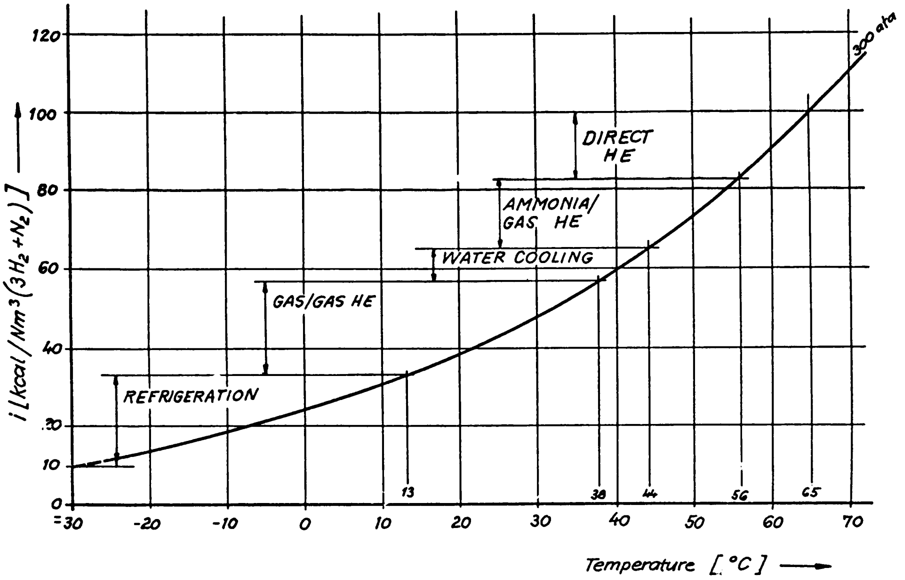

Figure 5. Enthalpy–temperature diagram for synthesis gas (3 N_2 + H_2) saturated with NH_3

separated from the catalyst through evaporation, is thus brought into contact with water. Both reaction partners are separated again in a distillation section at top and bottom of the column, the ammonia is fed back to the third stage. The enriched water is fed to a single-stage distillation column. The heavy water with a content of over 99.8% D_2O can finally be withdrawn from the bottom of the distillation column.

Based on this consideration the final concentration has been designed and supplied by Sulzer Bros., Winterthur.

Operation of the Plant. The different sections of the plant - the gas purification section with transfer column, the first stage with stripping system, the second and third stage and lastly, the final purification section, can be operated independently; that means if one of them has to be shut down, the others can still be operated. This reduces the process control problems and increases plant reliability. It is a characteristic feature of the process that the steady state conditions, i.e. the final concentration profile in the columns, are reached only after a period of a few days. Also therefore each section is provided with a separate collecting tank for the liquid hold up in order to avoid mixing of liquids with different isotope concentrations, and so to facilitate re-starting.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

Engineering Problems

Apart from questions dealing with the process design engineering there were also several mechanical engineering problems to be solved. The plant is designed for much the same pressure and temperature range as an ammonia synthesis plant; consequently, the same sort of techniques can be used for the design. This applies particularly to the heat exchangers as well as the choice of other equipment.

The high-pressure columns involve new problems. The diameter of the cold column in the first stage is 2 m and the diameter of the corresponding hot columns is larger still due to the greater gas and liquid load. The columns are up to 40 m high. The cold columns of the enrichment system and of the transfer section are divided in two parts in series.

At an operating pressure of 325 kg/cm^2 the column weight is considerable. The largest column, which has a dead weight of 270 t, must be transported to the plant site in one piece and erected there. Therefore the transportation conditions should be reviewed carefully before deciding on the location for a plant of this kind.

All towers are equipped with sieve trays, which provide a good mass transfer between the phases. According to the special features of the system with regard to the kinetics of the reaction and the hydrodynamic characteristics of the fluids, the design of the sieve trays differs from the design normally used for distillation or absorption towers.

Oxygen-bearing substances are completely removed from the gas due to the presence of potassium amide. It is well known that hydrogen of extreme purity reduces the notch impact strength of high-grade steels. Tests have shown, however, that such a risk is unlikely under the conditions prevailing here. For safety reasons steels are preferred, which have a relatively low strength and good ductility, even at low temperatures, as is the case for higher nickel-alloyed steels.

Potassium amide in ammonia acts very strongly on organic materials, so even materials like Teflon corrode within a short time. A variety of materials were examined in autoclave tests in order to find materials which are resistant to potassium amide at the prevailing operating conditions. Later these materials are tested under operating conditions in a special facility. Even today this is done to test material for pump seals and stuffing boxes which are new on the market. All these questions have been examined very carefully, first on a laboratory scale and then on a pilot-plant scale in order to find a reliable solution for the design of a commercial plant.

Integration of Heavy Water Plant and Ammonia Synthesis

This process is based on hydrogen as the source of deuterium. This hydrogen can be obtained for example from the gasification unit of the ammonia plant. The heavy water plant is stripping the deuterium from the syngas, which is then returned to the ammonia synthesis loop. This coupling is of vital importance for the operation of ammonia plants. It must be certain that the production and also the on-stream time of the ammonia plant are not affected.

Figure 6 shows the scheme of integration of a heavy water plant with an ammonia plant.

1. The synthesis gas produced in the gasification section is purified in the usual way and fed to the synthesis gas compressor, where it is brought up to the pressure of the ammonia synthesis unit and admixed to the synthesis gas cycle as feed gas. After the last stage of the syngas compressor, the synthesis gas is diverted to the heavy water plant. The synthesis gas which is depleted of deuterium is then returned to the ammonia synthesis unit. The heavy water plant in fact constitutes a by-pass to the ammonia synthesis unit.
2. The synthesis gas passes only through the gas purification column and the transfer column of the heavy water plant resulting in a certain pressure drop. This pressure drop would have to be made up by the synthesis gas compressor. However, it is better to install an additional booster compressor which compensates for this pressure drop. In the

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

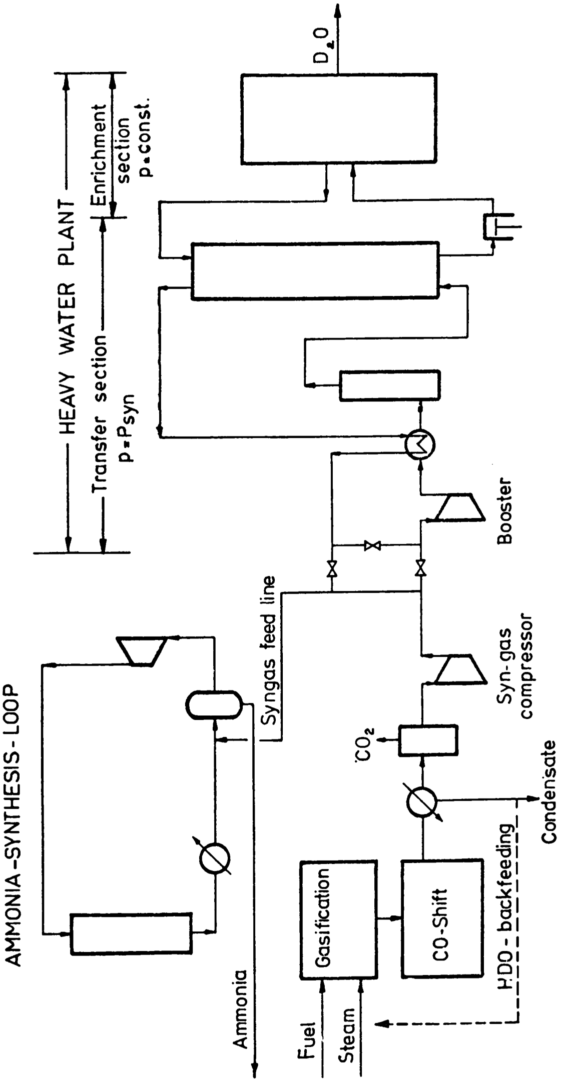

Figure 6. Integration of heavy water plant with ammonia plant

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

event of failure of the NH_3 synthesis unit, the gas purification column and the transfer column can be operated in a closed circuit. Also in this case there is no need for a valve in the by-pass line, thus establishing an open by-pass. In the case of fluctuation in the gas flow the heavy water plant runs under constant conditions; only the direction flow in the by-pass line will be changed. The flow can slowly be adjusted to new conditions accordingly. The same is the case if there are disturbances in the heavy water plant.

3. The synthesis gas which is returned to the synthesis unit is saturated with ammonia at a dew point of $-28°$ C corresponding to the temperature at the top of the cold transfer column. At a pressure of 200 kg/cm^2 in the synthesis unit, the ammonia content of this stream is thus approximately 1.2%. If this gas is admixed to the recycle gas of the synthesis unit upstream of the first separator, it has no effect on the synthesis cycle. However, if the gas is fed to the recycle gas directly upstream of the converter, as is the case sometimes in synthesis units where nitrogen scrubbing is used for gas purification, the gas entering the converter would have a slightly higher ammonia content and this would result in a corresponding decrease in the NH_3 conversion rate in the converter. This can be compensated by increasing the pressure of the synthesis loop, but it is better to compensate this higher ammonia content by slightly increasing the cold duty of the last separator of the ammonia synthesis unit, in order to keep the design conditions of the converter constant.
4. The temperature of the return gas is lower than that of the feed gas, because the heat exchanger must have a certain temperature gradient.
5. Furthermore, the gas contains no traces of either CO or oxygen which usually have a detrimental effect on the ammonia catalyst. The last two factors mentioned have a favourable effect on the operation of the ammonia synthesis unit, although the benefits cannot be defined quantitatively.
6. An essential point of the integration concerns the gasification section. The gas purification should be designed in such a way as to keep the content of oxygen-bearing impurities as low as possible in order to reduce the load on the gas purification section of the heavy water plant. However, the deuterium content in the gas is more important and should, of course, be kept as high as possible. The deuterium content is determined by the deuterium content of the feedstocks used for the ammonia, e.g. methane and water; but, as we have seen from numerous measurements of the deuterium content of samples taken at various parts of ammonia plants, it can be negatively influenced by processes within the gasification section. A deuterium exchange can

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

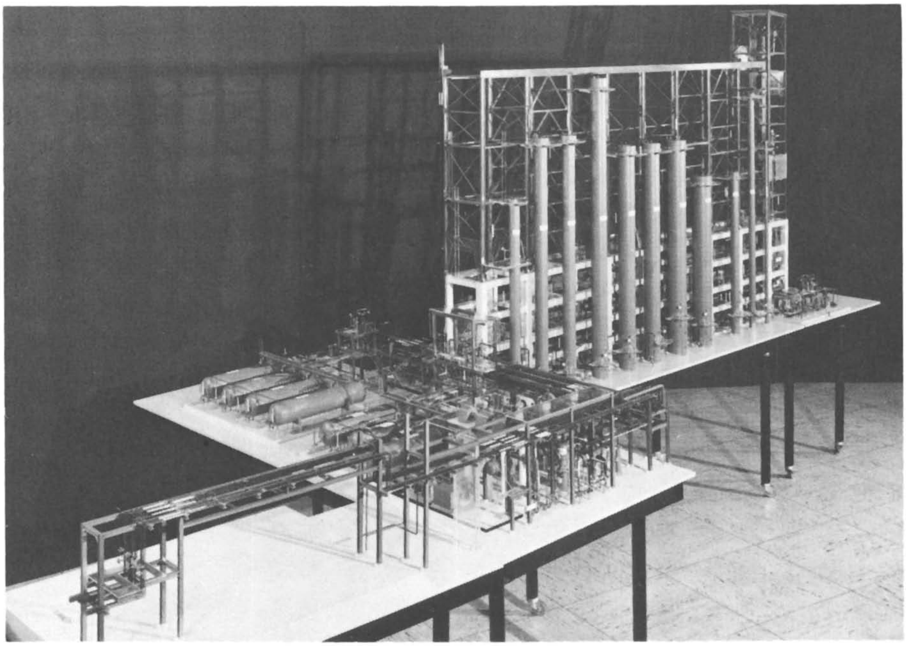

Figure 7. Model of a heavy water plant (capacity 63 t/yr)

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch006

take place between the hydrogen and the excess steam in the CO shift conversion, the deuterium being transferred to the steam. The hydrogen thus becomes depleted of deuterium and the steam becomes enriched. This steam is condensed upstream of the CO_2 scrubbing unit and is discharged from the plant. The condensate is usually not returned to the plant and the deuterium contained in it would be lost and this would result in a proportionate reduction in the production of the heavy water plant. These losses can be avoided if this enriched condensate is transformed to steam and this steam is then used as process steam in the steam reformer. However, this involves a greater load on the steam system of the ammonia plant which cannot be realized in the case of existing ammonia plants. This problem can be avoided by an isotope exchange of the enriched condensate with the process steam which is being fed to the steam reformer or to the shift conversion. The equilibrium between water and water vapour is nearly equal to unity; that means the condensate leaving the exchange system has the normal deuterium concentration again.

These points show that an ammonia plant and a heavy water plant can be integrated without any particular difficulties.

Conclusion

A heavy water plant with a capacity of 63 t D_2O per year will be built at Talcher/India. The plant is coupled with a 900 t per day ammonia plant and will be put on stream beginning 1978. Figure 7 is a photo of the model.

A comparison of the production costs based on the calculation for this plant shows with regard to the investment as well as to the operating costs that this process can compete with other processes or may even be superior.

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RECEIVED October 28, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch007

7

Novel Catalysts for Isotopic Exchange between Hydrogen and Liquid Water

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Canada's atomic power program requires large quantities of heavy water that are currently produced by the Girdler-Sulphide or GS process. This process is based on exchange of hydrogen isotopes between hydrogen sulphide gas and liquid water as given by the following chemical exchange reaction:

$$HDS_g + H_2O_{liq} \rightleftharpoons HDO_{liq} + H_2S_g \qquad (1)$$

At Chalk River we have a strong interest in trying to develop new and more efficient processes for the production of heavy water. A very attractive process and one with many inherent potential advantages is based on the hydrogen-liquid water isotopic exchange reaction.

$$HD + H_2O_{liq} \rightleftharpoons HDO_{liq} + H_2 \qquad (2)$$

The hydrogen-water isotopic exchange reaction is more attractive primarily because it has a higher separation factor, α, defined in terms of the deuterium (D) to protium (H) atom ratios in the two species at equilibrium.

$$\alpha = (D/H)_{liq} \Big/ (D/H)_g \qquad (3)$$

At low deuterium concentrations, α is equal to the equilibrium constant for both of these exchange reactions.

Figure 1 gives the separation factor for the hydrogen-liquid water (1) and the hydrogen sulphide-liquid water (2) exchange reactions in the temperature range 0-200°C. Over the entire temperature range, the separation factor, α, for the H_2-H_2O system is about a factor of 2 higher than that for the H_2S-H_2O

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch007

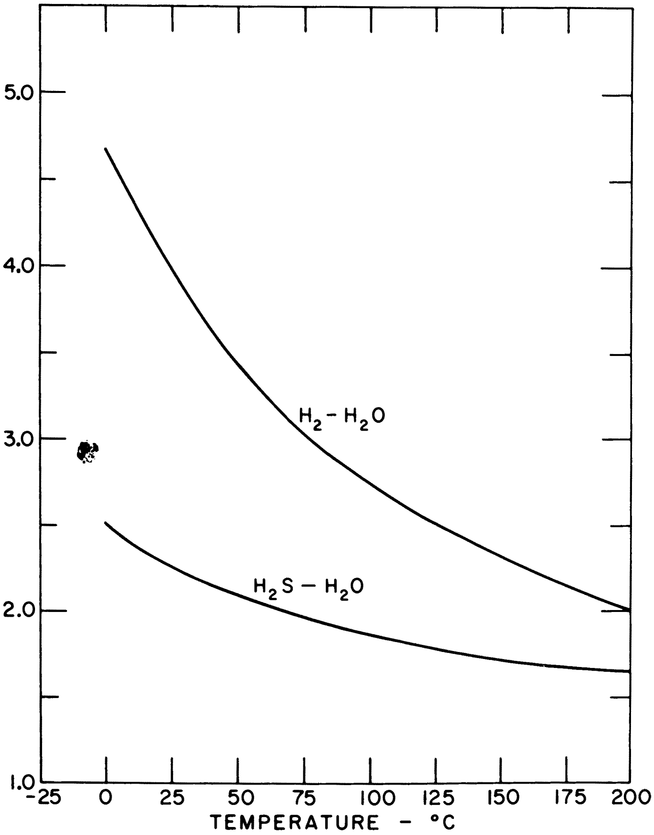

Figure 1. Separation factor, α, as a function of temperature for the hydrogen–water and hydrogen sulfide–water systems

exchange reaction. As a result, a process based on the H_2-H_2O reaction will have a higher recovery of deuterium from natural water and, as a consequence, a smaller plant will be required. Theoretical recoveries of 50% are possible for a bithermal process based on the hydrogen-water reaction compared to 21% for the GS process.

Catalyst Development

Although the hydrogen-water isotopic exchange reaction is very desirable for the separation of hydrogen isotopes, the difficulty has been to obtain a catalyst that can operate efficiently in the presence of liquid water (3). Effective noble metal catalysts for the vapour exchange reaction have been known for many years but these catalysts lose their activity in contact with water.

Our new approach is to use a catalyst suitable for the vapour exchange reaction, such as highly dispersed platinum metal deposited on γ-alumina, and to coat the catalyst body with a very thin layer of a water repellent material, such as a silicone polymer, to prevent wetting (4). To illustrate the effectiveness of the silicone wetproofing, Figure 2 shows what happens when catalyst pellets of platinum on alumina, a commercial catalyst produced by Engelhard Industries, are immersed in water. The untreated pellets release a stream of small bubbles of air as water immediately enters the pores of the alumina. The pellets become jet black, indicating that the surface is completely wetted. In contrast, the silicone treated pellets shown in Figure 3 have large gas bubbles adhering to their surface and the surface remains light grey in colour, which is characteristic of the wetproofing action of the silicone. These silicone treated, or wetproofed, catalysts are quite effective for the hydrogen-liquid water isotopic exchange reaction.

Subsequently, catalysts were prepared by depositing platinum on porous polytetrafluoroethylene in an attempt to provide an improved hydrophobic environment for the platinum crystallites (5). A more successful approach has been to deposit platinum on high surface area carbon and to bond the platinized carbon to a variety of column packings or carriers using Teflon as both the bonding and the wetproofing agent. These latter catalysts have proven very effective for the hydrogen-liquid water exchange reaction.

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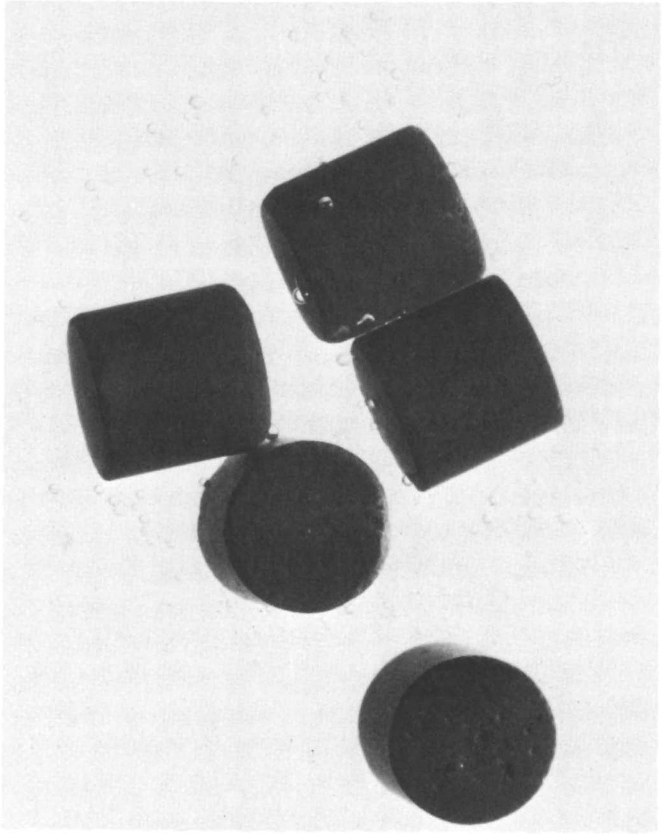

Figure 2. Untreated 0.5% Pt–Al_2O_3 Engelhard catalyst immersed in water

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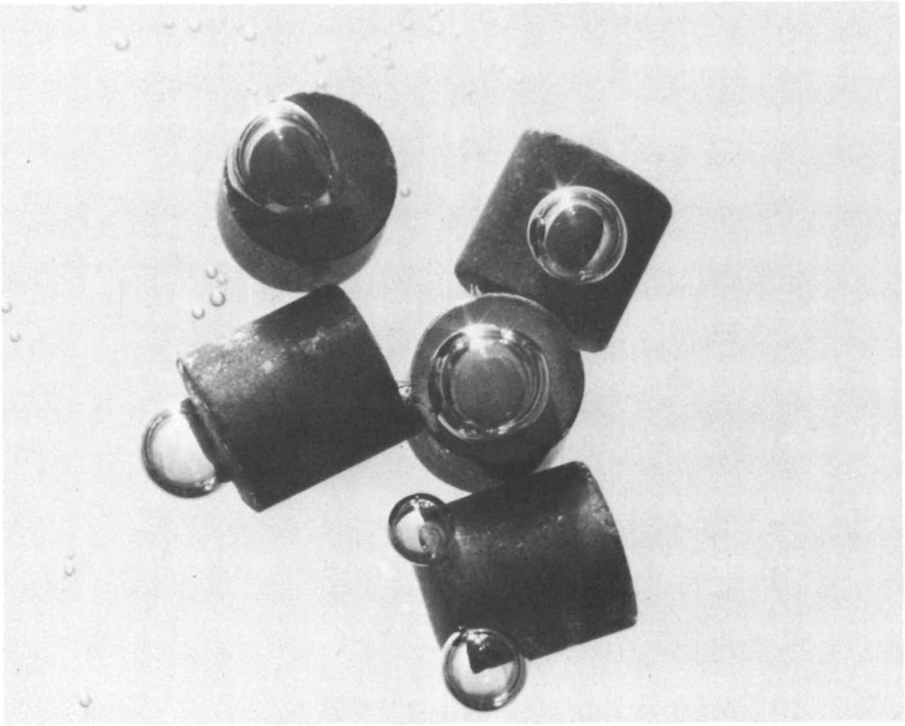

Figure 3. 0.5% Pt–Al_2O_3 Engelhard catalyst treated with Dow Corning 773 Silicone and immersed in water

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Catalyst Performance

To measure the performance, or the activity, of these catalysts we have used a single pass trickle bed reactor shown diagrammatically in Figure 4. A known quantity of catalyst is packed in a 2.5 cm diameter glass column to depths varying from 5 to 75 cm. About 15 cm of non-catalytic packing is placed directly below the catalyst bed to aid in establishing uniform gas flow patterns through the bed. The entire packing is supported on a stainless steel screen (mesh size, 40 x 40). Natural water (D/H = 144 ppm) is introduced at the top of the column through a water distributor and flows downward through the catalyst bed assembly. Purified dry hydrogen, enriched in deuterium (D/H = 300 ppm), flows countercurrently upward through the humidifier where it becomes saturated with water vapour which is in isotopic equilibrium with the liquid water leaving the catalyst bed. The gas and water vapour then continue upward through the catalyst bed. The deuterium concentration in the inlet and outlet hydrogen gas streams is measured with an on-line mass spectrometer (6). For the operating conditions described, the enriched hydrogen gas becomes depleted in deuterium in passing through the column while the natural water feed is enriched. For example, for a given catalyst operating at 25°C where the separation factor, α, is 3.81, the hydrogen gas stream leaving the top of the column may have a D/H = 150 ppm, while if equilibrium had been established between the two phases the concentration would be 37.8 ppm.

The activity of the various catalysts for the isotopic exchange reaction in the hydrogen-water system is determined by the nearness of approach to isotopic equilibrium between the two phases after passing through the column. This degree of approach is expressed in terms of a column efficiency, η, defined as the ratio of the actual change in the deuterium concentration of the hydrogen to the change that would have occurred had the hydrogen gas stream reached equilibrium with the feed water. With mixtures of hydrogen and water at low deuterium isotopic composition, the column efficiency, η, for the catalyst bed is given by the expression

$$\eta = \text{Fractional Approach to Equilibrium Between the Two Phases}$$

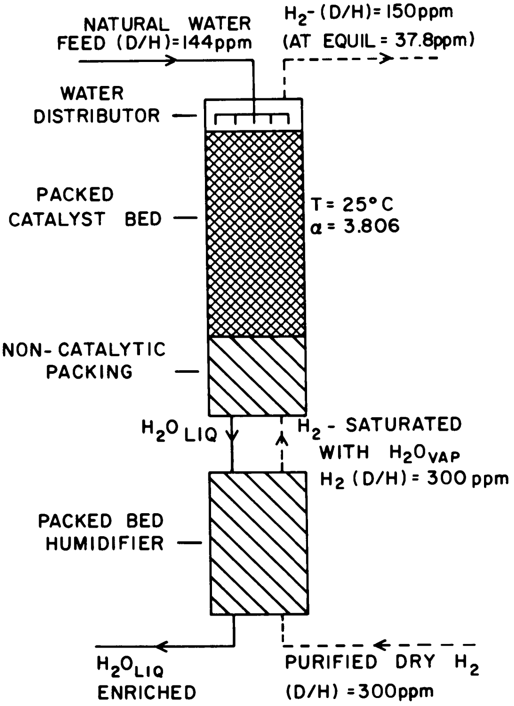

Figure 4. Trickle bed reactor used for hydrogen–liquid water isotopic exchange studies

$$= \frac{(D/H)_b - (D/H)_t}{(D/H)_b - (D/H)_{eq}} \qquad (4)$$

where (D/H) is the atom ratio and the subscripts, b and t, refer to the inlet and outlet hydrogen gas streams at the bottom and top respectively of the exchange column. The subscript, eq, refers to the deuterium concentration of the hydrogen in equilibrium with the liquid water. From a measurement of the column efficiency, η, the overall transfer of deuterium from hydrogen to liquid water can be calculated. For hydrogen and water flowing countercurrently in a packed column, the transfer of deuterium from the hydrogen to the water is characterized by an overall gas-phase mass transfer coefficient, T_ya, expressed in gram atoms per unit time, per unit volume of bed, for unit displacement of the deuterium mole fraction from the equilibrium value. For a small test reactor where the concentration of deuterium in the water does not vary significantly throughout the reactor, the rate of deuterium transfer from the gas to the liquid phase in a small volume element of the reactor, dV, of cross sectional area A and height dh, is given by the following differential equation:

$$-G \cdot A \cdot dy = T_y a(y - y^*) A \cdot dh \qquad (5)$$

where G is the molar flow rate of hydrogen per second per unit area, y is the actual mole fraction of deuterium in the hydrogen at a given height, h, and y* is the value at equilibrium with the liquid water. Integrating equation 5 over the height of the catalyst bed, h, gives

$$T_y a = \frac{G}{h} \left[-\ln(1 - \eta) \right] \qquad (6)$$

Since gas flow rates are normally measured in terms of volume, we have found it convenient to use a volume transfer coefficient, K_ya given by the expression

$$K_y a = \frac{F}{h} \left[-\ln(1 - \eta) \right] \qquad (7)$$

where F - superficial hydrogen flow rate, $m \cdot s^{-1}$ at STP

h - height of the catalyst bed, m

K_ya - gas-phase volume transfer coefficient, m^3 (of H_2 at STP)$\cdot s^{-1} \cdot m^{-3}$(of catalyst bed).

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The rate of the overall isotopic exchange reaction is first order in the approach of the deuterium concentration of any of the species to its final equilibrium value and thus K_ya is a first order rate constant and dimensionally it has the units of s^{-1}.

We have studied the effect of many parameters on the activity of the catalyst, K_ya, and Figure 5 shows the effect of hydrogen gas flow rate and temperature for a 0.37% Pt-C-Teflon catalyst on 6.1 mm ceramic spheres. For this catalyst, K_ya increases approximately as the 0.3 power of the hydrogen flow rate in the range 0.05 to 1.4 m/s at STP. We are dealing here with a very fast isotopic exchange reaction: for example, at a temperature of 25°C and a hydrogen flow rate of 1.0 m/s at STP, K_ya = 1.2. This is equivalent to a half-time for the exchange reaction of 0.18 s. The half-time is calculated using the actual hydrogen flow rate which is 3.1 times the superficial flow rate for this particular catalyst bed assembly (the volume fraction of gas in the operating column is 0.32). The solid points in Figure 5 were obtained using enriched hydrogen (D/H = 250 ppm), where the deuterium is transferred from the hydrogen gas to the liquid water, while the open points were obtained using enriched water (D/H = 1130 ppm),where deuterium is transferred from the liquid water to the hydrogen gas. From the data no difference can be detected in the rate of deuterium transfer for the net reaction occurring in either direction. The effect of temperature on the activity of the catalyst is also illustrated in Figure 5. For an increase in temperature from 25° to 60°C, K_ya increases by a factor of 2.4. The temperature coefficient of K_ya for this catalyst in the range 15° to 60°C is equivalent to an Arrhenius activation energy of 21 $kJ \cdot mol^{-1}$ or about 5 $kcal \cdot mol^{-1}$.

The effect of platinum metal surface area on the activity of the catalyst is shown in Figure 6 where K_ya, the volume transfer rate constant, is plotted against the platinum metal surface area, measured by hydrogen chemisorption, and expressed as m^2 per cm^3 of packed bed. Although K_ya increases with metal area, the increase is not directly proportional to the area. For metal areas below 0.06 $m^2 \cdot cm^{-3}$, K_ya increases as the 0.75 power of the metal surface area and at higher metal areas the rate of increase of K_ya is less. The curve appears to be approaching a maximum value. These results indicate that another reaction besides the catalytic one is limiting the overall exchange reaction rate.

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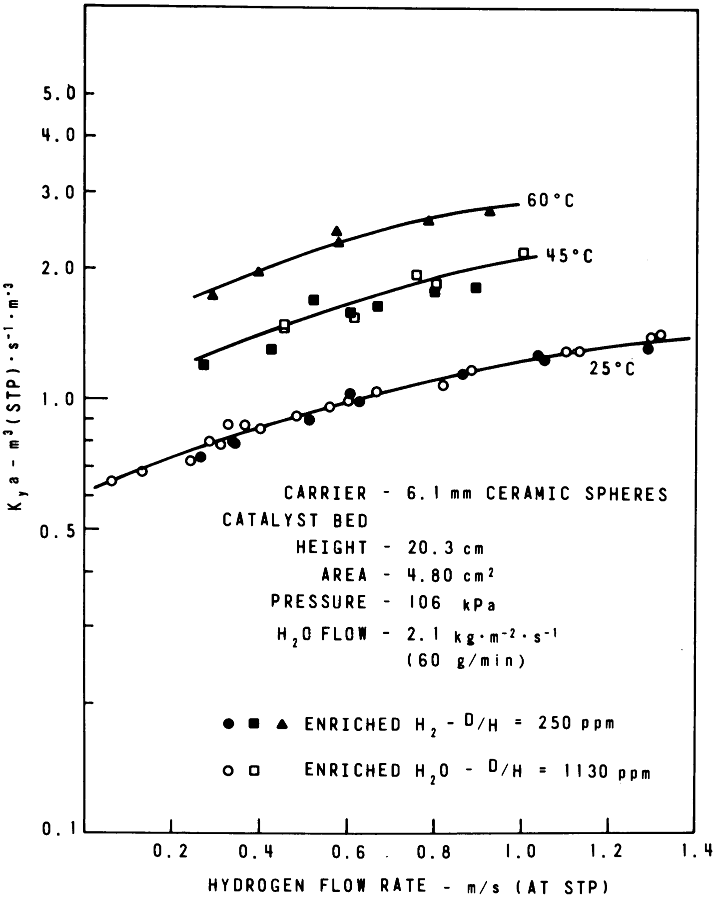

Figure 5. Effect of hydrogen gas flow rate and temperature on the activity, K_ya, *of a 0.37% Pt–C–Teflon catalyst*

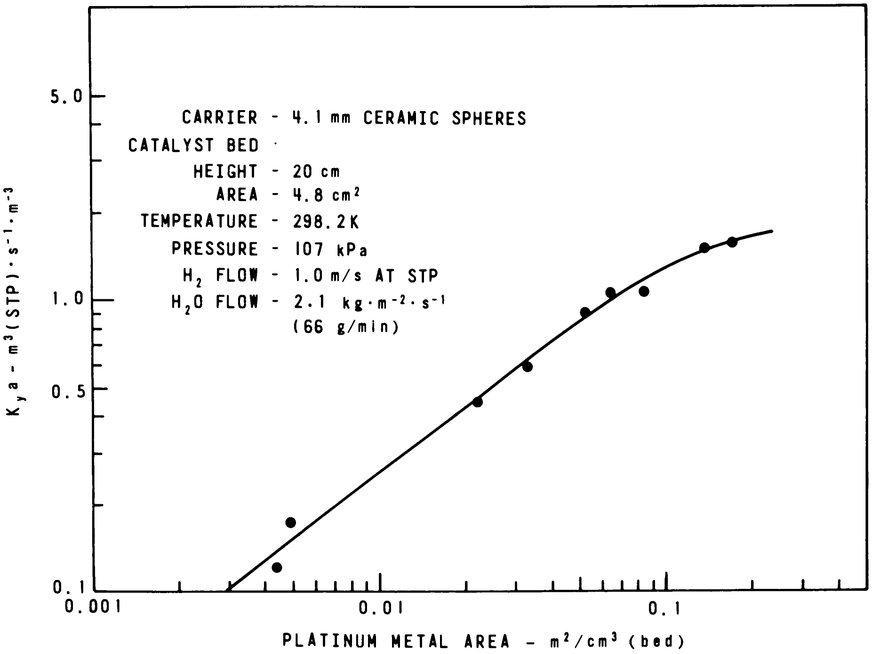

Figure 6. Dependence of the transfer rate constant, K_ya, *on the platinum metal area of Pt–C–Teflon catalysts*

Mechanism of the Exchange Reaction

As a first approximation, the overall rate of transfer of deuterium between streams of hydrogen and liquid water over these wetproofed catalysts can be considered in terms of two transfer steps. The first corresponds to the catalytic rate of transfer of deuterium from an enriched hydrogen stream to water vapour and the second corresponds to the transfer rate from water vapour to liquid as shown in equations [8] and [9].

$$HD + H_2O_{vap} \rightleftharpoons HDO_{vap} + H_2 \qquad (8)$$

$$HDO_{vap} + H_2O_{liq} \rightleftharpoons HDO_{liq} + H_2O_{vap} \qquad (9)$$

The catalytic reaction [8] occurs on active catalyst sites while the vapour-liquid transfer reaction [9] occurs on any surface. The latter transfer step can be considered as a condensation-evaporation reaction. Techniques have been developed so that, in a trickle bed reactor, the overall rate and the individual transfer rates (reactions [8] and [9]) can be determined simultaneously (7). The magnitudes of these separated rates are both about a factor of 2 larger than values from direct measurements made on these two reactions independently. These results have led to the conclusion that the overall mechanism for the exchange reaction is not as simple as first assumed and that there is a third process independent of the water vapour involved in the transfer of deuterium from hydrogen gas to liquid water. The exact nature of this third process is not yet known.

Studies have been made of the effect of some 20 different parameters on the activity of the catalysts and these will be discussed in future publications.

Improvements in Catalyst Performance

Innovations resulting in improved catalyst performance are summarized in Table 1. The activity, K_ya, of each catalyst in a trickle bed reactor is given for a column operating at 25°C, at about 1 atmosphere pressure (0.106 MPa) and a superficial hydrogen gas flow rate of 1.0 m/s at STP. Also listed in Table 1 is the specific activity of each catalyst, K_ya^*, defined as the overall transfer rate per unit concentration of platinum in the catalyst bed,

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ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

TABLE 1

Improvement in Catalyst Performance

	Catalyst	$K_y a$ $m^3 \cdot s^{-1} \cdot m^{-3}$	$K_y a^*$ $m^3 \cdot s^{-1} \cdot (kg\ Pt)^{-1}$	Rel. Specific Activity
1.	Pt-Charcoal, Taylor	0.017	0.0022[a]	2.0
2.	0.05% Pt-Al_2O_3 Untreated	0.005	0.0011	1.0
3.	0.5% Pt-Al_2O_3 Silicone Treated	0.22	0.046	42
4.	0.4% Pt-Porous Teflon	0.20	0.064	58
5.	0.4% Pt-C-Teflon	0.58	0.146	133
6.	0.14% Pt-C-Teflon	1.20	1.44	1300
7.	0.087% Pt-C-Teflon	0.98	2.18	1980
8.	0.39% Pt-C-Teflon Ordered Packing	2.40	2.84	2580

[a] Calculated from data given in reference (8).

$$K_ya^* = K_ya \Big/ \text{kg Pt per m}^3 \text{ bed} \qquad (10)$$

The specific activity gives a measure of how effectively the platinum is being used in a given catalyst. The last column gives the specific activity relative to catalyst #2, an untreated,0.5% Pt catalyst on 3.2 mm pellets of γ-alumina. Catalyst #1, platinum on powdered charcoal, was patented by Taylor for this exchange reaction in 1954 (8). Treatment of catalyst #2 with silicone (Cat. #3) improved the performance by a factor of 40. In an attempt to further improve the hydrophobic environment of the platinum crystallites, platinum was deposited on porous Teflon (Cat. #4) and this enhanced the activity slightly. Depositing platinum on high surface area carbon and bonding this to a carrier with Teflon (Cat. #5) made a significant improvement in the specific activity. By decreasing the platinum loading and increasing its dispersion on the carbon black (Cat. #6) the relative specific activity was increased by a factor of 10. By further decreasing the platinum loading to 0.087% (Cat. #7) a further increase was obtained. This latter catalyst has a specific activity about 2000 times higher than the untreated 0.5% Pt-Al_2O_3 catalyst, #3, and is about 1000 times more active than the catalyst patented by Taylor (8) for this exchange reaction (Cat. #1). In catalyst #8, the platinized carbon was bonded with Teflon to corrugated metal sheets arranged in an ordered fashion in the exchange column. Although this catalyst has a higher platinum content, 0.39%, the concentration of platinum per unit volume of bed is essentially the same as catalyst #6. However as a result of the improved geometric configuration of the catalyst, both the activity and the specific activity are twice that of catalyst #6. Since the height of the column required for a given separation is inversely proportional to K_ya, the spectacular improvements in catalyst activity reported here make a hydrogen-water exchange process for deuterium enrichment look very promising.

Process Features of Hydrogen-Water Exchange

Processes based on the hydrogen-water exchange reaction potentially have many attractive features for the separation of hydrogen isotopes relative to the GS process.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch007

ADVANTAGES OF HYDROGEN-WATER PROCESSES

1. HIGHER SEPARATION FACTOR
2. HIGHER RECOVERY
3. LOWER WATER AND GAS FLOWS
4. SMALLER EXCHANGE COLUMNS
5. SIMPLE CHEMISTRY
6. NON-CORROSIVE SYSTEM
7. NON-TOXIC
8. LOW ENVIRONMENTAL IMPACT, POLLUTION-NIL
9. USES ONLY ONE EXCHANGE REACTION

These generic advantages are generally applicable to any process based on the hydrogen-water exchange reaction and are particularly relevant to the Combined Electrolysis Catalytic Exchange (CECE) process. The CECE process which couples a hydrogen-water catalytic exchange column to the hydrogen gas stream from an electrolysis cell offers a very effective system for the enrichment of deuterium. The process is discussed in more detail by Hammerli, et al. (9) in the next paper. Since the separation factor, α, for the hydrogen-water exchange reaction is higher than that for the GS system, a higher deuterium recovery is possible, 70% from natural water compared to 19% for the GS process. Higher recovery permits lower water and gas flow rates in the plant. The very active catalysts that have been developed mean that the exchange columns will be quite small. Although most of the separatory work is accomplished in these columns, their volume would only be about 4% or 1/25 of the exchange volume in current GS plants for the same production of heavy water.

The chemistry of the hydrogen-water system is simple and operating conditions of the CECE process are near ambient. The system is non-corrosive, an important feature since many of the shut-downs in GS plants result from corrosion. The system is non-toxic and non-polluting and would have a very low environmental impact. The CECE process yields two valuable products - heavy water and large quantities of hydrogen, a very useful chemical. Electrolytic oxygen may also be considered as an additional product. Finally the process utilizes only one exchange reaction for the complete enrichment of deuterium from natural water to reactor grade heavy water, 99.8% D_2O. This removes many of the complexities of other heavy water processes which require different processes at various stages in the enrichment.

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The major disadvantages of the process are that it requires a large amount of electrical power for the electrolysis cells and it requires a stable platinum catalyst which is somewhat expensive. However active catalysts have been developed with low platinum loadings so that the platinum represents only about 30% of the cost of the finished catalyst. Further, the amount of catalyst required is small and it has been estimated that the catalyst cost will be only a very small percentage of the total capital cost of a heavy water plant. Likewise catalyst replacement is not expected to add significantly to the operating costs.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch007

Acknowledgements

We thank J. den Hartog and F.W. Molson for their assistance in the development of these wetproofed catalysts. We express our thanks to W.M. Thurston for the development of an automatic mass spectrometer system for on-line analysis of deuterium in hydrogen gas streams, at near natural abundance. Only with his equipment and assistance in the analysis of thousands of gas samples has this research been feasible.

Abstract

Catalytic isotopic exchange between hydrogen and liquid water offers many inherent potential advantages for the separation of hydrogen isotopes which is of great importance in the Canadian nuclear program. Active catalysts for isotopic exchange between hydrogen and water vapour have long been available, but these catalysts are essentially inactive in the presence of liquid water. New, water repellent platinum catalysts have been prepared by: 1) treating supported catalysts with silicone, 2) depositing platinum on inherently hydrophobic polymeric supports, and 3) treating platinized carbon with Teflon and bonding to a carrier. The activity of these catalysts for isotopic exchange between countercurrent streams of liquid water and hydrogen saturated with water vapour has been measured in a packed trickle bed integral reactor. The performance of these hydrophobic catalysts is compared with non-wetproofed catalysts. The mechanism of the overall exchange reaction is briefly discussed.

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RECEIVED October 10, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch007

8

Combined Electrolysis Catalytic Exchange (CECE) Process for Hydrogen Isotope Separation

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

In the preceding paper (1) a novel platinum-carbon-Teflon catalyst for efficient separation of the hydrogen isotopes in the presence of liquid water has been discussed. This paper deals with the Combined Electrolysis Catalytic Exchange (CECE) processes which use this catalyst for separating the hydrogen isotopes, namely the CECE-HWP (-Heavy Water Process) and the CECE-TRP (-Tritium Recovery Process).

The isotopic separation principles inherent in the CECE processes are:
(a) the equilibrium isotope effect in reactions of the type:

$$HD_{gas} + H_2O_{liquid} \rightleftarrows H_{2\,gas} + HDO_{liquid} \qquad (1)$$

and its isotopic analogues, and
(b) the kinetic isotope effect (2) inherent in the electrolytic hydrogen evolution reaction. There are thus two relatively large isotopic separation factors involved in these processes which, as we might expect, lead to many of their advantages, discussed later. Both separation factors favour concentration of the heavier isotope in the liquid water relative to the hydrogen gas.

The CECE-HWP is a new, yet old process, for it utilizes the same basic principles as Canada's first industrial heavy water plant operated by Consolidated Mining and Smelting Company from 1943 to 1956 at Trail, B.C. (3). The Trail process was also a combination of electrolysis and hydrogen-water exchange, but the exchange reaction had to be carried out in the gas phase because liquid water poisoned the catalyst. In the exchange column, deuterium was transferred from hydrogen to water vapour in a heated catalyst bed, and then a pair of bubble cap trays promoted deuterium exchange between the water vapour and liquid water. This sequence was repeated many times throughout the column. Heavy water produced by the Trail process was too costly because of the size and complexity of the exchange columns and the excessive energy required for the steam preheaters to repeatedly vapourize any liquid water in the gas stream. It should be noted that the catalyst beds occupied only 4 percent of the total volume of the towers.

If a catalyst could be developed that would remain active in the presence of liquid water, the need for the complex Trail-type columns could be eliminated, and packed liquid-vapour contactors could be used. Becker and co-workers (4) developed a slurry catalyst consisting of platinum on finely divided charcoal for the hydrogen liquid water exchange reaction. The exchange rate for their catalyst depended primarily on the dissolved hydrogen concentration so that the catalyst could only be used at very high pressures, 20 MPa. Low catalyst activity, high inventory of platinum and losses of the finely divided catalyst are the main reasons the process proved uneconomic.

With Stevens' invention of the wetproofed catalyst (5), it became possible to effect a very efficient deuterium exchange between hydrogen and liquid water at low pressures. This catalyst allows the very close coupling of the two exchange reactions. Preheaters and bubble cap trays become unnecessary and the exchange column can be operated at lower (ambient) temperatures where the separation factor is larger (6). Thus the volume of the column for the CECE-HWP is reduced by a factor of about 20 relative to the Trail process.

Because the wetproofed catalyst in the CECE-HWP has drastically altered the exchange column of the Trail-type process, the designation CECE will only apply to processes incorporating this type of catalyst, even though the same basic isotope separation principles apply to both.

Before discussing the CECE-HWP in more detail, it is worth mentioning that this process involves three products, H_2, D_2O and O_2, of which the first two have considerable commercial value at present. The large amount of electrical energy required to produce one kilogram of reactor grade heavy water can be offset somewhat by the value of the hydrogen, either as a chemical or as a fuel (equivalent to $\sim$20 MWh/kg D_2O). Nevertheless, it must be understood at the outset that the major disadvantage of the CECE-HWP is its relatively large specific energy requirement ($\sim$50 MWh/kg D_2O), the energy being of the highest grade and cost.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

The CECE-HWP will become increasingly more attractive for the large scale production of D_2O from natural water, to the degree that the cost of fossil fuels escalates faster than the cost of CANDU* nuclear power.

The CECE-HWP

Basic Description of the Process. In the CECE-HWP (see Figure 1) the electrolytic hydrogen, already depleted in deuterium relative to the electrolyte by virtue of the kinetic isotope effect inherent in the hydrogen evolution reaction, steadily loses most of its remaining deuterium as it moves up the catalyst column in counter-current flow with the feed water trickling down into the electrolysis cell. The water becomes enriched in deuterium according to reaction 1 as it passes down the catalyst bed. The overall deuterium profile is one in which the deuterium concentration in the water increases along the length of the column from top to bottom, while in the gas phase the deuterium concentration decreases from the bottom to top.

The dehumidifier is necessary if the depleted hydrogen gas must be dry. This unit also transfers the deuterium in the water vapour carried by the hydrogen gas to the feed water.

The scrubber between the catalyst column and the electrolysis cell serves the following functions:
(a) removes entrained electrolyte in the hydrogen gas,
(b) adjusts the humidity of the hydrogen gas to the conditions prevailing in the column, which need not be the same as those in the cell,
(c) thermostats the humidified gas to the column temperature, and
(d) transfers deuterium from the water vapour entrained in the hydrogen gas to the liquid water.
The latter function is very important since the deuterium concentration of the water vapour in the hydrogen gas stream leaving the electrolysis cell could easily be about 3 to 10 times larger than that in the water at the bottom of the exchange column. This difference is mainly dependent on the magnitude of the effective electrolytic H/D separation factor, which in turn depends on the cathode material and the operating conditions of the electrolysis cell.

Any type of electrolysis cell incorporating a separator between the anode and cathode compartments may be used in the CECE-HWP. If the cell contains a liquid electrolyte, such as 25 weight % solution of KOH, the salt of the electrolyte must be removed from the

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*CANada Deuterium Uranium

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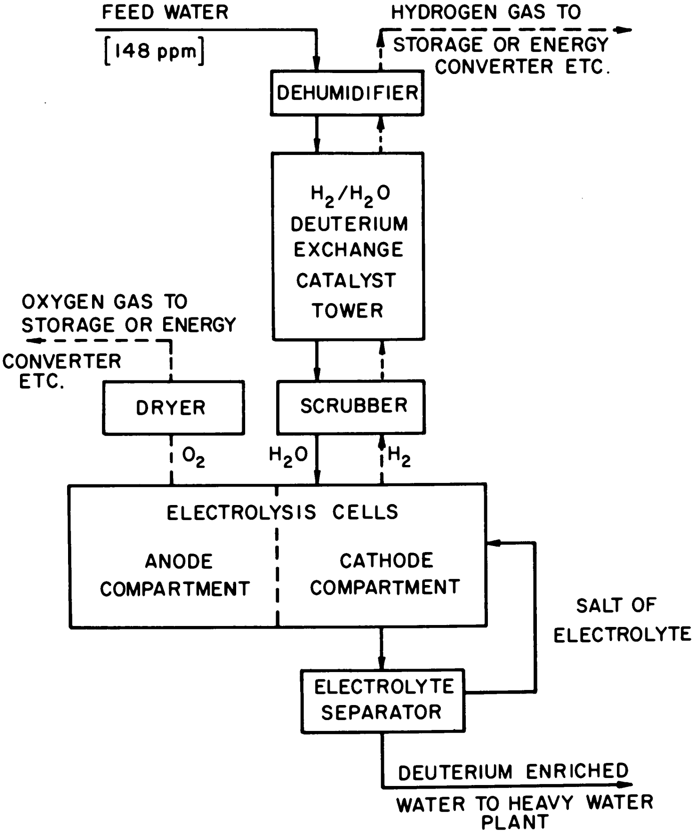

Figure 1. Combined Electrolysis Catalytic Exchange–Heavy Water Process (CECE–HWP)

product stream before it can be fed to the next higher stage. Electrolyte removal may best be accomplished by flash evaporation (7), which would also remove simultaneously the excess heat generated in the cell.

It is important to dry the co-liberated oxygen because the first stage product could easily be about 20 times richer in deuterium than the feed water at the top of the column (8), so that losses would otherwise be intolerable.

Results from Laboratory Unit. The small laboratory unit used to demonstrate the principles of the CECE-HWP consists of a catalyst column, 36 cm long and 2.54 cm in diameter, and a G.E. electrolysis module containing 2-unit cells. The apparatus is shown schematically in Figure 2. Because the G.E. electrolysis module contains a solid polymer electrolyte (SPE), the electrolyte separator (see Figure 1) is not required. The electrolysis cell was operated at a current of 2 x 20 = 40 A.

With operating conditions such that the feed water rate is adjusted to equal the electrolysis rate and no product is withdrawn (total reflux), one would expect to see a linear increase in the deuterium concentration in the cell-water circuit as a function of electrolysis time providing the following conditions pertain:
(a) the cell current remains constant,
(b) the deuterium concentrations in both the feed water and the effluent hydrogen remain constant, and
(c) there are no extraneous deuterium losses in the system.
Condition (a) is easily satisfied with a constant current power supply. The deuterium concentration in the feed water is also easy to keep constant, but that in the effluent hydrogen gas is a function of the column parameters including catalyst activity, as well as the deuterium concentration in the electrolytic hydrogen. However, the catalyst bed parameters were chosen so that the column operated at near 100% efficiency for a product concentration up to about 0.1%. This can be seen by the almost horizontal line for the deuterium concentration in the depleted hydrogen gas in Figure 3. The deviation of the deuterium build-up in the water from the theoretical line is thus mainly attributable to losses associated with incomplete drying of the oxygen gas. These losses naturally become larger as the deuterium concentration increases in the cell water.

The slope of the calculated liquid phase line in Figure 3 is a function of the volume of water in the

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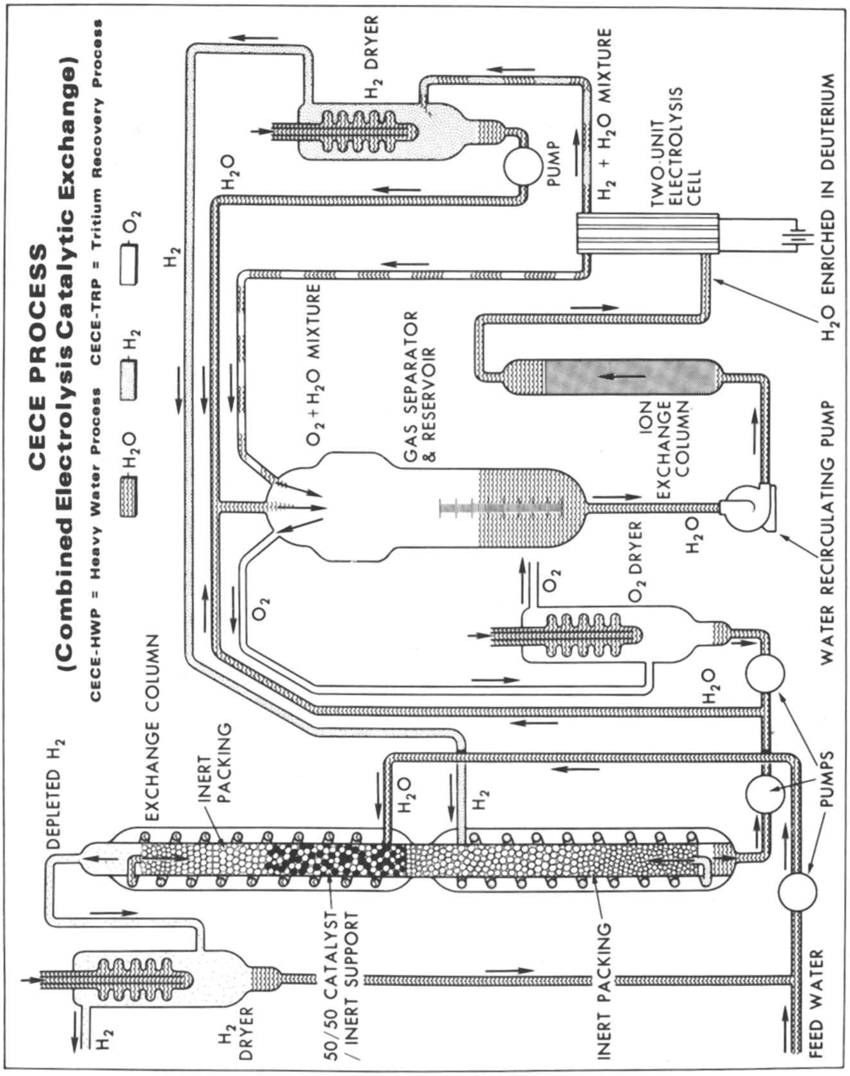

Figure 2. Laboratory CECE–HWP demonstration unit. The unit incorporates a General Electric solid polymer electrolyte electrolysis module.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

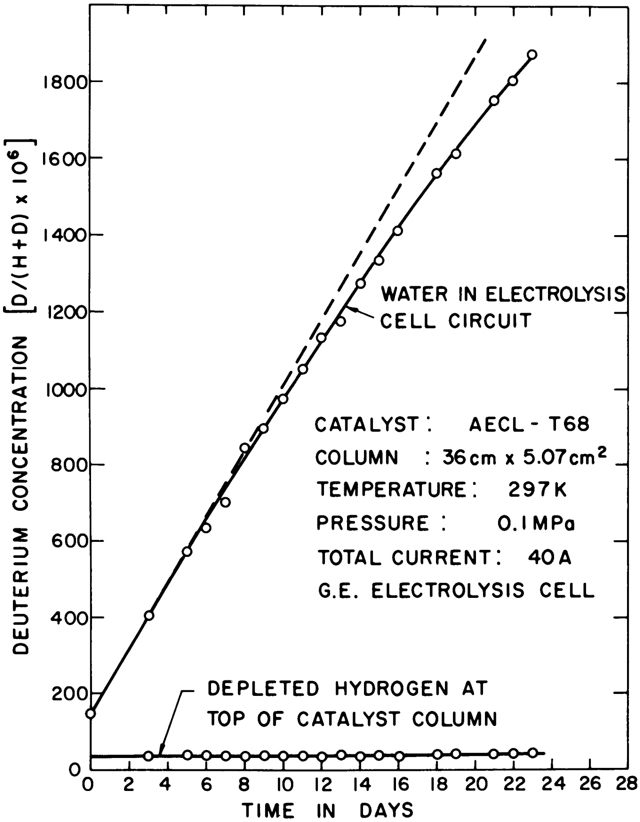

Figure 3. Deuterium concentration in the electrolysis cell water circuit as a function of electrolysis time. The feed water flow rate equals the electrolysis rate, and the product flow rate is zero. The dashed line is calculated assuming no deuterium loss from the system (see text).

cell-water circuit, the deuterium concentration in the feed water, the operating temperature of the column, and the rate of electrolysis. Thus it has no fundamental significance.

It is worth emphasizing that both the water and hydrogen linear flow rates are about two orders of magnitude smaller than the optimum flow rates for the 2.54 cm diameter column, because of the low current, 40 A, in the electrolysis cell. Linear hydrogen flow rates of 1 to 2 $m{\cdot}s^{-1}$ at S.T.P. appear optimum for efficient utilization of the novel catalyst (1) for a column operating at near atmospheric pressure. This column would require an electrolysis current of 4,365 A to 8,730 A to produce the required linear hydrogen flow rates. These figures point to the fact that the electrolysis plant will be considerably larger than the corresponding catalyst column in an optimum CECE-HWP plant.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

Deuterium Recovery. In the CECE-HWP, the theoretical fraction of the deuterium which can be recovered from the feed water is governed solely by the value of the equilibrium constant of reaction 1, and hence the temperature of the top of the column. It may be expressed in terms of the separation factor for the column, α_C, which is identical to the equilibrium constant, as follows:

$$\text{Theoretical Recovery} = \frac{D_F - D_F/\alpha_C}{D_F} \qquad (2)$$

where D_F is the deuterium concentration in the feed water.

In practice, it is prudent to choose a deuterium concentration in the effluent hydrogen gas which is about 10% larger than the calculated equilibrium value, D_F/α_C. Then catalyst requirements, which would otherwise approach infinity, are reasonable. The practical range of deuterium recoveries for the CECE-HWP will probably be in the range 66-75% corresponding to a temperature range of about 60°C to 15°C respectively. This is a high recovery for a deuterium production process (9).

Synergistic Effects. Several synergistic effects result from combining electrolysis with H_2/H_2O deuterium exchange relative to either cascaded conventional electrolysis alone or cascaded H_2/H_2O exchange alone. In the latter case, a bithermal exchange process must be used, similar in principle to the present Girdler-Sulphide (GS) process (9) based on the H_2S/H_2O exchange reaction.

The synergistic effects of the CECE-HWP are summarized in Tables I and II.

In Table I, electrolysis alone, operating as an ideal cascade, is compared to electrolysis in the CECE-HWP assuming the electrolytic H/D separation factor, α_E, is 6 for both. This value is certainly attainable in practice. For example, the electrolytic heavy water Upgrading Plant at CRNL has operated for several years with an effective α_E of 8 to 9 at cell temperatures from 35°C to 25°C respectively. However, these cells incorporate mild steel cathodes and operate at lower temperatures than is the current practice in commercial cells. Since the trend is towards higher operating temperatures and other cathode materials*, including precious metals, an α_E of say, 3, might be more realistic in the future. Any value of α_E less than 6 would, of course, increase the differences in Table I.

The factors which lead to a reduction in catalyst requirements for the CECE-HWP versus the bithermal H_2/H_2O-HWP are tabulated in Table II. Since the specific catalyst requirement (amount of catalyst required per unit of D_2O production per unit of time) is directly proportional to the gas flow rate but the deuterium production is directly proportional to the liquid flow rate, increasing the L/G ratio (L and G are the molar water and gas flow rates respectively) decreases the catalyst requirement directly. Data in Table II serve to illustrate the effects of the different parameters on the catalyst volume for a given D_2O production rate and are not necessarily optimum values.

For the bithermal H_2/H_2O-HWP, the deuterium recovery is limited by the difference in the practical cold and hot column temperature attainable, since it is based on the temperature coefficient of α_C. For a given deuterium concentration in the feed, the specific volume of water which must be processed per unit of D_2O produced is directly dependent on the recovery.

The third parameter which is compared in Table II is the number of transfer units (N.T.U.) required for a deuterium concentration in the product of 0.1% [1000 ppm D/(H+D)] when α_E = 6, and the feed water contains 148 ppm deuterium, which coincides with the Great Lakes waters (10). The specific catalyst volume for a given catalyst is directly dependent on the N.T.U.'s (9). It is important to point out that only

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*Iron or mild steel cathodes yield the largest α_E values for a given set of operating conditions relative to other metals.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

Table I

SYNERGISTIC EFFECTS OF THE CECE-HWP

Conventional Electrolysis (Ideal Cascade) Compared to Electrolysis in the CECE-HWP

	Parameter	Ideal Cascade	CECE-HWP	Remarks
1.	Reflux, n_E	1.7	1.0	∿70% reduction in energy costs
2.	No. of Stages	∿17	3	Less complicated plant
3.	α_E	Size of electrolysis plant directly dependent on α_E	Size of electrolysis plant not affected	Catalyst volume increases somewhat as α_E decreases

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Table II

SYNERGISTIC EFFECTS OF THE CECE-HWP

Reduction in Catalyst Requirements for the CECE-HWP versus the Bithermal H_2/H_2O-HWP

Parameter	Bithermal H_2/H_2O-HWP	CECE-HWP	Catalyst Reduction Factor	
L/G	0.43	1	2.3	∿15
% Recovery	∿33	∿66	2	
N.T.U. for 1000 ppm	12.3*	7.4	1.66	
Pressure	7 MPa	∿1 MPa	∿2	
Electrolytic Separation	Nil	$\alpha_E = 6$	1.6‡	
∴ TOTAL REDUCTION FACTOR			∿24	

*Calculated only for the cold column

‡The N.T.U.'s for the CECE-HWP are reduced by this factor since the deuterium concentration in the column liquid product needs only be = 265 ppm instead of 1000 ppm if α_E is 6 instead of unity.

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

catalyst for the cold column in the bithermal process is considered here. Additional catalyst would of course be required for the hot column in the bithermal process but not in the CECE-HWP. On the other hand, electrolysis cells are required in the CECE-HWP.

The bithermal process must operate at high pressures to avoid an excessively large hot column as a result of the vapour load at the hot column temperature (∿$200^{o}C$). On the other hand, the catalyst column in the CECE-HWP could operate at about atmospheric pressure, although 1 to 2 MPa may be preferable in the 1st stage. Several pressure effects combine to produce the approximate factor shown in Table II.

Assuming for the moment that α_E is unity, a value which would be approached in a high temperature (≃$1000^{o}C$) electrolysis cell, the catalyst requirements for the CECE-HWP would be about 15 times less than that for only the cold column of the bithermal H_2/H_2O-HWP. If α_E is 6, the overall catalyst reduction factor is approximately 24. In the above analysis, the 2nd and 3rd stages have been ignored. This is justifiable since these stages would together require only 10% additional catalyst or less depending on the deuterium concentration of the 1st stage product (8).

Applications of the CECE-HWP and CECE-TRP

The development of both the CECE-HWP and the CECE-TRP is based mainly on about 7 years of laboratory research (1). The results from this work have led to commitments of small pilot plants for both processes. The CECE-HWP pilot plant will be located at Chalk River Nuclear Laboratories (CRNL). The CECE-TRP pilot plant is a cooperative project between CRNL and the Energy Research and Development Administration (ERDA) of the U.S. Government, and is located at the Mound Laboratory, Miamisburg, Ohio. Preliminary results from the Mound pilot plant have been reported by Rogers et al. (11).

Despite the success achieved in the catalyst development program, we have not yet prepared a platinum-carbon-Teflon catalyst (1) with sufficient activity to make a full scale bithermal H_2-H_2O heavy water plant economically feasible. With our present catalysts the amount required would be too large. Furthermore, a satisfactory hydrophobic catalyst for the hot column has not been developed. Our present catalysts are sufficiently active, however, to perform effectively in the CECE-HWP where the catalyst requirements are relatively small, only about 4% of that required in the cold column of a bithermal plant. Several small scale

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

applications of the CECE-HWP and the CECE-TRP that could now be used in the nuclear power industry are outlined below.

(1) Upgrading of D_2O - The heavy water used in CANDU reactors as moderator and coolant that has become downgraded with light water can be re-enriched to reactor grade, 99.8% D_2O, by the CECE-HWP.

(2) Final Enrichment Stage for GS Plants - The GS system produces 10-20% D_2O which is currently enriched to reactor grade by water distillation. This could be done more effectively by the CECE-HWP.

(3) Recovery of Tritium from the D_2O in CANDU Reactors - Tritium builds up in the heavy water during the operation of CANDU reactors. The recovery of this tritium would reduce the radiation field in some areas of the power station and its removal may become an environmental necessity. Tritium may also become a saleable commodity for the development of experimental nuclear fusion reactors.

(4) Tritium Recovery from Light Water - Tritium can be recovered from light water wastes from ERDA contractors in the U.S.A. As already noted, pilot studies of this application are being made at the Mound Laboratory (11). This application will also be required in nuclear fuel reprocessing plants since tritium is a product of the fission process.

The disadvantage of the high energy requirement for the full scale production of heavy water by the CECE-HWP does not apply to these applications, primarily because of the much smaller liquid flows.

For the CECE-HWP applications 1 and 2, the overall separation required is considerably less (enrichment factor of $\sim$10) than that required to produce pure D_2O from natural water (enrichment factor $\sim$7000). Thus the electrolysis energy required is reduced by a factor of about 700 from 50 MWh to 70 kWh per kilogram of D_2O.

For the CECE-TRP applications 3 and 4, the water flows will be at least a thousand times smaller than for a full scale heavy water plant. Furthermore, the energy requirements for the CECE-TRP are smaller than for other processes currently being considered, such as water and hydrogen distillation, because the separation factors are larger.

Larger scale applications of the CECE-HWP, if pilot plant studies warrant these, would include:

(1) Small D_2O Plant - A small ($\sim$70 Mg/a) complete D_2O plant would be economically feasible where a market exists for the electrolytic hydrogen and the heavy water.

(2) Simultaneous D_2O and Peak Power Production - The CECE-HWP could be coupled with either H_2/O_2 gas turbine-

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

generators or fuel cells through appropriate H_2 and O_2 storage facilities to produce D_2O (during the off-peak periods) and peak power. This load levelling scheme (8) is being considered by Ontario Hydro, Canada's largest electric utility, as one alternative for their future load-levelling requirements.

(3) Electrolytic H_2 as Natural Gas Supplement or Chemical - It might be feasible to use excess hydro electric power, wherever it exists, to produce hydrogen and D_2O using the CECE-HWP. The hydrogen could be used as a natural gas supplement in a pipeline and a feasibility study of a 100 MW prototype plant is underway. Alternatively the hydrogen could be used as a chemical, e.g. hydrogenation of bitumen or chemical intermediate, e.g. methanol production which could serve as a gasoline supplement.

All of the above potential applications must await pilot plant studies before plants can be committed. Furthermore, the relative economics of electrolytic hydrogen versus hydrogen produced from fossil fuels will play a major role in any decision to proceed in each of these applications. The current value of the D_2O by-product will also be important and to a lesser extent, the value and marketability of the co-liberated oxygen. It need hardly be said that successful development of efficient, relatively low cost electrolyzers is also a key requirement for these larger applications. Moreover, current emphasis to conserve all our non-renewable resources will increase the stimulus to develop the CECE process over the next decade or so. When fossil resources become sufficiently scarce, and/or expensive, the move towards a hybrid hydrogen-electric economy will be accelerated and consequently larger amounts of by-product heavy water could be produced by the CECE-HWP.

Summary

The CECE process is a very efficient method for the separation of hydrogen isotopes. The catalytic exchange columns where most of the separatory work is accomplished would be very small compared to the exchange column used in either a bithermal H_2/H_2O process or the present bithermal H_2S/H_2O (GS) process. Laboratory studies have demonstrated the salient features of the CECE process and if pilot plant studies at CRNL and Mound Laboratory are successful, the process will undoubtedly be used in the nuclear power industry in a number of the small scale applications discussed in this paper. As large hydrogen gas streams become

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

available the process could also be used for the full scale production of large quantities, 70-100 Mg/a, of heavy water.

Acknowledgements

We thank A.S. Denovan for technical assistance in operating the laboratory demonstration unit of the CECE process and for performing the deuterium analyses in gas and water samples. We also thank W.M. Thurston and M.W.D. James for constructing and maintaining the mass- and infrared-spectrometer systems used for the deuterium analyses.

Abstract

Hydrogen isotopes can be separated efficiently by a process which combines an electrolysis cell with a trickle bed column packed with a hydrophobic platinum catalyst. The column effects isotopic exchange between counter-current streams of electrolytic hydrogen and liquid water while the electrolysis cell contributes to isotope separation by virtue of the kinetic isotope effect inherent in the hydrogen evolution reaction. The main features of the CECE process for heavy water production are presented as well as a discussion of the inherent positive synergistic effects, and other advantages and disadvantages of the process.

Several potential applications of the process in the nuclear power industry are discussed.

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RECEIVED October 18, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch008

9

Heavy Water Distillation

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch009

The motivation for the current heavy water research program at Ontario Hydro comes from our growing dependence on CANDU-based nuclear power plants. About 15% of the capital cost of these plants is for the heavy water moderator and coolant. We hope to be able to provide economically and technically viable options for heavy water production in the 1990's by developing alternative production methods to an industrially useful degree by that time.

The Heavy Water Group at Hydro Research Division has assisted in establishing the scientific feasibility of two heavy water production methods: laser-induced dissociation of formaldehyde, and low-temperature water distillation using waste heat and hopes to continue development of both these methods.

In this talk, I will describe the experiments carried out to demonstrate the feasibility of low-temperature distillation with a parallel-sheet packing developed at the Research Division. The cost environment of heavy water distillation will also be discussed.

Distillation Systems - Physical

To refresh your memory, I will show in Figure 1 (a) a schematic representation of a distillation system. The main features of the system are upward moving vapour streams and falling liquid films in close proximity, maintained by a temperature gradient between the heat source (boiler) at the bottom and the heat sink (condenser) at the top of the system. A convenient way of bringing the counter-flowing phases close to each other is to provide vertical sheets of material over which the liquid flows as a thin film, while the vapour rises in narrow channels between the sheets, as shown in Figure 1(b).

What makes a heavy water system "different" is that the component to be separated out, HDO, is present in very low concentration, about one part in 3500, in natural water fed to the system, so that enormous volumes of vapour must be passed through the separating system to extract sufficient HDO.

Cost Components. From our estimate (and those of many prior workers) of the cost of heavy water from a distillation plant, if we were to pay for fossil fuels, or if we used the heat from a nuclear reactor which would otherwise be generating electricity, the cost of this energy would itself amount to well over the current cost of heavy water.

Since thermal generating stations are only about 40% efficient in converting the thermal energy released from fuel into electricity, ~60% of it is available as low grade heat (water at about 26°C) costing only the price of transporting it to the point of use.

Our objective, then, has been to utilize this waste heat, by operating between about 26°C and the lake water temperature which is typically 20° lower. If we can utilize waste heat, then the remaining high-cost components are the material, or packing, used to bring the liquid and vapour into close proximity, the structures (vacuum buildings) used to house the packing, and the heat exchangers and boilers for maintaining the flow of heat through the system. The relative magnitudes of these components, based on D_2O at $200/kg is shown in Figure 2. The greatest cost component, by far, is the packing for the columns.

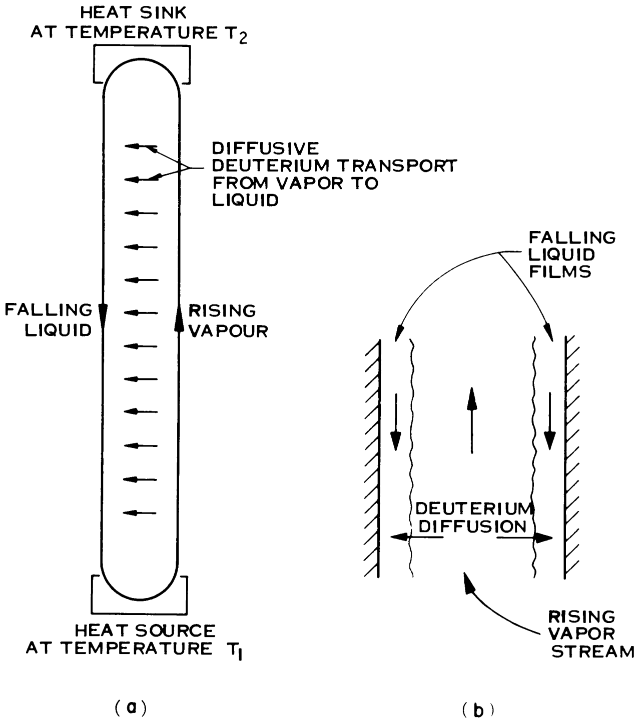
400 Ton Plant Conception

Figure 3 shows our present conception of a low-temperature distillation plant capable of producing 400 tons of heavy water per year. It is divided into several hundred units housed in separate towers, each operating independently to distill the heavy water out of clean lake water and bring it to a concentration of about 1%. The subsequent concentration step to 99.8% for reactor use costs only 15% to 20% that of performing the first step, and is carried out in a separate distillation "finishing" unit.

Experimental Packing

The major gap in the plant concept was the packing. Heavy Water distillation packings for the low-tempera-

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch009



(a) (b)

Figure 1. Elements of a distillation system

COMPONENT	RELATIVE COST $/kg D_2O
WASTE HEAT	6.5
COOLING	20
VACUUM BUILDINGS AND PLUMBING	5.5
CONDENSERS AND BOILERS	14
PACKING AND SUPPORTING STRUCTURES	96
OPERATION AND MISCELLANEOUS *	58
	200

* WATER CLEANUP, INSTRUMENTATION, CONSTRUCTION LABOR, COMMISSIONING

Figure 2. Relative component costs in heavy water distillation

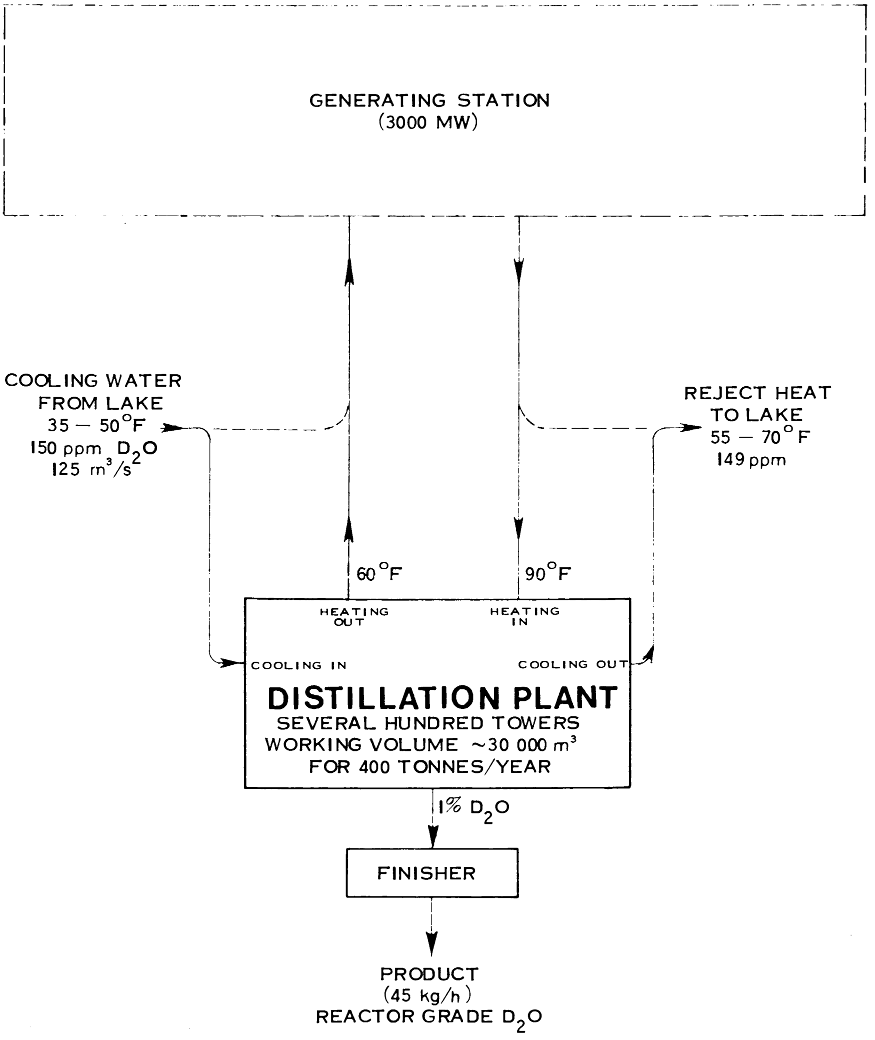


Figure 3. Concept for a heavy water distillation plant using waste heat from a generating station. 400 tonne/year D_2O plant.

ture and pressure regime had not been developed commercially. A theory of the process predicted that a useful degree of separative power could be achieved using simple parallel sheets carrying downward-moving water films, with upward-moving vapour between them. The packing developed at the Research Division is based on this concept, and is shown schematically in Figure 4. A series of tubes carries condensed water to the tops of the sheets to flow downward over their surfaces, while vapour moves up between them. The sheets used to date have been nylon fabric under tension, with a surface treatment to improve the uniformity of the water film. The performance of this module is expected to depend on the two mass and deuterium flow parameters, the velocity, and the diffusion time in each phase.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch009

Packing Performance - Experimental

The basic mechanism which causes isotopic separation in distillation systems is the difference in vapour pressure of H_2O and HDO, at the same temperature. In distillation, the ratio of the equilibrium vapour pressures of H_2O and HDO is called α, as shown in Figure 5.

$\alpha(T) = \frac{P_{H_2O}}{P_{HDO}}$, typically, α is around 1.08 in this temperature region, rising at lower temperatures towards 1.10.

We can gauge the performance by measuring the isotopic enrichment of the water flowing out the bottom C_{Bottom}, the depletion of the vapour leaving at the top C_{Top}, taking the natural logarithm of their ratio and dividing by the natural logarithm of the average α value for the system; this is a measure of the number of stages, each carrying out a separation of α, in the column. The number of such stages per metre of column height is a performance parameter for the packing:

N(number of stages/m) $\approx \ln\left(\frac{C_{Bottom}}{C_{Top}}\right)/H\ln\alpha$, where H is the column height.

Current experimental values of N run from 2.5 to over 3 stages per metre.

Using this parameter, and the corresponding mass flow rate, we can estimate the total surface area of the sheets required to produce 400 tons of D_2O per year. The figure also shows the "earning power" of our experimental packing and the theoretical limit to it as a function of the F-number (related to the mass

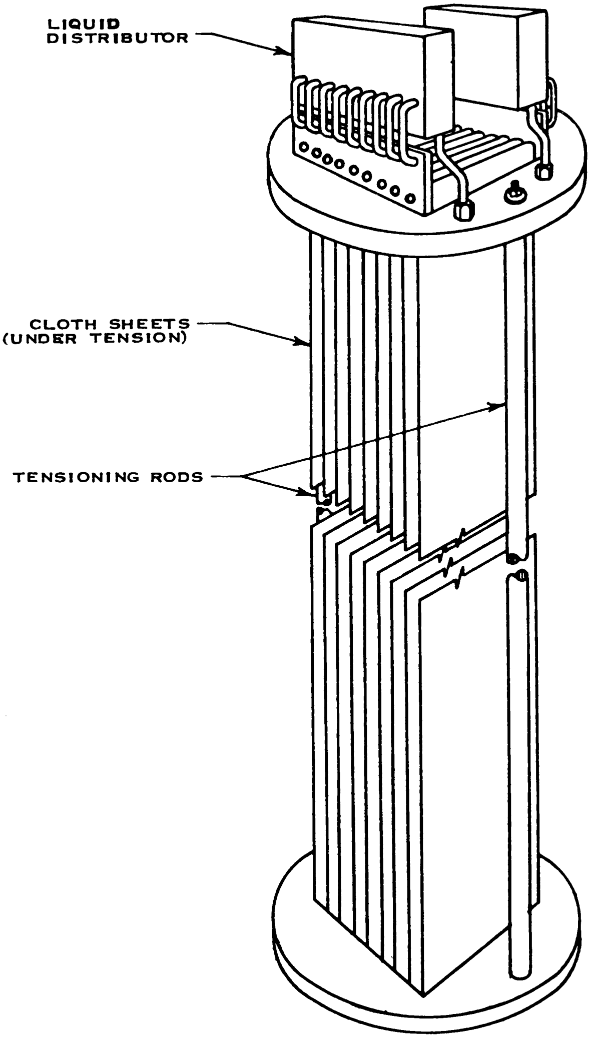


Figure 4. Parallel plate packing module (without glass envelope)

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch009

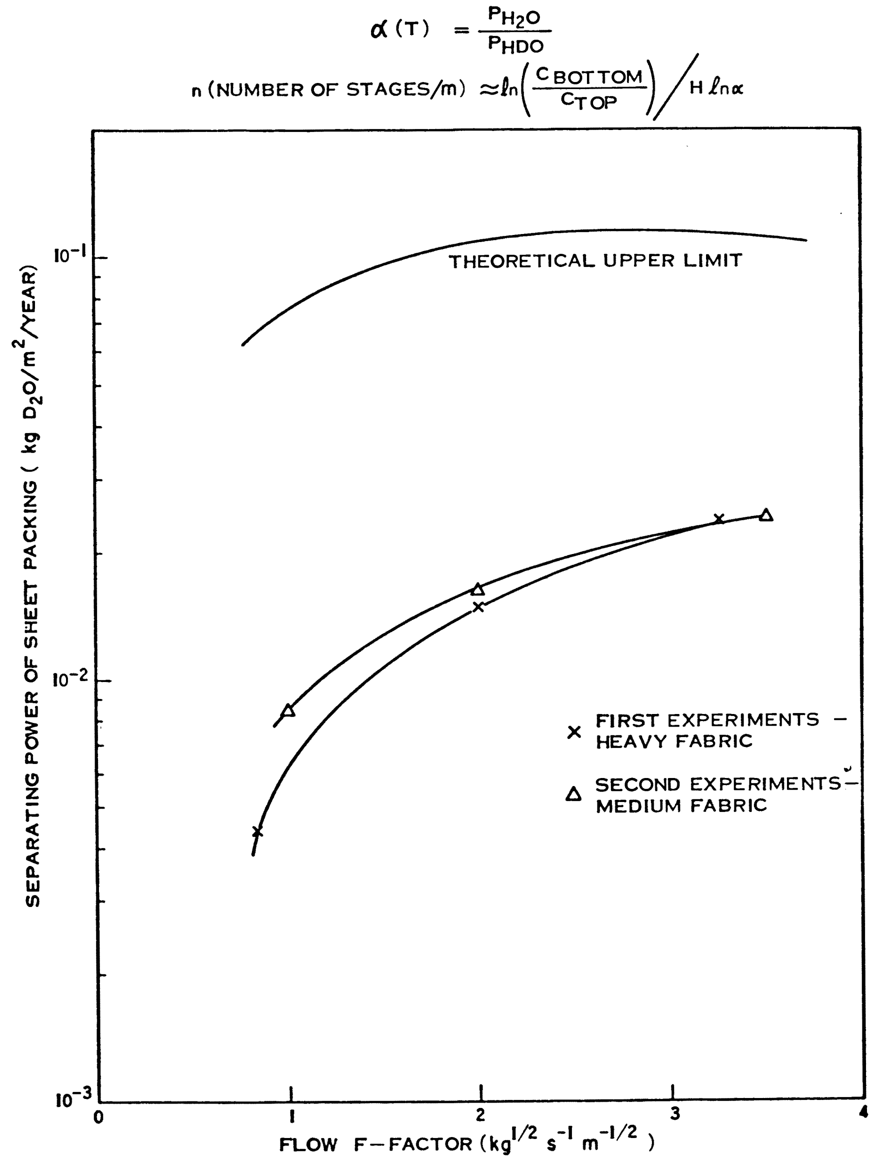


Figure 5. Earning power of two experimental packings

flow) in the system. Each square metre of packing can be considered to produce about 0.2 kilograms (~40 dollars worth) of D_2O per year. The upper curve is the predicted maximum earning power for this type of packing system. As you can see, our results while showing that the system works, can still be considerably improved. The triangles show more recent work with a different material; as our understanding of the desirable and undesirable features of these materials grows, we believe we can come still closer to the theoretical limit. This would bring our heavy water cost estimate down towards $200/kg. Further work on a larger scale would also be required to study how well the packing unit can be scaled up to an industrially useful size.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch009

Summary

I can summarize what we have learned as follows: recent work at the Research Division has demonstrated the feasibility of performing heavy water separation by distillation at low temperature, using a newly developed packing system. We believe that the current performance can be considerably improved, and that the cost of heavy water from distillation can be made comparable to that from the current production method. Tests on a larger scale will be required to demonstrate that this performance can be successfully scaled up to an industrially useful degree.

Abstract

A review of distillation as a heavy water separation method has identified areas of high cost: energy and packing material. At temperatures around 25°C, large amounts of energy are available as waste heat from thermal generating stations. If a suitable low-cost packing can be developed for use in this temperature region, distillation could become economically competitive.

Results of theoretical packing work, and experiments on a prototype packing for heavy water plants are discussed.

RECEIVED August 30, 1977

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Deuterium Isotope Separation via Vibrationally Enhanced Deuterium Halide–Olefin Addition Reactions

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

Over the past few years, there has been much excitement in the scientific community about the prospects for efficient separation of isotopes, particularly uranium-235 and deuterium, using laser techniques. Of the various laser methods which have been suggested, those which involve the use of IR photons to enhance the rate of isotopically selective photochemical reactions have received much attention, and this paper discusses one example--vibrationally enhanced gas phase deuterium halide addition into olefins. The incentive for using IR photons is clear; to quote from a recent review article (1): "The attractive feature of vibrational photochemistry for isotope separation is the promise of using low energy IR photons from an efficient molecular laser to get a good yield of product. Since 1 mole of photons at 3000 cm^{-1} is 10^{-2} kwh and some IR lasers are about 10 per cent efficient, processing of bulk chemicals might even be economic." Thus, a deuterium separation process with 1% quantum efficiency that utilized 2000 cm^{-1} photons from a 10 per cent efficient CO laser would require a laser process energy of 6.6 kwh/mole D, equivalent to a laser operating cost of 13¢/mole D $\equiv$ \$13/kg D_2O, assuming electricity at 20 mills per kwh. The specific laser capital investment, assuming a price of \$20 per optical watt of 10 per cent efficient laser power, would be roughly \$152/kg D_2O/yr., equivalent to approximately \$30/kg D_2O at a capital charge rate of 20 per cent/year. To put these numbers in perspective, we note that the current Canadian price for heavy water made by the H_2S/H_2O exchange (G-S) process is about \$150/kilogram, of which 60 per cent is due to capital charges, 25 per cent due to energy, and 15 per cent for operations and maintenance (2). Since heavy water is a much cheaper commodity than U-235, this approximate calculation illustrates the challenge in developing a laser deuterium separation process which is economically competitive with the existing technology (3).

In this paper we illustrate the problems and prospects involved by examining in some detail a specific deuterium separation process based on deuterium halide-olefin addition reactions. In Section II we describe the basic reaction mechanism, with particular attention to the problem of exciting the deuterium halide with existing lasers. Section III is devoted to the crucial question of the expected effectiveness of vibrational excitation for this class of reactions. In Section IV, we focus on the "back-end" of this separation scheme in the context of a possible flow-sheet for the overall process. We conclude with a summary of our results and the implications thereof in Section V.

II. Hydrogen Halide-Olefin Addition Reactions

An ideal isotopically selective laser photochemical process would use a single IR photon to excite the fundamental mode of the isotopic molecule of interest, followed by a gas phase, vibrationally-enhanced bimolecular reaction, leading to an isotopically enriched reaction product which could easily be separated. A primary consideration in the choice of reaction is the activation energy. It must be high enough to minimize the (thermal) reaction rate in the absence of vibrational excitation, but low enough so that the reaction rate of the vibrationally excited species exceeds the rate of scrambling reactions, e.g., V-V and V-T energy transfers, which lead to the loss of isotopic selectivity. In this section we discuss a class of reactions, deuterium halide-olefin additions, with thermal equilibrium activation energies in the range 15-40 kcal/mole.

The initial step of this process involves sequential absorption of several quanta near 5 microns from a pulsed CO laser to excite DBr or DCl up their vibrational ladders to the $v \geq 3$ vibrational level. Alternately, a pulsed DF laser near 4 microns can sequentially excite DF or HDO to $v \geq 3$. In pure DX, collisions of the type $DX(v = 1) + DX(v = 1) \rightarrow DX(v = 2) + DX(v = 0)$ can also excite higher vibrational levels, but this mechanism is not feasible in natural HX containing only 0.015% DX. The vibrationally excited DX molecule (X = Br, Cl, F, OH) then will preferentially react with unsaturated hydrocarbons (for example, DBr reacting with ethylene) to yield a deuterium-tagged addition product, e.g., ethyl bromide-d_1. These steps may be written

$$DX + nh\nu \rightarrow DX^* \ (v{=}n) \qquad n \geq 3 \qquad (1)$$

(pulsed CO or DF laser excitation)

$$DX^* + R_1R_2C{=}CH_2 \rightarrow R_2-C(R_1)(X)-CH_2D \qquad (2)$$

$(R_1, R_2 = H, CH_3, CH{=}CH_2, \text{etc.})$

This type of addition reaction into unsaturated hydrocarbons in the gas phase occurs by a homogeneous, bimolecular, four- or six-center process (4,5). Both the forward reaction (2) and the reverse reaction (unimolecular elimination of HX) have been very well studied in the gas phase(6,7). Kinetic parameters for the gas phase thermal addition reaction are well represented by the Arrhenius rate expression

$$k(\text{sec}^{-1}) = [C]\cdot Ae^{-E_a/RT} \qquad (3)$$

where $[C]$ = olefin concentration (moles/liter)
A = frequency factor (liter/mole•sec)
E_a = thermal activation energy (kcal/mole)

Arrhenius parameters for HX addition into simple and conjugated olefins are given in Table I, which illustrates the variation of activation energy E_a and frequency factor A, according to the choice of reagents.

Examination of Table I reveals that activation energies in the range 10-50 kcal/mole are available, depending on the choice of reagents. Lowest activation energies occur for HI addition with increasing activation energy for lighter HX, such that $E_a(HI) < E_a(HBr) < E_a(HCl) < E_a(HF) < E_a(H_2O)$. Table I also shows that activation energy decreases with increasing substitution, with E_a decreasing by about 5 kcal/mole per methyl ($-CH_3$) group and by about 9 kcal/mole per vinyl ($-CH{=}CH_2$) group on the α- or halogen-receiving carbon atom. Among C_4 olefins, 2-methylpropene and 1,3-butadiene have nearly identical activation energies, but 1,3-butadiene is a far superior reagent choice because of its approximately 200-fold higher frequency factor (A value).

Although HI has the lowest activation energies for reaction, it is probably not an acceptable choice in a large scale process because of its tendency to decompose. HF and H_2O are probably relatively unattractive, since they have significantly higher activation energies; this leaves HBr or HCl as the most likely reagent choice. Also, use of HF or H_2O would require excitation by a DF chemical laser, which is an inherently more expensive and less efficient device than the CO laser, primarily due to the cost of regenerating the fluorine. The CO laser is an efficient, well-developed device (11) which is quite suitable for a large-scale industrial process.

To evaluate the suitability of the CO laser for excitation of DBr or DCl, a computer comparison was made of the calculated wavelengths of CO emission lines and DBr or DCl absorption lines. For these diatomic molecules, accurate frequencies may be generated from a Dunham equation for the energy levels:

$$E(V,J) = \sum Y_{k\ell}\left(V+\tfrac{1}{2}\right)^{k} J^{\ell}\left(J+1\right)^{\ell} \qquad (4)$$

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

TABLE I

Arrhenius Parameters for HX Addition to Olefins: X = I, Br, Cl, F, OH

Unsaturated Hydrocarbon	Frequency Factor[a] $\text{Log}_{10}A$	Activation Energy E_a (kcal/mole) HI	HBr	HCl	HF	H_2O
ethylene[b]	8.3[c]	28.5	34	40	50	57
propylene[b]	7.9[c]	23.5	28.5	34	45	52
2-methylpropene[b]	6.5[c]	18.5	23.5	28	41.5	49
Phenylethylene[b]	7.4[d]	20	24	30	38	--
1,3-butadiene	8.8[e]	18.7[e]	24[i]	29[g]	--	--
2-methyl-1,3-butadiene	8.4[f]	15[f]	20[i]	26[g]	--	--
1,3-pentadiene	7.7[h]	14.7[h]	20[i]	25[g]	--	--
2-methyl-1,3 pentadiene[i]	7.4[j]	11	16	21	--	--
4-methyl-1,3-pentadiene[i]	6.3[j]	10	15	20	--	--

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[a] Units of A are liters•mole^{-1}•sec^{-1}. $\text{Log}_{10}A$ is constant ± 0.3 for all HX compounds.

[b] E_a values from Reference 6.

[c] Reference 4.

[d] Computed from A of back reaction. See Reference 7.

[e] Reference 8.

[f] Computed from kinetic data of Reference 5.

[g] Computed from kinetics of back reaction. See Reference 9.

[h] Reference 10.

[i] Estimated E_a value. Probable accuracy: ± 2 kcal/mole.

[j] Estimated value for $\text{Log}_{10}A$. Probable accuracy: ± 0.4.

For normal and isotopic carbon monoxide, the coefficients $Y_{k\ell}$ yield computed emission frequencies accurate to 0.001 cm^{-1} (Ref. 12) or even a few megahertz (13). For $D^{35}Cl$, directly measured values for the $Y_{\ell k}$ were available (14). For $D^{37}Cl$, the $Y_{k\ell}$ were computed from $D^{35}Cl$ using the Dunham isotope relations (15) and the appropriate atomic reduced masses (16). For $D^{79}Br$ and $D^{81}Br$ the earlier reported absorption frequencies (17) were not sufficiently accurate. Therefore, accurate $Y_{k\ell}$ were generated for HBr using the accurate rotational constants (18) and recent higher level vibrational constants (19). The appropriate reduced masses (16) and Dunham isotope relations (15) then were used to derive all $Y_{k\ell}$ except Y_{10} for $D^{79}Br$ and $D^{81}Br$. Y_{10} was then fixed by requiring the computed 1-0 band to be 0.25 cm^{-1} higher than its measured value (17), according to the correction suggested in Ref. 20.

The derived Dunham coefficients for DCl and DBr thus provided calculated absorption line center frequencies for a computer search to find near-coincidences with CO laser emission frequencies. For each near coincidence, the absorption coefficient was computed using a standard Lorentz line shape formula, equation (5), which also included the temperature dependence of the rotational level population:

$$\alpha(\Delta\nu) = \frac{Km\ e^{-\beta m(m+1)/kT}}{1 + \ (\Delta\nu/0.5\gamma P)^2} \qquad (5)$$

In equation (5), $\alpha(\Delta\nu)$ is the absorption (in cm^{-1}) at a distance $\Delta\nu(cm^{-1})$ from DX line center at a pressure of P atmospheres. The values for the pressure-broadened linewidth $\gamma(cm^{-1}\ atm^{-1})$ depend on rotational number m, and were taken from Ref. 21 for DCl broadening by HCl. The rotational number is m = J-1 for R-branch and m = J for P-branch transitions. DBr values for γ were derived from the reported values for HBr(22). The parameters K and β in equation (5) were adjusted to match the reported DCl absorption line strengths(23), and DBr values for K and β were derived from the HBr values (22) by assuming $K(DBr) \cong 1/4\ K(HBr)$ and $\beta(DBr) \cong 2\ \beta(HBr)$, assumptions found to be reasonable for the DCl/HCl data (23).

Equation (5) thus permits reasonably accurate estimation of absorption in the 1-0 band of DCl and DBr by CO laser lines. Absorption strength of the higher vibrational bands (2-1 through 5-4 in this study) will increase approximately proportional to v (Ref. 24), but decrease due to the distribution of population over the several levels. As a first approximation, absorption strength for higher vibrational bands was thus taken to be the same as the 1-0 band.

Tables II and III summarize the computed absorption of $^{12}C^{16}O$ laser emission lines by the various isotopes of DCl and DBr. Data for Tables II and III were computed for atmospheric pressure and room temperature (298°K), and illustrate the ease

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

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TABLE II

ABSORPTION OF $^{12}C^{16}O$ LASER LINES BY $D^{35}Cl$ and $D^{37}Cl$, at P=1 ATM.

DCl Transition* • $\nu(cm^{-1})$	$^{12}C^{16}O$ LASER LINE	$\nu_{DCl}-\nu_{CO}(cm^{-1})$	ABSORPTION COEF. (cm^{-1})
1-0 $P(7)_{35}$ 2011.041	5-4 P(7)	-0.049	11.8
1-0 $P(3)_{37}$ 2055.146	3-2 P(9)	-0.012	5.4
1-0 $P(7)_{37}$ 2008.282	3-2 P(20)	-0.138	1.4
1-0 $P(4)_{35}$ 2046.609	3-2 P(11)	-0.349	1.1
2-1 $P(2)_{35}$ 2016.033	2-1 P(24)	0.007	12.6
2-1 $P(11)_{35}$ 1909.678	6-5 P(25)	-0.001	5.1
2-1 $P(4)_{37}$ 1991.114	5-4 P(12)	0.090	3.0
2-1 $R(3)_{35}$ 2077.340	2-1 P(10)	0.201	2.9
3-2 $P(2)_{35}$ 1963.140	7-6 P(6)	0.058	8.7
3-2 $P(11)_{35}$ 1858.853	10-9 P(13)	-0.044	3.6
3-2 $P(6)_{35}$ 1918.799	7-6 P(17)	-0.179	3.4
3-2 $P(2)_{37}$ 1960.514	4-3 P(25)	0.103	1.7
4-3 $P(5)_{35}$ 1878.238	10-9 P(8)	-0.017	18.5
4-3 $R(5)_{35}$ 1986.873	5-4 P(13)	-0.037	15.2
4-3 $P(2)_{35}$ 1910.507	7-6 P(19)	-0.024	11.8
4-3 $P(3)_{37}$ 1897.518	7-6 P(22)	-0.101	2.3
5-4 $P(7)_{35}$ 1804.358	12-11 P(14)	0.026	14.4
5-4 $P(1)_{35}$ 1868.160	9-8 P(17)	0.034	6.0
5-4 $R(2)_{37}$ 1903.939	9-8 P(8)	0.058	3.7

* Subscript 35 or 37 refers to $D^{35}Cl$ or $D^{37}Cl$ transitions, respectively.

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TABLE III

ABSORPTION OF $^{12}C^{16}O$ LASER LINES BY $D^{79}Br$ and $D^{81}Br$ at P=1 ATM.

DBr TRANSITION*	$\nu(cm^{-1})$	$C^{12}C^{16}O$ LASER LINE	$\nu_{DBr}-\nu_{CO}(cm^{-1})$	ABSORPTION (cm^{-1})
1-0 $R(2)_{81}$	1863.999	9-8 P(18)	0.011	3.2
1-0 $R(3)_{79}$	1872.378	8-7 P(22)	0.048	2.5
1-0 $P(9)_{79}$	1757.851	14-13 P(13)	-0.044	2.1
1-0 $P(3)_{81}$	1813.573	11-10 P(18)	0.057	1.9
2-1 $R(6)_{81}$	1847.163	9-8 P(22)	0.046	3.0
2-1 $P(8)_{81}$	1722.606	16-15 P(9)	0.003	3.8
2-1 $R(9)_{79}$	1867.966	8-7 P(23)	-0.032	2.0
2-1 $P(9)_{79}$	1713.497	15-14 P(18)	-0.046	2.0
3-2 $P(6)_{81}$	1696.517	16-15 P(16)	0.008	4.3
3-2 $R(2)_{81}$	1771.343	13-12 P(16)	0.017	3.1
3-2 $P(9)_{79}$	1669.172	18-17 P(10)	0.074	1.3
4-3 $P(4)_{81}$	1669.115	18-17 P(10)	0.017	3.7
4-3 $R(3)_{79}$	1732.808	15-14 P(13)	0.043	2.7
5-4 $P(7)_{79}$	1598.386	21-20 P(9)	0.016	4.0
5-4 $P(7)_{81}$	1597.983	20-19 P(16)	0.049	2.9

* Subscript 79 or 81 refers to $D^{79}Br$ or $D^{81}Br$ transitions, respectively.

in achieving sequential absorption of CO laser quanta to excite DCl or DBr up their vibrational ladders to v ≃ 5.

Examination of Table II indicates that the best matches of $^{12}C^{16}O$ laser emission with $D^{35}Cl$ yield absorption coefficients of about 12 cm^{-1} at 1 atmosphere. Similarly, the best CO laser-DBr absorption coefficients are about 3 cm^{-1}. At higher pressures, radiation from CO laser lines is easily absorbed without need for CO laser line selection. For example, at 5 atmospheres pressure <u>any</u> CO laser line in the 4.9-5.1 micron region is calculated to experience an average DCl absorption coefficient of 2 cm^{-1} for the 1-0 band, which increases to about 10 cm^{-1} when absorption from DCl vibrationally excited states is included. Only the "best" matches were given in Tables II and III for each level of vibrational excitation. Table II shows that most DCl absorption of $^{12}C^{16}O$ laser emission will occur in the 4.9-5.4 micron region, and useful DBr absorption will occur in the 5.4-6.2 micron region. At natural deuterium abundance, the 1/e absorption depth would be about 5 meters for DCl and 20 meters for DBr.

Since a typical reaction mixture would also contain an olefin at near-atmospheric pressure, it would be important to insure that the olefin is sufficiently transparent at these wavelengths (α < 0.1 $meter^{-1}$). This is essential to allow the CO laser emission to excite primarily DBr or DCl, and not waste photons by optically heating the olefin. Examination of simple and conjugated olefin absorption bands (25) in the 5-6 micron region reveals quite strong C = C stretch absorption at 6.0-6.2 micron. Potentially troublesome combination band absorption occurs at 5.1μ and especially at 5.6μ in 1,3-butadiene and isoprene, probably the best reagent choices from Table I.

Gas phase absorption spectra were examined and showed an absorption coefficient (to base e) of about 0.5 cm^{-1} Atm^{-1} for both 1,3-butadiene and isoprene near 5.6 micron. This is about 2-3 orders of magnitude stronger than naturally occurring DBr absorption, rendering photon efficient excitation of DBr impossible. The situation is somewhat improved at 5.1 micron, where the absorption coefficients of these two olefins are about 0.05 cm^{-1} atm^{-1}, still about an order of magnitude stronger than DCl absorption at natural abundance. This suggests that linear conjugated olefins will be excessively absorbing, and prevent efficient CO-laser excitation of DCl and especially DBr. Cyclopentadiene and 1,3-cyclohexadiene should also exhibit low activation energies for hydrogen halide addition, similar to the linear conjugated olefins listed in Table I, and optical absorption spectra are somewhat more promising. Cyclopentadiene (26) appears transparent in the 5.0-5.3 μ region, potentially suitable for use with DCl, and 1,3-cyclohexadiene (27) appears transparent in the 5.4-5.75 μ region, making it potentially suitable for use with DBr. Elimination of olefin absorption will be essential for efficient photon utilization at low deuterium

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

concentrations. Only ethylene (25) shows extreme transparency, with no detectable absorption from 1550 cm^{-1} to 1750 cm^{-1}, making it optically suitable for use with DBr.

Non-reactive quenching of vibrationally excited deuterium halide will be an important process, as it competes with reactive addition of the excited species into the olefin. The reaction efficiency ϕ will be simply the ratio of reactive quenching to total quenching, or

$$\phi = \frac{R_v[C]}{(R_v+Q_c)[C] + Q_x[X]} \qquad (6)$$

where

[C] = Olefin concentration
[X] = Hydrogen halide concentration
R_v = Deuterium halide reactivity in vibrational level v
Q_c = Quenching rate/unit concentration of olefin
Q_x = Quenching rate/unit concentration of hydrogen halide

In addition to reaction, the vibrationally excited deuterium halide will experience non-reactive vibrational quenching by both the olefin and the hydrogen halide. Q_x denotes vibrational quenching of deuterium halide by hydrogen halide and has been measured for quenching of the DX v=1 level (28-31). For DBr, a value of Q_x = 0.2 (μsec • atm)$^{-1}$ was determined (28) for quenching by HBr. For DCl quenching by HCl, a value of Q_x = 0.4 (μsec • atm)$^{-1}$ may be inferred (29). Non-reactive vibrational quenching by the olefin may be 10-100 times faster than these rates, based on the observed rapid quenching of HBr (30), HCl (31) and DCl (31) by water and methane. Quenching rates of higher DX vibrational levels will be faster than for the v=1 level, rising approximately proportional to v (Ref. 29). Thus, equation (6) reduces to a simpler form when the olefin concentration [C] is raised to optimize ϕ,

$$\phi \approx R_v/(R_v+Q_c) \text{ if } [C] \approx [X] \text{ and } Q_c \gg Q_x \qquad (7)$$

since vibrational quenching by HX is slow compared to the expected olefin quenching rates. The upper limit of the DX reaction rate with a given olefin is simply the frequency A (Table I) and is expected to be approached as the DX laser-supplied vibrational energy exceeds the reaction-activation energy E_a. This assumption was examined for other reaction systems (32), and is discussed further in Section III. This places an upper limit on the reaction efficiency

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$$\phi_{max} \lesssim \frac{A}{A+Q_c} \qquad (8)$$

when one assumes (32) that A for a bimolecular reaction is independent of reagent vibrational excitation. The best value of A from Table I occurs for 1,3-butadiene, A ≃ 25 $(\mu sec{\cdot}atm)^{-1}$. If olefin non-reactive vibrational quenching is comparable to HX quenching rates by methane (30,31), or Q_c = 10-60 $(\mu sec{\cdot}atm)^{-1}$, then the maximum reaction efficiency, from equation (8), could lie in the range 0.1%-50%, with the higher reaction efficiencies corresponding to use of olefins with high values of A, such as 1,3-butadiene or ethylene.

The problem of non-reactive quenching of vibrationally excited DX by the olefin is related to the problem of excessive optical absorption by the olefin, namely the presence of olefin energy resonances near DX absorption frequencies. DX vibrational quenching by v-v energy transfer processes becomes very rapid near energy resonance (30,33), but should drop to acceptably low values, if the nearest resonances have an energy discrepancy of more than about 1000 cm^{-1}. Lower non-reactive quenching can be achieved by using fully halogenated olefins (34), which may also yield high olefin transparency at DX absorption frequencies. However, typical fluorinated olefin reagent choices, such as hexafluoro-1,3-butadiene (35), hexafluoropropene (36), or fluorinated ethylenes (36) have excessive optical absorption in the 5-6 micron region (35,36), and hence are not suitable. But when in the course of this work tetrachloroethylene optical absorption was examined in the gas phase, it was found to be highly transparent in the 4.2-5.2 μ region, and is thus potentially suitable for use with HCl. Experimental kinetic data on activation energies are not reported, but calculated values of E_a for HF or HCl reacting with perhalogenated ethylene are 5 kcal/mole lower than with normal ethylene (6). Some perfluorinated olefins are very toxic (37), and perchlorinated olefins require operating temperatures 100-200°C higher than normal olefins to achieve useful vapor pressure. Nevertheless, the potential for high IR transparency and low vibrational quenching makes this class of reagents (and tetrachloroethylene in particular) attractive to consider for a practical process.

There is presently very little experimental data on laser-excited HX addition into olefins. However, reaction was observed between 2-methylpropene and HCl(v=6) produced by intracavity dye laser excitation of the HCl fifth overtone (38). Quantum yields for reaction were estimated (38) to lie in the range 0.01-0.1%, consistent with the very low frequency factor for this olefin (see Table I). Use of 1,3-butadiene in this same experiement (instead of 2-methylpropene) was not tried, but should have yielded a reaction quantum yield of 2-20%, based on its 200-fold higher frequency factor. Economic analysis of laser-related costs in heavy water production by the DX-olefin process discussed here indicate that reaction efficiencies must exceed 5% for this process to be economically viable (39). Additional costs due to the "back-end" of this process (see Section IV) will probably set a practical lower limit of 10% for an acceptable reaction efficiency. In this context, the classical quantum efficiency is the reaction efficiency ϕ divided by n, the average number of absorbed quanta per DX molecule. The assumption of n = 5 places an approximate lower limit of 2% on an economically acceptable quantum efficiency for deuterium halide addition into olefins as a potential photochemical route to heavy water production.

In this section we have shown that the CO laser permits sequential excitation of DBr or DCl up the vibrational ladder to at least the v = 5 vibrational level. At natural deuterium abundance, the 1/e absorption depth for selected CO laser line radiation is about 5 meters for DCl and about 20 meters for DBr, at a hydrogen halide operating pressure of one atmosphere. At 5 atmospheres operating pressure, unrestricted multiline operation of the CO laser is sufficient, but some line tuning (according to Tables II and III) facilitates DX absorption at one atmosphere pressure. Troublesome olefin optical absorption and vibrational quenching may be reduced by using tetrachloroethylene. Unwanted olefin optical absorption may also be avoided by using ethylene, cyclopentadiene, or 1,3-cyclohexadiene. The large choice of Arrhenius parameters available for typical reagent choices (Table I) permits reagent optimization for acceptable process reaction efficiency. Experimental evaluation of the deuterium halide/olefin process for heavy water production is in progress at the Lawrence Livermore Laboratory.

III. Effectiveness of Vibrational Excitation

In the preceding section, we have shown that excitation of low-lying vibrational levels of deuterated halides should lead to significant enrichments via isotopically selective addition reactions, if the halide vibration and reaction coordinates are essentially identical. That vibrational excitation of hydrogen halides leads to enhanced rates for diatomic-atom exchange reactions of the type

$$A + BC \underset{K_r}{\overset{K_f}{\rightleftarrows}} AB^{\dagger} + C \qquad (9)$$

have been experimentally confirmed; perhaps the most striking example is the fact that HCl (v = 2) was found to react with bromine approximately 10^{11} times faster than HCl (v = 0) (40).

The theoretical explanation of these rate enhancements runs as follows: Since the forward, exoergic reaction leaves the product AB in a highly vibrationally excited state ($AB^{\dagger}$), then

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

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microscopic reversibility at the same total energy implies that the rate of the reverse, endoergic reaction will be enhanced more effectively when energy is put into AB vibration rather than into relative translation of AB and C. In considering more general reactions involving vibrationally excited reagents, it is important to note that the reversibility argument can be applied independent of whether the reaction which leads to a vibrationally excited product is endoergic or exoergic. We stress this because, while it is generally believed that the endoergic reactions utilize vibrational energy more effectively than exoergic reactions (41), the existing experimental evidence, as analyzed by Birely and Lyman (32), does not show any strong correlation between the effectiveness of reagent vibration in lowering the activation energy and reaction exoergicity. It follows that insight into the effect of vibrational excitation of hydrogen halides on the rate of exoergic addition reactions can best be gleaned from the experimental data on the energy disposal of the reverse reactions, i.e., unimolecular hydrogen halide eliminations from, e.g., haloalkanes and haloölefins, following chemical or photochemical activation. There is an extensive literature in this area: The experimental evidence is summarized by Berry (42) who concludes that, irrespective of the activation mechanism, the total available energy (E_T), or the molecular complexity of the reactant, all HX elimination products acquire ∿ 15-40% of the potential energy (E_p) available to the reactants (defined as the threshhold energy for HX elimination minus the reaction endoergicity) as vibrational energy. The remaining energy is channeled into HX rotation, olefin product rotation and vibration and relative translational energy of the recoiling products. We note that all the data pertains to experiments in which $E_T >> E_p$. Of greater relevance as far as effectiveness of HX vibration on the rate of the inverse addition would be data on HX eliminations for which $E_T \simeq E_p$. Nevertheless, the availability of many internal degrees of freedom of the product olefin makes it improbable that rate enhancements for HX addition reaction comparable to those for HX-atom exchange reactions can be achieved. Experiments to test this conjecture are in progress at the Lawrence Livermore Laboratory.

IV. "Back-End" of the Separation Cycle

In common with most other deuterium separation schemes, the economic viability of an enrichment process based on laser enhanced deuterium halide addition reactions necessitates provision for recycling the working fluid. That is, it is not feasible to use, e.g., hydrochloric acid, on a once-through basis as feed for a deuterium separation plant since even if all the D in natural HCl (natural abundance $\simeq 1.5 \times 10^{-4}$) were removed with 100% efficiency, the HCl feed cost alone would be

$$\frac{\dfrac{\$0.1}{\text{kgHCl}} \times \dfrac{36\ \text{kg HCl}}{\text{kg mole HCl}}}{1.5 \times 10^{-4}\left(\dfrac{D}{H}\right) \times \dfrac{1\ \text{mole } D_2O}{2\ \text{mole DCl}} \times \dfrac{20\ \text{kg } D_2O}{\text{kg mole } D_2O}} = \$2400/\text{kg } D_2O \quad , \tag{1}$$

assuming HCl costs 10¢ per kilogram. Thus, the economic viability of this process depends on the ability to redeuterate the HCl which has been depleted of D by the isotopically selective addition reaction. The "obvious" way to accomplish the redeuteration is by isotopic exchange of HCl with natural water (43). For specificity, we discuss this reflux operation in the context of the prototype system shown in Figure 1. The deuterated product of the addition reaction (DACl) is thermally dissociated to produce isotopically pure DCl (and eventually D_2O through exchange with natural water), while the olefin is recirculated to the laser irradiation area. The material flows in the reflux tower assume equilibrium operation at 108°C (44). At this temperature the separation factor α for the exchange reaction

$$DCl + H_2O \rightleftarrows HCl + HDO \tag{2}$$

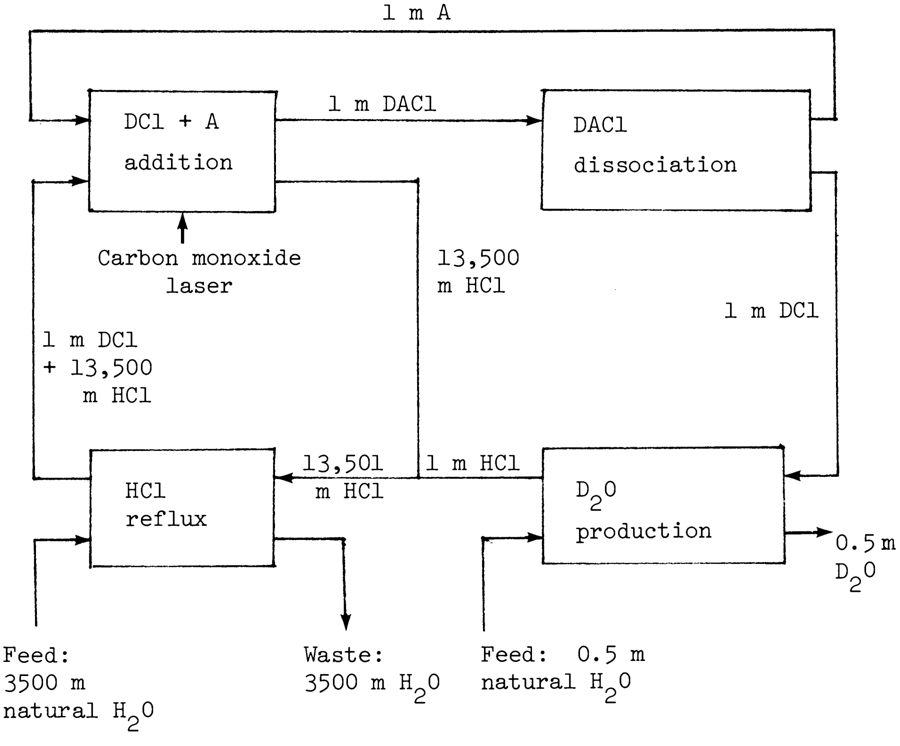
is (43)

$$\alpha = \frac{\left(\frac{D}{H}\right)_{H_2O}}{\left(\frac{D}{H}\right)_{HCl}} = 1.9$$

Besides the fact that all the hydrogen halide-water exchange reactions are characterized by an unfavorable equilibrium as far as reflex is concerned, i.e., the deuterium tends to concentrate in the water, there are two other practical difficulties associated with the use of these systems: (1) they are highly corrosive, necessitating the use of special materials, e.g., Monel, and, (2) they form constant boiling (azeotropic) mixtures.

The significance of the latter is that it is impossible by successive distillations at a given pressure (or at a given temperature) to obtain both components as pure products from a hydrogen halide-water mixture. At some point in the distillation process, the azeotropic concentration will be reached (44); when this azeotropic feed is partially vaporized, the vapor has the same composition as the liquid and no further separation of components is possible. One convenient way to break the azeotrope and separate the phases after the isotopic exchange process has been completed is to make use of the so-called "salt effect" in vapor-liquid equilibrium. The addition of a non-volatile salt such as calcium chloride, $CaCl_2$, to the HCl/H_2O mixture has the effect of simultaneously increasing the vapor pressure of the HCl via the common ion effect and decreasing the vapor pressure of the water, thus generating vapor of higher HCl concentration than that characteristic of the azeotrope. We have not been able to

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010



LEGEND:

m = Mole
A = Olefin
DACl = DCl + Olefin addition product

Figure 1. Process flow diagram for D_2O production by laser-augmented deuterium-chloride addition into olefins

find information in the literature on the $HCl/H_2O/CaCl_2$ system; however, from data on Isopropanol/$H_2O/CaCl_2$ (45) and $HCl/H_2O/H_2SO_4$ mixtures (46)(H_2SO_4, while not a common ion, behaves similarly to a non-volatile salt in reducing the vapor pressure of H_2O), we conjecture that the concentration of $CaCl_2$ required will be approximately 2-4 wt.%.

A detailed discussion of the design of the HCl/H_2O exchange process incorporating the equipment necessary to generate redeuterated, anhydrous HCl for reflux to the laser tower would carry us too far afield (47); however, the basic concept is as follows. The isotopic exchange takes place on a series of trays with the HCl bubbling up and H_2O flowing down in a countercurrent fashion. The liquid stream from the exchange column, and a salt solution are fed to a concentrated stripper which produces vapor of high purity (> 99 mole % HCl); this is recycled to the bottom of the isotopic exchange column. The liquid from the concentrated stripper, having a concentration lower than the azeotrope, passes to an evaporator where the salt is recovered for recycle to the concentrated stripper, and vapor is produced which is subsequently stripped to produce two streams: a water stream which is washed before discharge, and an azeotropic HCl/H_2O mixture. The latter, mixed with incoming fresh water, is fed to the top of the isotopic exchange column. Many variations of the above are probably feasible; our main point here is to indicate that while the use of hydrogen halides introduces complications in the design of the "back-end" of the separation scheme, these can be overcome.

V. Conclusion

Optical production of heavy water is beginning to receive serious consideration. Laboratory-scale photochemical separation of deuterium via dissociation of deuterated formaldehyde (HDCO) to yield HD and CO has already been demonstrated in the UV(3) using a single photon, and in the IR at 10.6 microns using multi-photon absorption (48). To be economically viable, the former process awaits efficient low cost tunable ultraviolet lasers near 340 nm (39,49), while the latter process requires significant improvement in photon utilization ($\sim 10^6$ photons are presently required per separated HD (48)). All photochemical deuterium enrichment processes will probably require deuterium optical isotopic selectivity of 1000-fold or better for efficient photon utilization (39,49), about an order of magnitude higher than has been demonstrated (3,48).

The deuterium separation process just presented proposes to utilize existing, efficient, high average power CO laser technology to promote deuterium halide addition into unsaturated hydrocarbons. Spectroscopic studies of CO lasers and deuterium halides have shown that both DCl and DBr can be sequentially excited by the CO laser near 5-6 microns to at least the v = 5

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

level, as summarized in Tables II and III. Addition into unsaturated hydrocarbons should occur with activation energies in the range of 15-40 kcal/mole using HCl or HBr as the working gas, as indicated in Table I. The effectiveness of hydrogen halide vibrational energy toward lowering the addition reaction activation barrier is not known, but probably lies in the range of 30-100%, suggesting that perhaps 5-8 quanta of DX vibrational excitation will be required for usefully fast reaction to occur. Two significant problems to be resolved are photon loss by olefin combination band absorption in the 5-6 micron region and potentially low reaction quantum yields due to non-reactive vibrational quenching by the olefin. These problems appear solvable by suitable olefin structural design. The problems at the "back-end" of the separation cycle, specifically the breaking of the HX/H_2O azeotrope, also appear solvable. Research currently underway will examine the effectiveness of vibrational catalysis on the reaction rate and reaction quantum yield as a function of olefin structure.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

Acknowledgement

One of the authors (M.M.M.) would like to thank Professors M. Benedict and J. E. Vivian for helpful discussion.

Abstract

The feasibility of a gas phase deuterium separation process is examined which would use IR lasers to augment addition reactions between HX (X = Br, Cl, F, OH) and unsaturated hydrocarbons. High vibrational levels ($V \geq 4$) of DF or HDO may be excited by a pulsed DF laser. Similar high vibrational excitation of DCl or DBr may be achieved by a pulsed CO laser and spectroscopic details for excitation up to $V = 5$ are examined. The thermal reaction between HX and unsaturated hydrocarbons is characterized by activation exergies between 15 and 57 kcal/mole, depending on olefin structure and choice of HX. The effectiveness of HX/DX vibrational energy in lowering the reaction barrier is discussed. Primary emphasis is given to an overall deuterium separation process utilizing HCl as a closed cycle working gas with aqueous phase redeuteration. Preferred olefin reagents are indicated compatible with CO laser excitation of DCl at a wavelength of 4.9-5.3 micron.

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RECEIVED September 12, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch010

11

Proposed H/D/T Separations Based on Laser-Augmented A + B ⇄ C Reactions

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch011

The separation of H/D/T by laser photolysis of selected congeners in the infrared does not require high spectral resolution but does depend on the retention of selective excitation and rapid reaction of the species which initially absorb the photolyzing radiation. Except for the vibration augmentation of three center abstraction reactions $[A + B^{\ddagger}C \rightarrow AB + C]$, all isotope fractionations achieved to date involving polyatomics are based on fragmentation of the irradiated species by coherent absorption of a large number of photons under essentially collision free conditions, to excited states considerably above the critical level for dissociation. A thermodynamic and kinetic analysis, which constitutes the first part of this report indicates that the inverse process i.e. the bimolecular association should also be isotopically selective. In the second part of this report several specific cases are proposed for testing this concept. The emphasis here is on chemical properties, not on spectroscopy, since it appears that the required irradiating frequencies are either available now or shortly will be from sufficiently powerful lasers. All the systems considered are presumed to be in the gas phase at pressures sufficiently low such that individually each species behaves ideally. While in some respects the analysis appears elementary, it is basic and merits formulation in a consistent manner.

Thermodynamic and Kinetic Relations

Consider the direct synthesis of an adduct:

$$A + B \underset{\varkappa_1}{\overset{\varkappa_{-1}}{\rightleftarrows}} C^{\ddagger} \underset{\varkappa_2}{\overset{\varkappa_{-2}}{\underset{(M)}{\rightleftarrows}}} C \qquad (1)$$

Reference to Figure 1 provides definitions of the conventional symbols used. For a system which is in statistical equilibrium $N_{A;B}(E,T)$ represent a normalized Boltzmann distribution of populations of the reactants; the hashed levels represent the weighted mean energies of the reactants, transition state, and products. The zero of energy for each species, per convention, is measured from the corresponding zero-point level. Thus,

$$\Delta E_T^o = \Delta E_o^o + \int_0^\infty E_{A;B}\, N_{A;B}\,(E,T)\, dE - \int_0^\infty E_C\, N_C\,(E,T)\, dE \qquad (2)$$

$$\Delta H_T^o = (\Delta E_T^o - RT) < 0 \quad ; \quad \Delta S_T^o < 0$$

These are thermodynamically favored reactions.

$$K_{p,eq} = \left.\frac{p_C}{p_A \cdot p_B}\right\}_{eq} = e^{-1} \exp\left\{- |\Delta S_T^o| / R + |\Delta E_T^o| / RT\right\}$$

$$= (\mathcal{R}T)^{-1}\, \frac{\varkappa_1}{\varkappa_{-1}} \cdot \frac{\varkappa_2}{\varkappa_{-2}} \qquad (3)$$

The units of $\varkappa_1$ and $\varkappa_2$ are in molecule^{-1}cm^{3}s^{-1}. Clearly, on raising the temperature, i.e. for $T_1 > T$, both distribution functions get steeper and $K_{eq}(T_1) < K_{eq}(T)$.

For a system which is in statistical equilibrium at the temperature T, *except* for a steady burning of a hole at level E_β and maintenance of an overpopulation at E_α, most of the reactant populations are unchanged, Figure 2. The magnitude of the second term in the right member of (2) is obviously increased and $K_p^*(T)$ is greater than $K_{p,eq}(T)$. The reverse applies when the hole in the population is burned at E_ρ and the overpopulation established at E_σ. These qualitative relations apply *independently of the magnitude* of E_a, which can be positive or zero. For example, the steady state irradiation of a mixture of $B(CH_3)_3$ and NH_3 with a CO_2 laser should *increase* the magnitude of the "perturbed equilibrium constant" for the reaction (1),

$$NH_3^{\ddagger} + B(CH_3)_3 \rightleftarrows (CH_3)_3B{:}NH_3 \qquad \Delta H^o_{300} = -14.2 \text{ kcal/mole (unirradiated)}$$

even though the adduct is presumed to be generated without an activation energy. A similar argument applies to the adsorption of gases onto a solid surface, where the amount adsorbed under steady state irradiation should increase when either the adsorber or the adsorbate undergo a resonant transition which is matched by the irradiating frequency. Here, the equivalent of the condition $\varkappa_2[M] > \varkappa_{-1}$ is rapid intrasurface-layer vibrational relaxation.

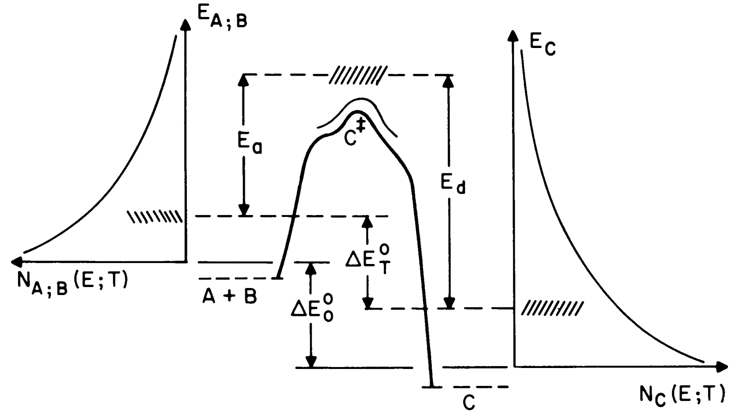


Figure 1. Potential energy diagram for an $A + B \rightleftarrows C$ *system and a population distribution when it is in statistical (but not chemical) equilibrium at* T

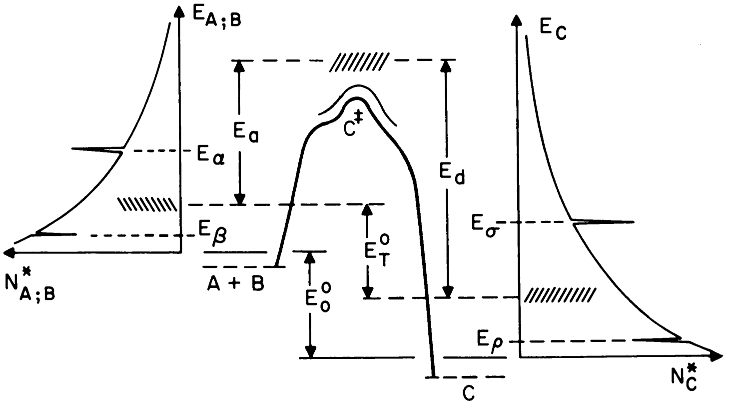


Figure 2. Change in population distribution at steady state because of pumping by $\beta \rightarrow \alpha = (E_\alpha - E_\beta)/h$ *or* $\nu_{\rho \rightarrow \sigma} = (E_\sigma - E_\rho)/h$*, assuming the statistical temperature remains at* T

The kinetic formulation provides addition details for the above analysis. To eliminate the dependence on [M] we must stipulate that $\varkappa_2[\mathrm{M}] > \varkappa_{-1}$. Then the unidirectional rate of production of $\mathrm{C}^{\ddagger}$ from the reagent is determined by the product of the individual state densities and the cross sections for association:

$$\mathfrak{R}_1 = \sum_{i,j} \varkappa_1^{(i,j)} \rho_A^{(i)} \rho_B^{(j)} \xrightarrow[\text{equil.}]{\text{at stat.}} \sigma_{A,B} \left[\frac{g_A g_B}{Q_A \cdot Q_B} \exp\left(- \frac{E_A + E_B}{kT} \right) \right]_a \rho_A \rho_B \tag{4}$$

$$\mathfrak{R}_{-1} = \tau_{C^{\ddagger}}^{-1} \rho_{C^{\ddagger}}, \quad \text{with} \quad \tau_{C^{\ddagger}}^{-1} \approx \nu_C^* \left(1 + \frac{E_d}{skT} \right)^{1-s} \tag{5}$$

where s is the equivalent number of classical oscillators assigned to the transition state ($\mathrm{C}^{\ddagger}$) and,

$$\nu_C^* = \prod_{i=1}^{s} \nu_i^{+} \left(\prod_{j=1}^{s-1} \nu_j^{\ddagger} \right)^{-1}$$

Similar expressions apply to the second step in the conversion. Hence for a system at steady state, with a hole burned at E_β and overpopulated at E_α,

$$\left(\mathfrak{R}_1^* - \mathfrak{R}_1 \right) = \varkappa_1^{(\beta)} \left[\rho_{A;B}^{(\beta)} - \rho_{A;B}^{(se,\beta)} \right] + \varkappa_1^{(\alpha)} \left[\rho_{A;B}^{(\alpha)} - \rho_{A;B}^{(se,\alpha)} \right]; \tag{6}$$

$\rho^{se,\beta}$ is the molecular density at E_β at statistical equilibrium. Because the perturbed system is generated by direct pumping, the increments in densities at α and β are equal but of opposite sign; however, $\varkappa_1^{(\beta)} < \varkappa_1^{(\alpha)}$ and $(\mathfrak{R}_1^* - \mathfrak{R}_1) > 0$. The net rate $(\mathfrak{R}_1^* - \mathfrak{R}_{-1}^*)$ is larger than $(\mathfrak{R}_1 - \mathfrak{R}_{-1})$ since the reverse rate is minimally affected by pumping $\beta \rightarrow \alpha$; recall $\varkappa_2[\mathrm{M}] > \varkappa_{-1}$. Note that the sign of the increment in the unidirectional flux is determined by the perturbed population, again, irrespective of the magnitude of E_a. However, the size of the increment depends on $(\varkappa_1^{\alpha} - \varkappa_1^{\beta})$ which is small when $E_\beta > E_a$ (2).

Clearly, to maintain the spiked distribution at the steady state, without allowing the system temperature to rise indefinitely, one must continually remove as much energy as is pumped into it by radiation. Imagine that the reactants and the reactor's walls are initially at a uniform temperature, $T_0 < T$. Upon turning on the radiation there will be a transient condition wherein, on a time scale of τ(vib) → (transl), the reactant temperature rises, but on a longer time scale (τ_r) it levels off, due to conduction and convection, to the operating temperature T which is determined by the rate of heat transfer to the walls, maintained at T_o. Thus the gas temperature tends toward, but does not attain a uniform distribution (3). The steady state population in level α is established by the balance between the pumping rate and the combined loss by relaxation and reaction. The efficiency of any LIS will be determined by the selectivity and intensity of pumping ($\beta \rightarrow \alpha$) and limited by $v^{(i)} \rightarrow v^{(j)}$ transfer efficiencies among the congeners, as well as by v → R, T processes which raise the operating temperature.

Classification of Adduct Production

To select suitable systems for isotope separations based on the above relations a broad range of criteria must be considered, but the principal step is to find conditions under which laser radiation does augment the rate of adduct production. In many cases the apparently simple reaction indicated in Eq. (1) proves to follow a much more complex mechanism. Toward this end it is useful to compile proposed reactions according to the magnitudes of their activation energies (E_a). Values of (30-40) kcal/mole are typical for the addition of mineral acids, water and hydrogen sulfide to olefins (4); these are the inverse of (α, β) eliminations. The addition of mineral acids or water to aldehydes and ketones require (12-18) kcal/mole. Also the addition of HBr and HI to conjugated dienes are in this group. Lewis acid-base adducts and hydrogen bonded complexes are generated with little or no activation energy (0-5 kcal/mole).

A small sub-set of the first group which is the largest and the most extensively investigated, is the addition of HF to $H_2C{=}CF_2$ and other variously substituted fluoroethylenes, illustrated in Figure 3. Many lower activation energy pairs in this category are cited by Marling (5). Numerical values for the pertinent energy parameters for the HF/ethylene additions are listed in Table I. The estimated lowest activation energy is that for HF/C_2F_4. Indeed, one may anticipate that excitation of HF would accelerate its addition across the double bond in view of the observed vibrationally excited HF generated from mixtures of CH_3 and CF_3 radicals. However, it appears (6) that of the 72 kcal/mole which the radical pair $H_3C^{\ddagger}CF_3$ incorporates [measured from the CH_2CF_2 + HF level], about 30 kcal/mole are statistically distributed prior to $HF^{\ddagger}$ elimination. Hence the application of detailed balance suggest that $C_2H_nF_{4-n}$ excitation may be just as essential as that of the HF to promote significant enhancement of the rate. Indeed we reached that conclusion after obtaining negative results by simply exposing mixtures of HF and various olefins to a pulsed HF laser with the cell at room temperature (Table II). Thus, the conditions outlined in the preceeding section are necessary but not sufficient, particularly for combinations which consist of a sizeable polyatomic acceptor and a strongly bonded intruder (HF;

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch011

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch011

TABLE I. Values of Parameters for Figure 3

HF/Ethylene Adduct	D(C–C) kcal mol^{-1}	E_C kcal mol^{-1}	ΔH^{o}_{T} kcal mol^{-1}	E_{ex} kcal mol^{-1}	E_R kcal mol^{-1}
CH_3CH_2F	88	57	11	31	46
CH_3CHF_2	~93	62	24	33	38
CH_2FCH_2F	89.6	62	10	28	52
CH_3CF_3	99	69	27	30	42
CH_2FCF_3	92	71	~28	21	43
CHF_2CHF_2	91	69	~26	22	43
CHF_2CF_3	94	72	~40	22	31

TABLE II. Attempts to Augment HF Addition

HF laser operation: pulsed, 2/s; ≈150 mJ/p

p(HF)/p(substrate): 3/1 to 1/3; 10^2 pulses

p(HF) = 0.5 torr; cell temp $\left[\begin{array}{l}25°\text{C (low T)}\\190°\text{C (high T)}\end{array}\right.$

Mass spectral analysis for products

Compounds tested, no reaction with $HF^{\ddagger}$ ---

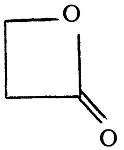
C_2F_4 (ℓ,h); $CH_2{=}CF_2$ (ℓ); $H_2C{=}CH\cdot COOEt$ (h)

C_5H_6-cpd (h); C_3H_6-allene (ℓ); $H_3CC{\equiv}CH$ (ℓ)

c-C_4H_8O (h); c-$C_4H_6O_2$ (h); $COC\ell_2$ (ℓ,h)

SiH_4 (h); CD_4 (h); $HC\ell CF_2$ (h)

$HF^{(0)}$ reacts with the following, on mixing



$H_2C{=}CO$

$H_2C{=}CH\cdot OCH_3$

H_2O; CH_3OH). Then vibrational activation of the acceptor is probably essential for significant augmentation of the rate of addition across the double bond.

An interesting combination of reagents which is related to, but is not strictly a member of, the first category involves an (α, α) elimination of $DC\ell$ from $DC\ell CF_2$. This is diagramed in Figure 4 and conceived as a by-pass attached to a polyfluoroethylene production plant (7).

There are relatively few members of the second group of addition reactions. Also only sparse data are available on their thermochemistry and kinetic behavior. We looked for combinations which fitted the following criteria as closely as possible:

(a) One or both of the combining reagents (if one uses two irradiation frequencies) should have strong ir absorption bands in the region of currently developed, high powered lasers.

(b) The thermal recombination rate should be limited by an activation energy which equals the equivalent of a few photons of the irradiating frequency, such that addition of $DX^{\ddagger}$ would be favored strongly over HX.

(c) The adduct can be separated from the mixture rapidly enough to avoid H/D exchange with the residual XH.

(d) The system is scalable for large throughput. This implies that the H/D carrier can be readily equilibrated with a natural source of deuterium (natural gas or water).

We found several combinations which satisfy criteria (a) and (b) and thus constitute good candidates for laser augmented rate trials, but as yet no such tests have been made. The equilibrium constants at room temperature for the addition of HF to tetrahydrofurane [C_4H_8O] is substantial (1.1×10^3, M^{-1}); addition to dimethylformamide [Me_2NCHO] is even larger, 4.6×10^3 M^{-1}; however, no kinetic data are available. It has been reported that perfluorocyclobutanon [C_4F_4O] readily adds HF but only qualitative observations have been mde. We selected for our initial experiments the production of gaseous hydrates of perfluoroacetone and trifluoroacetaldehyde. Their infrared spectra are shown in Figures 5 and 6, respectively. These compounds do satisfy criterion (a). Several rates of hydration and of decomposition of the adducts were measured (8) to check whether these comply with criterion (b).

For:

$$F_3C{-}CHO + H_2O \underset{k_a}{\overset{k_d}{\leftrightarrows}} F_3C{-}CH(OH)_2$$

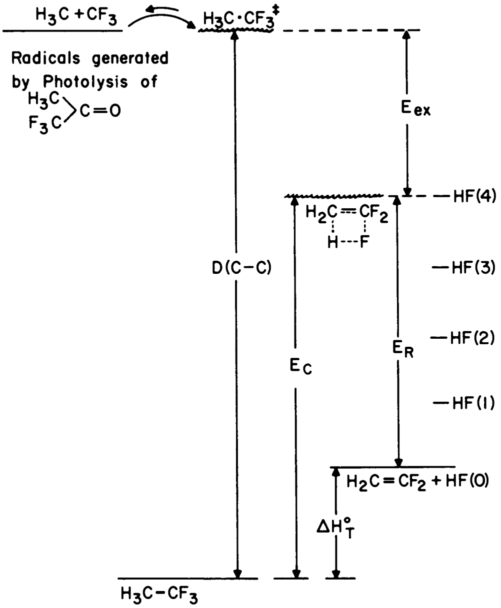


Figure 3. Energy level diagram for HF/ethylene pairs

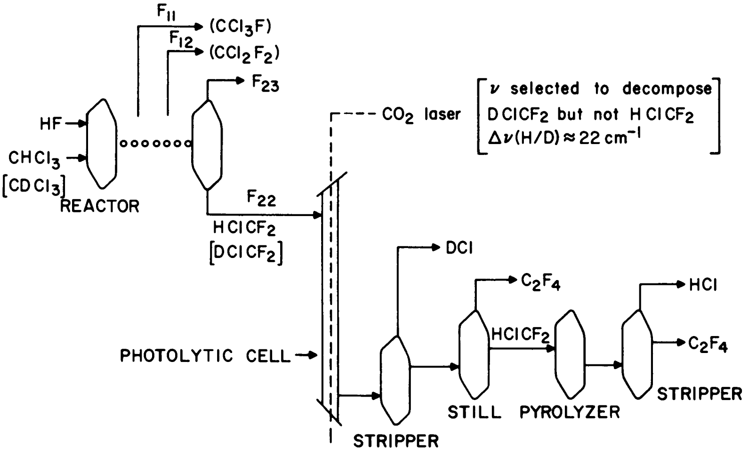


Figure 4. Flow chart for selective laser photolysis of $DClCF_2$ to generate DCl from natural abundance of D in chloroform, incorporated in a perfluoroethylene plant. Based on the total annual C_2F_4 production (USA), an optimum yield of ≈ 400 tons of D_2O could be developed. Recirculation of C_2F_4, F_{11}, F_{12}, and F_{23} to generate larger supplies of chloroform (via HCl) would be energy intensive.

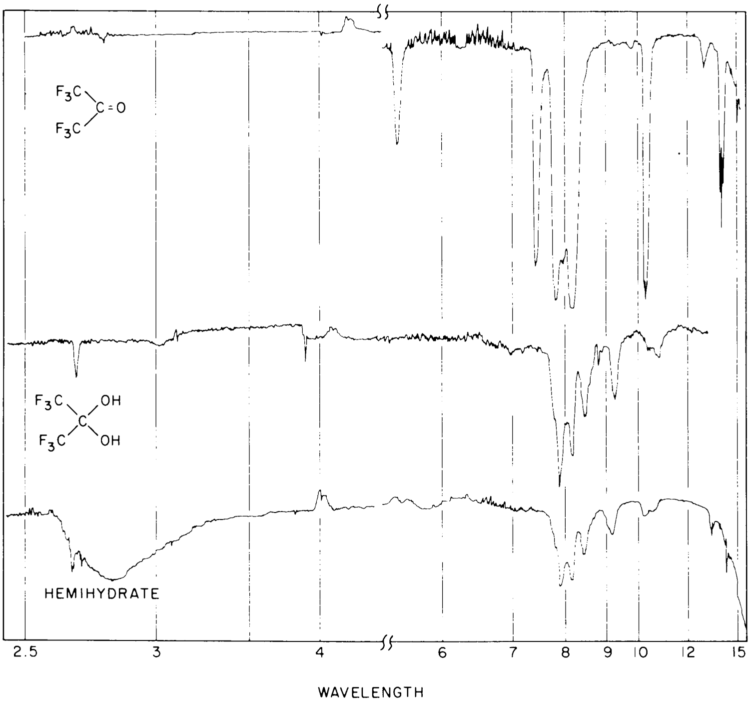


Figure 5. IR transmission spectra of perfluoroacetone, its mono-and hemihydrates

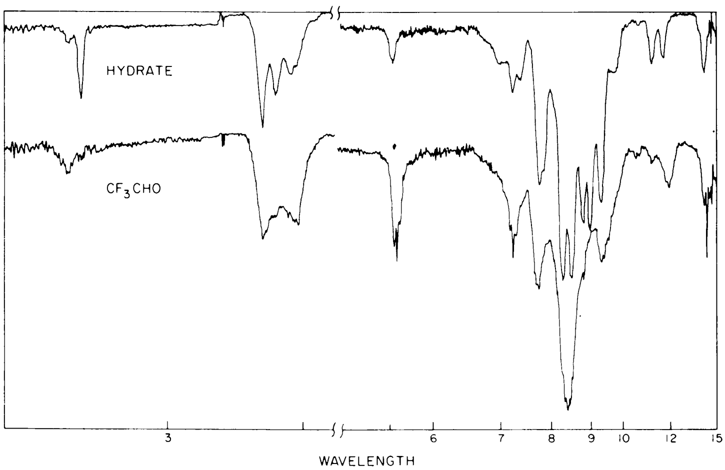


Figure 6. IR transmission spectra of trifluoroacetaldehyde and its monohydrate

$$\left.\begin{array}{l} k_a\ (75^oC) = 1.3 \times 10^2\ \text{mole}^{-1}\text{cm}^3\text{s}^{-1} \\ k_d\ (77^oC) = 6.23 \times 10^{-4}\ \text{s}^{-1} \\ \ (137^oC) = 3.75 \times 10^{-3}\ \text{s}^{-1} \end{array}\right] \quad \begin{array}{l} E_a = 19 \pm 3\ \text{kcal/mole} \\ E_d = 29.2 \pm 1\ \text{kcal/mole} \end{array}$$

For: $$(F_3C)_2CO + H_2O \underset{k_a}{\overset{k_d}{\leftrightarrows}} (F_3C)_2C(OH)_2$$

$$k_a\ (25^oC) = 1.5 \times 10^3\ \text{mole}^{-1}\text{cm}^3\text{s}^{-1}$$

Measurement of laser augmented rates will be made after our low pressure intracavity reactor (9) has been modified to minimize adsorption of these reagents on the cell walls.

We anticipate that the rates of adduct production in the third category, characterized by very low activation energies, would be slightly if at all augmented by laser irradiation of the precursors but the "perturbed equilibrium" composition of the adduct (at steady state, Figure 2) should be reduced upon its irradiation. Conceptually this can be utilized for an H/D separation in the following scheme, wherein the particular Lewis acid and base shown are examples selected from a large class of possible combinations (1):

$$BMe_3 + MeNH_2 \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} Me_3B{:}NH_2Me \qquad \Delta H^o_{300} = -18.2\ \text{kcal/mole}$$

$$GaEt_3 + MeNH_2 \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} Et_3Ga{:}NH_2Me \qquad = -19.8$$

Whereas both k_1 and k_2 are presumed to be large ($\approx 10^{12}$ $\text{mole}^{-1}\text{cm}^3\text{s}^{-1}$) and temperature insensitive, the reverse steps are much slower since k_{-1} and k_{-2} have Arrhenius exponential factors with (-18.2/RT) and (-19.9/RT), respectively. Thus, were an equilibrium mixture of methylamine, the two Lewis acids, and the corresponding adducts in equilibrium, exposed to radiation which is selectively absorbed by $Et_3Ga{:}NHDMe$, the deuterium would be selectively trapped as Me_3BHDMe, possibly for a sufficient time to achieve separation. Other means for trapping laser shifted concentrations of dissociation products are conceivable. For example, the irradiation of matrix isolated samples followed by adjusted diffusion rates of the products (careful

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch011

temperature control) but these applications appear of little practical utility.

Abstract

Thermodynamic and kinetic analyses of adduct production: $A + B \underset{k_a}{\overset{k_d}{\leftrightarrows}} C$; $K_{eq} = k_a/k_d$, indicate how the steady state composition and rates (forward vs reverse) can be perturbed by absorbable radiation which generates a "spiked" steady state population distribution for one of the species. Three classes of reactions were considered, wherein E_a ranges from (30-40) kcal/mole; (12-16) kcal/mole; and (0-5) kcal/mole. These are of particular interest for H/D/T separation, in that one of the adducts can be water, a mineral acid (which rapidly equilibrates with water) or hydrogen. Our analysis and preliminary experiments indicate that the intermediate case ($E_a \sim 15$ kcal/mole) is particularly attractive for LIS.

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RECEIVED August 31, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

12

Operating Experience with the Tritium and Hydrogen Extraction Plant at the Laue–Langevin Institute

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The Institute Max Von LAUE - Paul LANGEVIN in GRENOBLE is a society founded in 1967 by a government agreement between FRANCE and GERMANY. In 1974 GREAT BRITAIN also joined the Institute.

The Institute operates the High Flux Reactor whose purpose is a large programme of nuclear physics research using the neutrons produced by the reactor.

This High Flux Reactor has a thermal performance of 57 MW with a single heavy water cooled and moderated circuit. Heavy water hold-up is about 40 m^3. The mean flux of thermal neutrons in the heavy water is equal to 1,8 . 10^{14} n/cm^2 sec, which leads to formation of tritium with a saturation activity of more than 80 Curie per litre (after 10 years about 30 Curie/l). This is similar to the value expected in the moderator circuit of the CANDU type reactor.

For safety reasons, tritium concentration in heavy water should not exceed 3 Curie per litre and in order to maintain moderator efficiency of heavy water, its fractional concentration should not be lower than 99,6 mol %. The installation fulfilling the mentioned duties was built by CCM/SULZER* in close co-operation with the C.E.A. (Commissariat ā l'Energie Atomique). SULZER already had experience in the low temperature distillation of hydrogen from a small heavy water plant in EMS Switzerland.

The installation at the LAUE-LANGEVIN Institute on the Grenoble Nuclear Centre site is the first known plant in operation for the simultaneous extraction of hydrogen and tritium from heavy water.

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* is Licensee of a patent owned by the CEA for this process

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

Design Data. - Tritium concentration of heavy water has to be stabilized at 1,7 Ci/l by an annual extraction of 160 000 Curie, equivalent to about 60 Nl of pure tritium.

- Content of heavy water has to be maintained at 99,6 mol % by an annual extraction of 160 litres of light water, equivalent to about 200 Nm^3 of hydrogen.

Principle of Operation. Figure 1 shows the mass flows with the corresponding contents at normal operation conditions in 1976, and furthermore, that the plant is made up of two main parts:

1. Catalytic exchange between heavy water vapour and deuterium gas at 200°C and about 1,2 bar, which allows the mass transfer of hydrogen and tritium from heavy water to deuterium to reach equilibrium according to the following reactions:

$$DTO + D_2 \rightleftarrows D_2O + DT$$

$$HDO + D_2 \rightleftarrows D_2O + HD$$

2. Low temperature rectification of the hydrogen isotopes $HD/D_2/DT/T_2$ at about 1,5 bar in two columns with extraction of HD at the top of the first column and pure tritium at the bottom of the second column.

The flow sheet Fig. 2 shows that the heavy water coming from the reactor is evaporated, superheated, and mixed with the deuterium to pass through the catalytic reactor where the isotopic exchange reactions occur ; it is then recondensed to be separated from the deuterium and transferred to the second and then to the third stage of the catalytic exchange.

The deuterium coming out of the catalytic exchange is dried and purified before being sent into a distillation column containing Sulzer packings. The partially tritium and hydrogen stripped deuterium coming out of the column returns to the catalytic exchange through an expansion vessel. The deuterium hydride drawn off with a content of about 80 mol % at the head is sent to a burner. The tritiated deuterium at the foot of the column is sent to a second column with dixon ring packing. In the middle of this column, DT is withdrawn in a tank to get tritium according to equilibrium reaction $2\,DT \rightleftarrows T_2 + D_2$. At the bottom of this column, pure tritium of about 98 mol % is drawn off periodically.

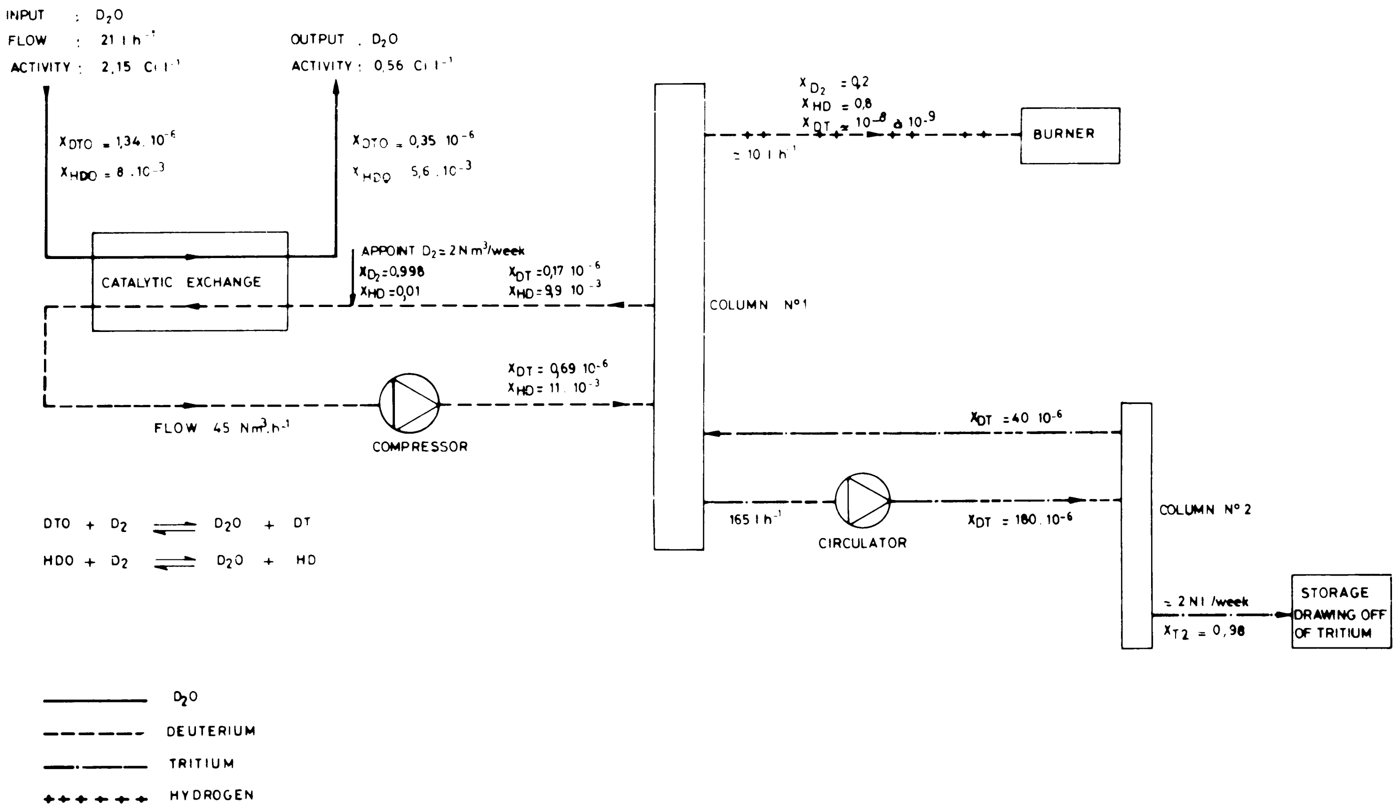
INPUT : D_2O
FLOW : 21 l h^{-1}
ACTIVITY : 2,15 Ci l^{-1}
OUTPUT . D_2O
ACTIVITY : 0,56 Ci l^{-1}
X_{DTO} = 1,34 . 10^{-6}
X_{HDO} = 8 . 10^{-3}
X_{DTO} = 0,35 10^{-6}
X_{HDO} 5,6 . 10^{-3}
CATALYTIC EXCHANGE
APPOINT D_2 = 2 N m^3/week
X_{D_2} = 0,998
X_{HD} = 0,01
X_{DT} = 0,17 10^{-6}
X_{HD} = 9,9 10^{-3}
X_{DT} = 0,69 10^{-6}
X_{HD} = 11 . 10^{-3}
FLOW 45 $Nm^3.h^{-1}$
COMPRESSOR
COLUMN N°1
X_{D_2} = 0,2
X_{HD} = 0,8
X_{DT} ≈ 10^{-8} à 10^{-9}
≈ 10 l h^{-1}
BURNER
X_{DT} = 40 10^{-6}
165 l h^{-1}
CIRCULATOR
X_{DT} = 180 . 10^{-6}
COLUMN N° 2
≈ 2 Nl /week
X_{T_2} = 0,98
STORAGE
DRAWING OFF
OF TRITIUM
$DTO + D_2 \rightleftharpoons D_2O + DT$
$HDO + D_2 \rightleftharpoons D_2O + HD$
D_2O
DEUTERIUM
TRITIUM
HYDROGEN

Figure 1

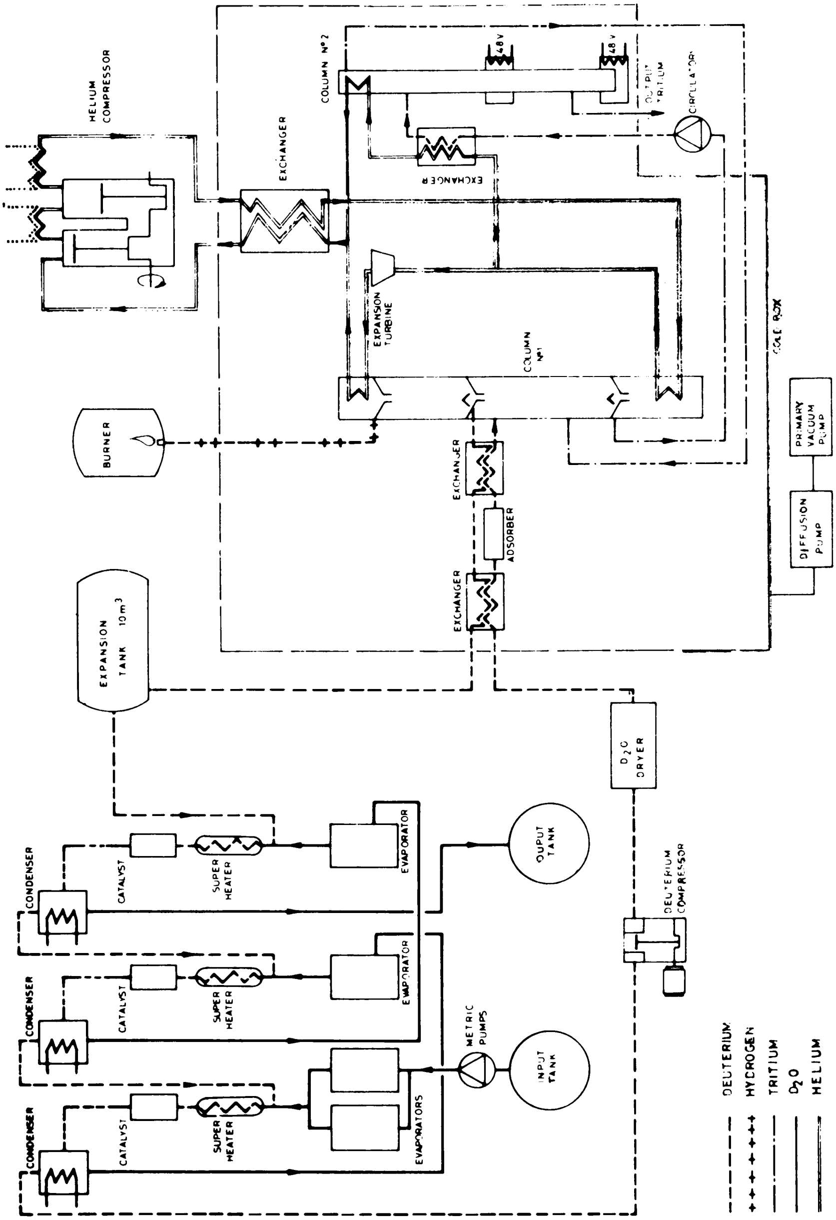
HELIUM COMPRESSOR
EXCHANGER
COLUMN N°2
48 V
48 V
OUTPUT TRITIUM
CIRCULATOR
EXCHANGER
EXPANSION TURBINE
COLUMN N°1
COLD BOX
BURNER
EXCHANGER
ADSORBER
EXCHANGER
PRIMARY VACUUM PUMP
DIFFUSION PUMP
EXPANSION TANK 10 m³
D₂O DRYER
CONDENSER
CATALYST
SUPER HEATER
EVAPORATOR
OUPUT TANK
CONDENSER
CATALYST
SUPER HEATER
EVAPORATOR
DEUTERIUM COMPRESSOR
METRIC PUMPS
CONDENSER
CATALYST
SUPER HEATER
EVAPORATORS
INPUT TANK
DEUTERIUM
HYDROGEN
TRITIUM
D₂O
HELIUM

Figure 2

Refrigeration power required to liquify deuterium is obtained by an auxiliary helium circuit. Helium is compressed to 15 bar and then expanded to 4 bar through a gas expansion turbine with oil bearings.

Plant Safety Precautions. The risks of explosion and radioactive contamination formed the basic criteria for the design, construction and operation of the installation. Very strict measures were adopted:

1. Location of the installation outside of the reactor but not in the open air. The external walls of the building are blowable to an open area to limit explosion damage.
2. Construction of the plant according to "hydrogen standards".
3. Constant ventilation of the premises.
4. Constant tritium and deuterium control of the atmospheric air of the premises.
5. Oxygen content in deuterium circuit is permanently registered at the inlet to the distillation column in order to have an indication about the quantity of ozone which could be formed by β-radiation of oxygen. Ozone in liquid or solid phase may decompose in an explosive manner.
6. In case of alarm from deuterium or tritium leakage, the plant is stopped and isolated in five parts. Each of these can be evacuated and rinsed automatically by nitrogen before repair works start.
7. A two stage membrane compressor can draw off the deuterium hold-up and fill into bottles under 200 bar.
8. Some main alarms and a main switch are repeated in the main control panel of the reactor.

Start-Up of the Plant and Operating Experience

The first tests with hydrogen began in August 1971. Start-up with deuterium and nontritiated heavy water followed quickly and separation performances between hydrogen and deuterium were controlled. It was only in August 1972 that the first introduction of tritiated heavy water from the High Flux Reactor was treated.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

By July 1973 the accumulation of tritium only reached 5 000 Curie. By the end of 1976 there was a tritium hold-up of 220 000 Curie in the plant and 230 000 litres of heavy water had been treated. About 85 000 Curie of pure tritium with an average molar content of 98% had been extracted in gaseous phase.

Since tritium production of the reactor is about 35 % lower and the admissible tritium concentration is now about 10 % higher compared with design data, and furthermore plant performance could be increased by about 25 % by variation of the ratio between heavy water and deuterium streams in the catalytic exchange, the plant is able to fulfil reactor requirements in only five months per year. That means plant overcapacity allows the treatment of tritiated water from other reactors.

The Institute has already treated about 16 000 l of heavy water with a concentration of about 6 Curie per litre for a French client.

At present, plant performance reaches an extraction of 240 000 Curie per year starting from a feed concentration of 2 Curie per litre. Tritium analysis made on the rectification columns showed that about 400 theoretical stages are installed.

Since leakage of light water into the heavy water circuit is smaller than presumed, the heavy water molar content has not reached 99,6 % up to now, and consequently light water extraction has been smaller than 160 litres per year.

Difficulties Encountered During Operation

Concerning the principal running of this process - catalytic exchange with deuterium rectification - no particular difficulties have been encountered.

The main difficulties which occurred during operation were:

- Two technological incidents on the helium circuit, the major being an accidental displacement of the molecular sieve, with subsequent distribution of its constituents through the whole helium circuit. This required complete cleaning of the helium circuit, particularly of the heat exchangers and caused a plant shutdown of several months.

- The other incident was the presence of mud and organic algae in the river water, which clogged the helium water cooler. Chlorination in the cooling water killed off the algae, but resulted in corrosion

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

of the welds on the carbon steel helium coolers, so that leakages of helium and ingress of water prevented the required refrigeration power being reached. Finally, new stainless steel coolers and a closed cooling water circuit were installed to get satisfactory conditions.

- The presence of alumina particles in the heavy water arriving from the reactor served as support for activation products - mainly cobalt and chrome - and resulted in high activity in the entrance of the catalytic exchange. The alumina particles have a size of 0,01 to 0,1 μ and pass through existing 0,22 μ filter. To prevent the presence of these activated alumina particles in tritium extraction plant, a supplementary separation plant has been installed in the reactor. This plant was put into operation satisfactorily some months ago.

- Fissure phenomena have appeared in the piping work containing heavy water vapor at the entrance in the first stage of catalytic exchange. The origin of these corrosions is not exactly known. Different experts think that these corrosions are due to the action of mechanical forces, caused by vibration and thermal expansion, acting in conjunction with a corrosive agent present in the heavy water. This agent may be chlorine. However, this fact is not yet proved.

- At the beginning nitrogen was used as cover gas in the reactor. Nitrogen dissolved in heavy water passed even through activated charcoal adsorber and was concentrated in the column evaporator reducing deuterium vapor load due to deterioration in heat transfer. Furthermore, a pH value of about 1 was noted in the heavy water leaving the burner, caused by nitric acid formed due to the presence of nitrogen coming from the nitrogen adsorber during its regeneration cycle. These inconveniences were resolved by replacing nitrogen by helium as reactor cover gas.

- During commissioning, different regulation systems could be improved but none of these improvements resulted from major problems.

- After about 23 000 hours of operation of the plant, the efficiency of catalysts has still not decreased.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

In the following I will indicate some operation conditions:

Plant operation is semiautomatic. Personnel are required to carry out various adjustments and maintenance concerned with the movement of heavy water and regeneration of the adsorbers and carrying out various analyses. During working hours, operation is ensured by four persons; outside working hours required supervision is transferred to the reactor main control room. At a stop, plant goes automatically into a safety position.

Operation of the plant is continuous, start up lasts about 12 hours and another 3 or 4 days are required to reach steady state conditions before treating tritiated heavy water.

The main consumptions are:

- Electricity	800 KW
- Cooling water	25 m^3/h
- Deuterium	2 Nm^3/week at todays conditions
- Compressed air	50 Nm^3/h

Hold-ups:

1 000	litres	of heavy water
85	Nm^3	of deuterium
200 000	Ci	of tritium
35	Nm^3	of helium

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RECEIVED August 22, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch012

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch013

13

Catalytic Detritiation of Water

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Mound Laboratory has, during the past four years, been actively involved in the development of methods to contain and control tritium during its processing and to recover it from waste streams. Initial bench-scale research was directed mainly toward removal of tritium from gaseous effluent streams. The gaseous effluent investigation has progressed through the development stage and has been implemented in routine operations. A test laboratory embodying many of the results of the research phase has been designed and its construction has been completed.

As the program at Mound Laboratory has progressed, the scope of the effort has been expanded to include research concerned with handling tritiated liquids as well. A program is presently under way to investigate the detritiation of aqueous wastes using the Combined Electrolysis Catalytic Exchange (CECE) process, a process very similar to the CECE-TRP process discussed at this symposium by Dr. Hammerli. As in the CECE-TRP process, the key to our CECE process is a precious metal hydrophobic catalyst developed by Dr. John Butler at Chalk River. Dr. Butler, who discussed this type of catalyst earlier in the symposium, made the catalyst for our system.

Catalytic Exchange

The catalytic exchange section of the process centers around two catalyst-packed columns, which are arranged in series to operate as if they were the upper and lower sections of a single column. (See Figure 1.)

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*Mound Laboratory is operated by Monsanto Research Corporation for the U.S. Energy Research and Development Administration under Contract No. EY-76-C-04-0053.

Each column is 7.5 m in length and has an inside diameter of 2.5 cm, which results in a superficial cross-sectional area of 5 cm^2 and a gross column volume of 3800 cm^3. The packing in each column consists of 4300 g of 0.6-cm diameter catalyst spheres. Liquid redistribution rings are placed at 45-cm intervals throughout the length of each column to limit channeling in the packed sections.

In operation, the liquid to be detritiated is supplied at approximately 5 cm^3/min. It is combined with the liquid stream exiting the upper column, and introduced at the top of the lower column. The 10 cm^3/min liquid stream from the bottom of the lower column is routed to the electrolysis section of the process where it is used as feed. Currently, the liquid stream entering at the top of the upper column is made up of distilled water, supplied from outside the process. Ultimately, however, this stream is expected to be a reflux stream, provided by a recombiner or fuel cell which would in turn be fed by the hydrogen product from the upper column.

The hydrogen stream from the electrolysis section is fed to the bottom of the lower column and then is routed to the bottom of the upper column. Upon exiting the upper column, it is currently vented to the atmosphere through a stack. As mentioned previously, however, it is anticipated that this stream will later be fed to either a fuel cell or a recombiner to provide reflux to the process and a detritiated liquid product.

Control of the catalytic exchange section of the process consists of five loops, serviced by a single microprocessor. In each of the loops the control element is a metering valve, driven by a stepping motor. For the gas stream passing through the columns, the sensing element is a turbine meter located downstream from the columns. The two liquid feeds to the process are sensed by hot-wire anemometers, and the levels maintained in the bottom of each column are monitored by capacitive level sensors. Although not used in the control of the process, tritium concentrations are monitored at various points by liquid scintillation counters for liquid streams and ion chambers for gas streams.

Electrolysis

The principal items of equipment in the electrolysis section are four General Electric electrolysis stacks. (See Figure 2.) Each stack consists of eight cells, each of which has an active area of 46.45 cm^2.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch013

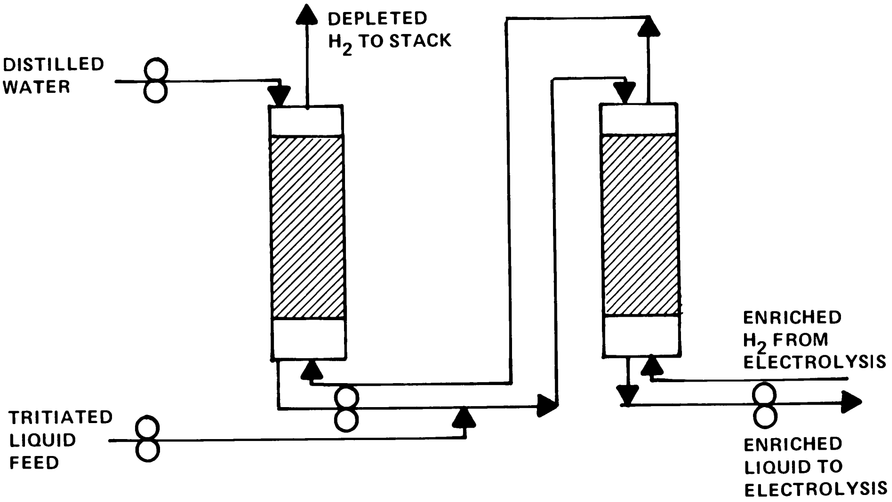

Figure 1. Catalytic exchange section

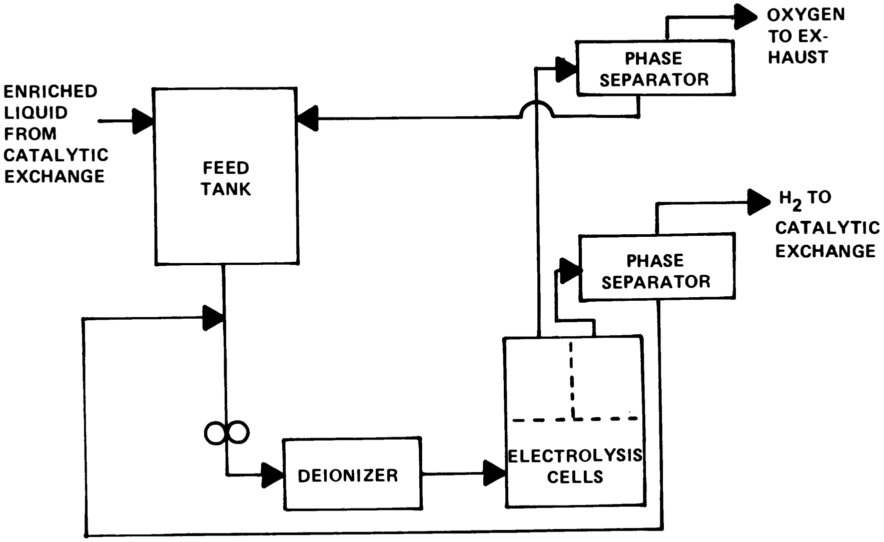

Figure 2. Electrolysis section

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Current density is 1.076 amp/cm for the maximum rated current of 50 amps. Rated stack voltage is 16.8 VDC. Operating at these conditions, each stack electrolyzes 2.45 cm^3 water/min to produce approximately 3000 cm^3 hydrogen/min and 1500 cm^3 oxygen/min. The maximum pressure is 100 psig and the upper limit temperature is 66°C. Proper stack operation requires that feed water resistivity be maintained at greater than 500,000 ohm-cm, and that a water circulation rate of approximately 400 cm^3/min per 8-cell stack be maintained.

Feed to the electrolysis section is supplied from a feed tank, which also provides recirculation capacity. From the feed tank, the water is pumped through a deionizer, and then to the cells. From the cells, the hydrogen stream passes through a cooler and a phase separator, and is returned to the catalytic exchange section. The oxygen stream, after being routed through a cooler and a phase separator, is currently sent to the air detritiation system for purification and disposal. It is anticipated, however, that this stream will ultimately be fed to a recombiner or a fuel cell supplying reflux to the catalytic exchange columns. The water removed from both the oxygen and hydrogen streams in the phase separators is mixed with the fresh feed upstream from the deionizer, and recirculated through the system.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch013

Preliminary Results

The CECE system was recently operated continuously for a period of approximately 48 hr. Water was fed both to the top of the first column and in between the columns, each at a rate of 3 cm^3/min. The top feed had a concentration of 0.028 μCi/liter while the mid-column feed, which can be considered the "hot" feed, had a tritium concentration of 304 μCi/liter. The total electrolysis stream, 7.2 liters/min, was returned to the bottom of the second column.

The depleted hydrogen stream exits the system at the top of the first column, where a portion of this stream is oxidized to water, collected in an ethylene glycol "bubbler", and analyzed for tritium using liquid scintillation counting. At the end of this 48-hr run, the water formed from this depleted hydrogen had a concentration of 0.006 μCi/liter, while the electrolysis water loop had been enriched to 386 μCi/liter. These results are summarized in Figure 3.

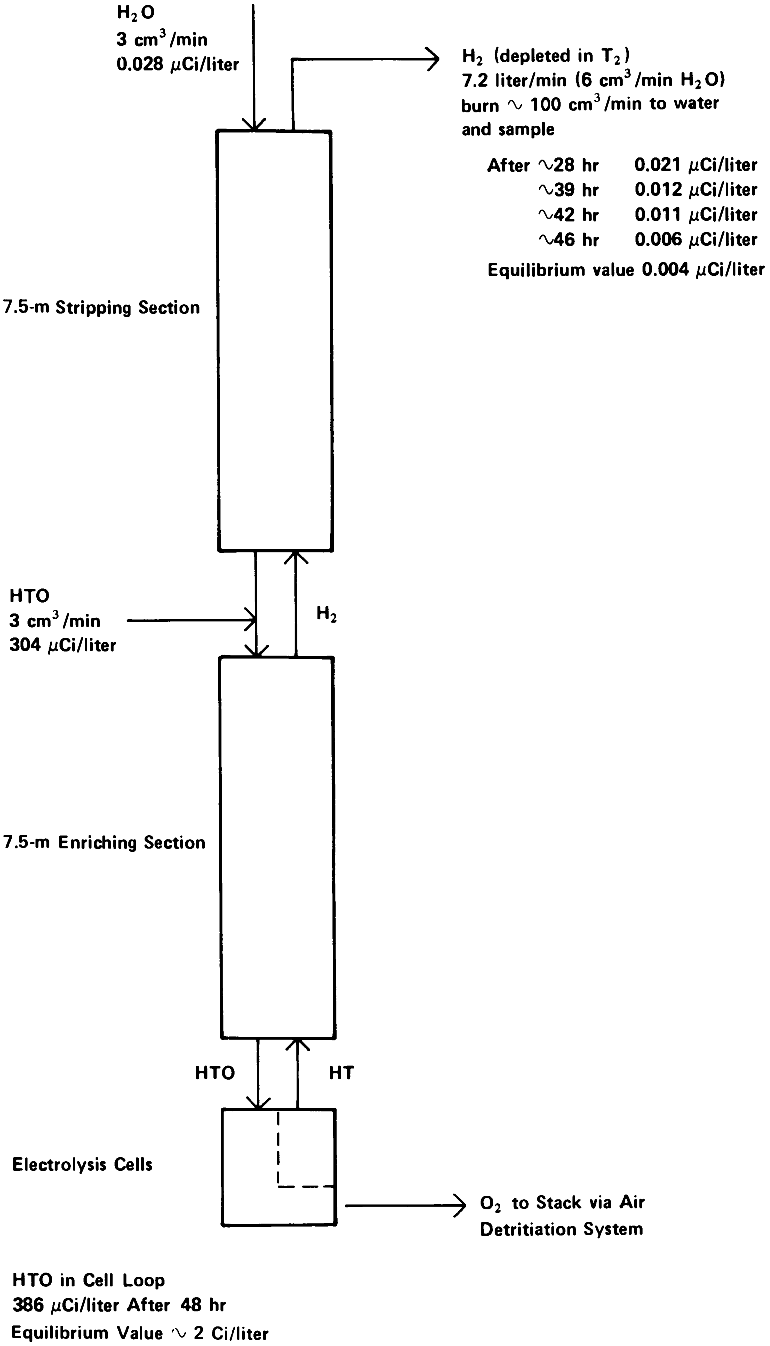

Figure 3. Preliminary results combined electrolysis catalytic exchange system (CECE)

Future Plans

The pilot CECE system will continue to be operated with goals of obtaining operating experience, determining scale-up parameters, and improving system dependability. Mound Laboratory also tentatively plans to build a larger system beginning in late 1978. This system would be used to treat aqueous tritiated waste for ERDA.

Abstract

A pilot-scale system has been used at Mound Laboratory to investigate the catalytic detritiation of water. A hydrophobic, precious metal catalyst is used to promote the exchange of tritium between liquid water and gaseous hydrogen. This catalyst was developed at Chalk River Nuclear Laboratories and is operated at 60°C. The catalyst is packed in two columns, each 7.5 m long by 2.5 cm i.d. Water flow is 5-10 cm^3/min and countercurrent hydrogen flow is 9000-12,000 cm^3/min. The equipment, except for the columns, is housed in an inert atmosphere glovebox and is computer controlled. The hydrogen is obtained by electrolysis of a portion of the water stream. Enriched gaseous tritium is withdrawn for further enrichment. This paper describes the system and outlines its operation, including experimental data.

RECEIVED August 10, 1977

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ch013

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Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ix001

In Separation of Hydrogen Isotopes; Rae, H.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1978.

Publication Date: June 1, 1978 | doi: 10.1021/bk-1978-0068.ix001

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