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PRELIMINARY STUDIES FOR THE SEPARATION OF
HD FROM H₂ BY RECTIFIED ABSORPTION

D. N. Hanson, C. d'A. Hunt, M. W. Cook, and J. L. Fick

March 17, 1952

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Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

March 17, 1952

ABSTRACT

The feasibility of rectified absorption for the recovery and purification of HD from H₂ streams has been investigated. The absorbent considered was liquid nitrogen at 78° K. The process appears to present no major engineering or operational problems. Cost calculations indicate that the process may be economically competitive with other processes. Process design was based on an estimated separation factor of 1.25 between H₂ and HD in this system. Experimental work has been undertaken to check the validity of this estimate and to investigate the possibility of using other absorbents such as hydrocarbons and fluorocarbons.

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INTRODUCTION

A review and evaluation of the methods proposed for the large scale production of heavy water up to 1945 is contained in Columbia Report No. A3229 by Maloney and Ray. In this report four processes were examined in detail. Of these the two which had been used during World War II, the electrolysis of water with catalytic exchange and the distillation of water, were found to be relatively unpromising. The two remaining processes, dual-temperature chemical exchange of H₂S and H₂O and distillation of hydrogen at 20° K were economically superior but involved development work which had not been completed up to that time. The H₂S - H₂O chemical exchange faced difficult corrosion problems. The low temperature distillation required hydrogen streams of extreme purity and development of operational techniques at the very low temperatures involved. However, the distillation process showed promise of being more economic than any others considered, and the Columbia report recommended that the major effort in future work go into its development.

The chief difficulty in the distillation process was associated with nitrogen impurity in the hydrogen feed stream. It was thought that unless

the nitrogen were completely removed before the stream entered the column, serious erosion and plugging might result. The number of hydrogen streams available in the country with a sufficiently low nitrogen content was small, enough to produce only 5 to 10 tons per month of heavy water, and the bulk of the hydrogen streams available contained nitrogen in such quantities that their use was not considered feasible.

An absorption process might also be considered for the separation of deuterium from gaseous hydrogen. If liquid nitrogen were employed as the absorbing medium, the nitrogen content of the hydrogen feed would not pose any serious problems, and the number of commercial hydrogen streams which might be processed would be greatly increased.

The use of absorption processes as alternatives to distillation for the recovery and purification of very light hydrocarbons has been studied extensively in the petroleum industry, and the results of those studies show that the two processes are economically competitive in that service. For H_2 - HD fractionation the absorption process operating at liquid nitrogen temperature levels would offer an advantage over distillation, since operational techniques at this level are well known in modern air separation plants.

In view of the results found in petroleum work and the advantages offered in the separation of HD from H_2 , an absorption process appears to have considerable promise, and a preliminary study has been made to determine its feasibility and cost.

GENERAL PROCESS DESCRIPTION

The possibility of a difference in the solubilities of H_2 and HD in a given liquid solvent indicates that an absorption process may be used to effect the recovery of HD from H_2 . In absorption alone the percent recovery of HD is determined by the characteristics of the absorbing section of a countercurrent flow column; however the maximum purity of HD in the absorbed product is limited by the equilibrium conditions between the feed and the absorbent.

If reasonable purities of HD are desired, then an enriching section below the absorbing section is added to the column. The vapor for the countercurrent gas - liquid flow which produces the enrichment is obtained from a stripping operation which separates the dissolved gas from the liquid stream and purifies the absorbent. The pure absorbent is then recycled to the top of the absorber, and the enriched gas product is withdrawn from the vapor returned to the enriching section. If necessary a feed preparation unit and an absorbent recovery unit are added to the system. This process is known as rectified absorption. (See Figure 1.)

The primary variables which must be considered in the design of such a process are temperature, pressure, relative liquid and vapor flows, and the nature of the absorbent. For any given absorbent there will be an optimum choice of the operating variables which can be determined only by detailed analysis based upon phase equilibrium data.

The solvent chosen for the first detailed analysis was liquid N_2 , because of the availability of phase data for the $H_2 - N_2$ system. The use of liquid nitrogen has the advantage that processing a $3H_2 - N_2$ feed stream

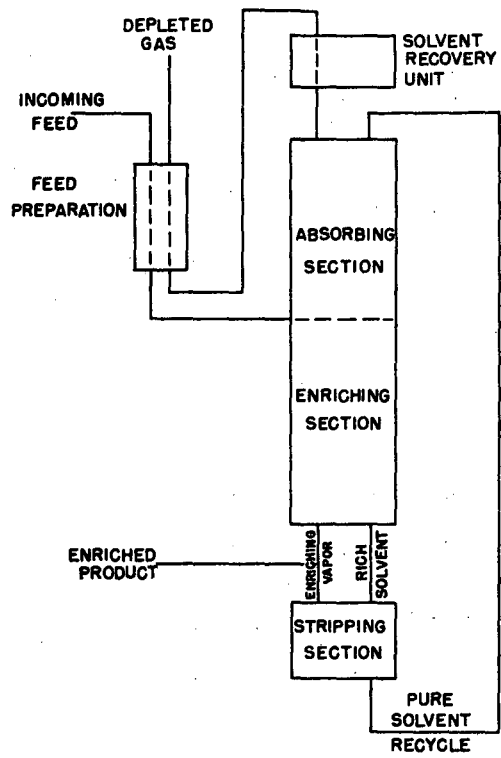


FIG. 1
SCHEMATIC DIAGRAM
OF
RECTIFIED ABSORPTION PROCESS

from an ammonia plant does not involve a solvent recovery unit or major feed purification.

The production of vapor for operation of the rectified absorber and the purification of the liquid nitrogen can be accomplished in different ways. Essentially these evolve into two extremes, a constant temperature process and a constant pressure process, although many combinations are possible.

In the constant temperature process, the stripping section consists of a series of practically isothermal throttling expansions of the liquid with recompression of the resulting flashed gas in order to return it to the enriching section. The lowest pressure reached is the vapor pressure of pure liquid nitrogen at the chosen temperature of operation. The liquid nitrogen is purified in a final stripping unit at the lowest pressure reached. Energy is added at each of the recompression stages; this energy is utilized as heat to provide vapors for the stripping unit and is finally removed by an auxiliary refrigeration system. (See Figure 2.)

The alternative process involves a constant pressure nonisothermal system. The liquid from the enriching section is preheated countercurrent to the purified absorbent returning to the absorber and is separated from the enriched gas in a distillation column. The stripping vapors for this unit are obtained by pumping the heat given up by the cold condensing vapors at the top of the column to the hotter liquid in the reboiler. In addition the temperature difference across the liquid stream heat exchanger requires additional heat pumping. As in the isothermal process an auxiliary refrigeration system is provided. (See Figure 3.)

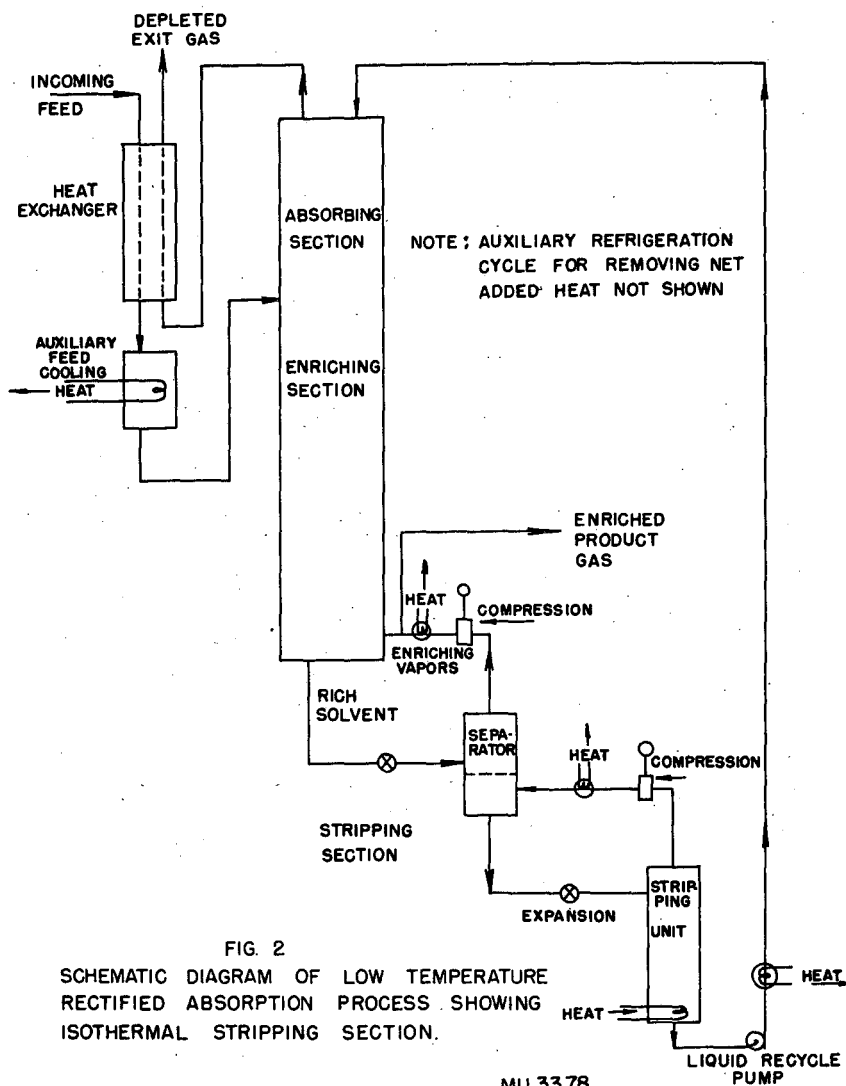
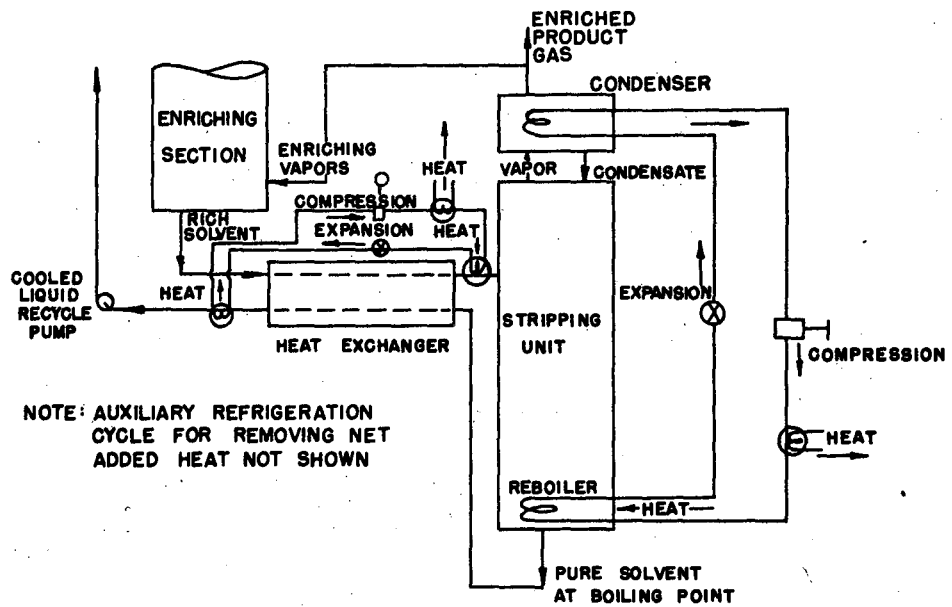


FIG. 2
SCHEMATIC DIAGRAM OF LOW TEMPERATURE
RECTIFIED ABSORPTION PROCESS SHOWING
ISOTHERMAL STRIPPING SECTION.

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NOTE: AUXILIARY REFRIGERATION
CYCLE FOR REMOVING NET
ADDED HEAT NOT SHOWN

FIG. 3

SCHEMATIC DIAGRAM OF NON ISOTHERMAL
CONSTANT PRESSURE STRIPPING SECTION
FOR RECTIFIED ABSORPTION PROCESS

MU33 79

ESTIMATION OF PHASE DATA FOR SYSTEM $H_2 - HD - N_2$

Two sets of data are available for the binary system $H_2 - N_2$ in the region of $68^\circ K$ to $113^\circ K$ and 12 atm to 90 atm.^{1,2} These data are reproduced in part on Figures 4, 5, and 6. The temperature selected for process design was $78^\circ K$ and the vapor liquid equilibria for use in this report were estimated at this temperature. Unfortunately, adequate data are not available below 17 atm and since much of the proposed process operates below this pressure it was necessary to extrapolate over a considerable range. For extrapolation of the nitrogen data, Raoult's Law was used, and for extrapolation of the hydrogen data, Henry's Law was used. In the latter case, however, the experimental data gave varying values of the Henry's Law constant, and it was decided to use a line corresponding to this variation. The uncertainty of these estimated data is expected to have only a secondary effect on process economics.

No data are available on the systems $D_2 - N_2$ or $HD - N_2$; however vapor pressure data are available for H_2 and HD . Since the solubilities of H_2 and HD in the nitrogen are low in the process under consideration, interactions in the liquid phase between the H_2 and HD may be assumed to be small, and ternary data may be estimated from data on the $H_2 - N_2$ system and the $H_2 - HD$ system. In Figure 7 the relative volatility of $H_2 - N_2$ has been extrapolated from the highest temperature at which this liquid - vapor system exists ($33^\circ K$) to the operating temperature of $78^\circ K$. As

1. Verschoyle, T.T.H., Trans, Roy. Soc., A, 230, 189 (1931).

2. M. Ruhemann and N. Zinn, Zeit. d. sowjetunion, 12, 389 (1937).

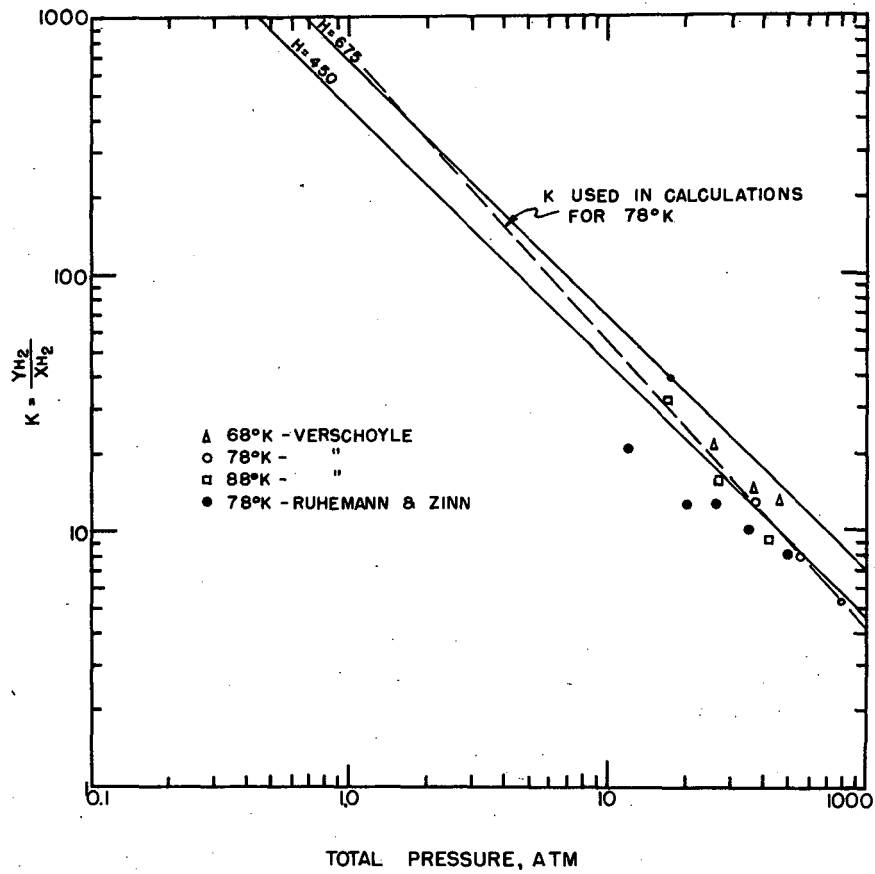


FIG. 4
EQUILIBRIUM CONSTANT FOR H₂ IN
THE SYSTEM N₂-H₂

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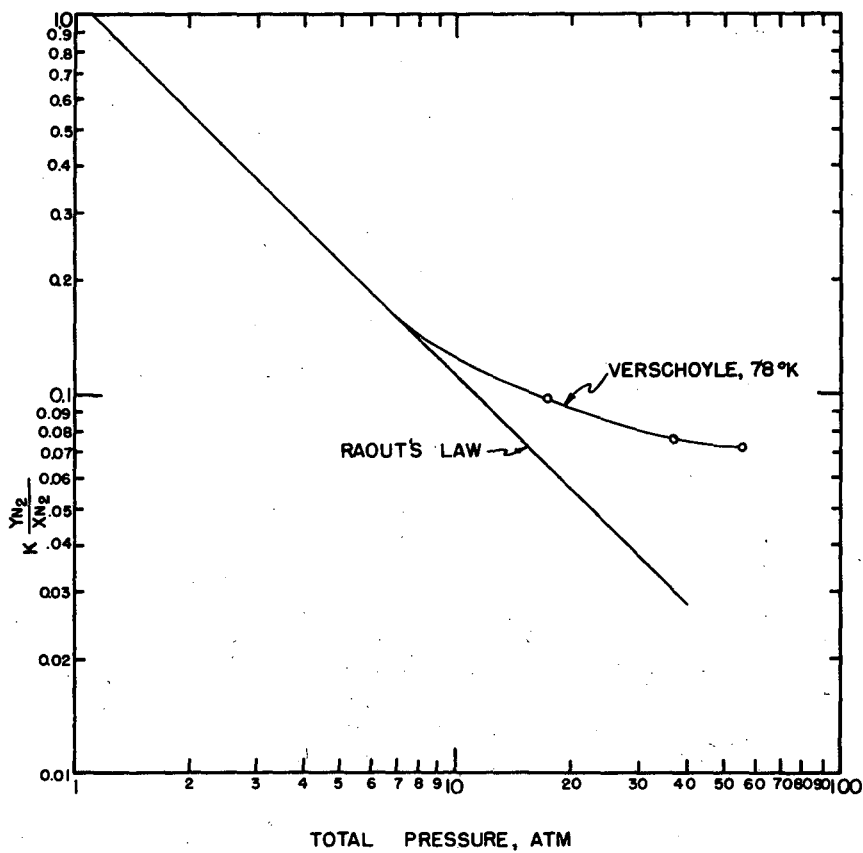


FIG. 5
EQUILIBRIUM CONSTANT FOR N₂ IN
THE SYSTEM N₂-H₂ @ 78°K

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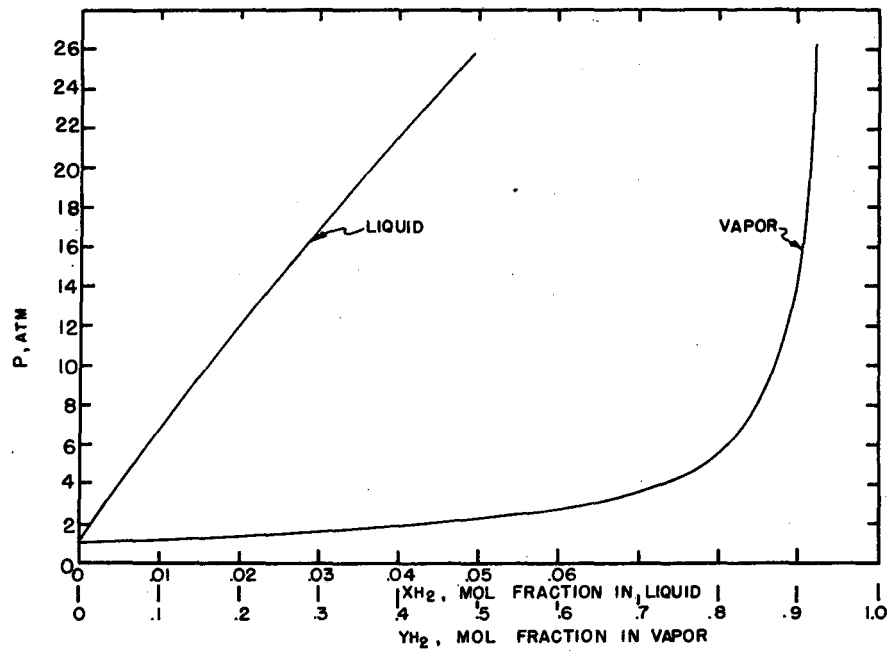


FIG. 6
TOTAL PRESSURE vs. COMPOSITION
VAPOR LIQUID EQUILIBRIA OF $H_2 - N_2$ SYSTEM
AT $78^\circ K$

MU3382

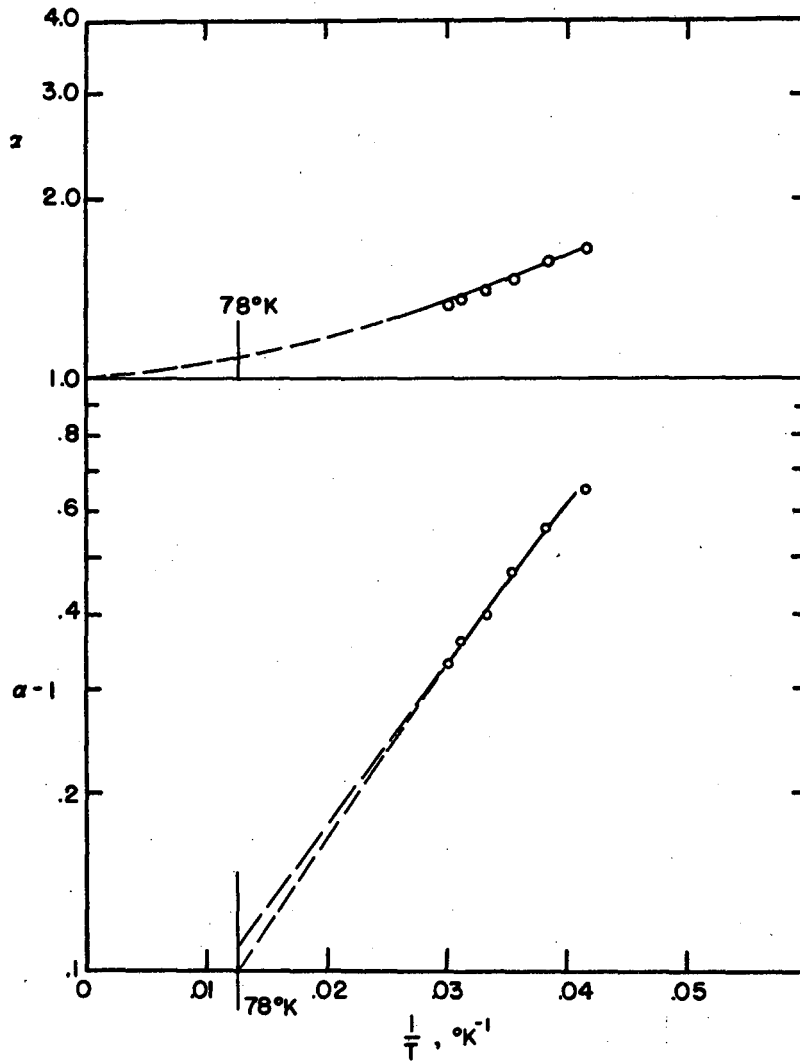


FIG. 7
EXTRAPOLATION OF IDEAL RELATIVE
VOLATILITY FOR H₂-HD
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will be noted from Figure 7 this extrapolation is uncertain but appears to give an ideal relative volatility of about 1.10. In addition to this relative volatility, due to the difference in extrapolated vapor pressure ratio, there is an additional effect due to the difference in degree of nonideality of the solutions of H_2 in N_2 and HD in N_2 . On the basis of regular solution theory¹ and using an ideal relative volatility of 1.10, the calculated relative volatility of H_2 to HD in liquid nitrogen is found to be 1.25. This figure was used as a basis for the cost calculations.

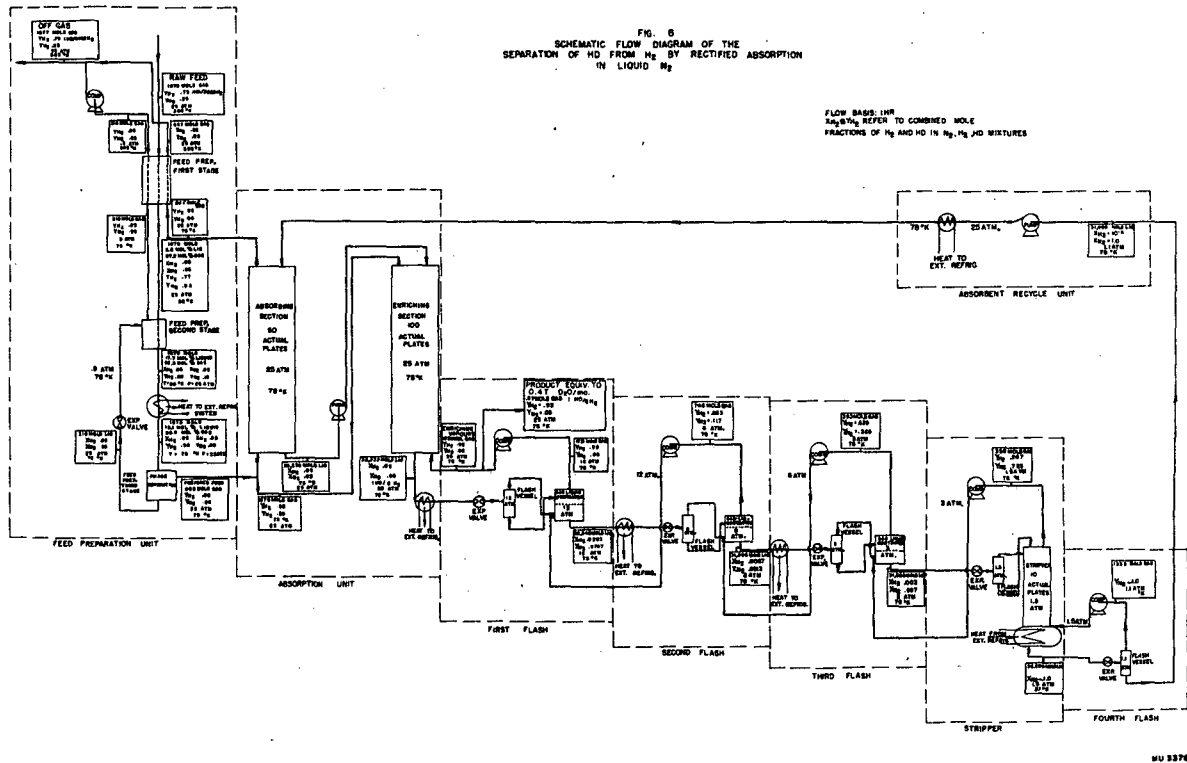
Detailed Process Description

A plant has been designed to produce 2.4 tons per month of D_2O by separating HD from a $3H_2 - N_2$ stream by means of rectified absorption in liquid nitrogen. The feed enters with a concentration of 1 mole of HD per 3500 moles of H_2 , and the product is enriched to 12.5 mole percent HD in this stage of the process. Further purification does not affect the economics significantly.

Figure 8 shows a schematic flow diagram of a unit with one-sixth of the total production capacity, and the complete process is six such units operating in parallel. An arbitrary upper limit of six foot diameter towers dictated this multiplicity of apparatus.

This process is to be operated in conjunction with an ammonia plant; so the feed of $3H_2 - H_2$ is assumed to be available at 25 atm and $308^\circ K$.

1. J. H. Hildebrand and R. L. Scott, "The Solubility of Non Electrolytes," A.C.S. Monograph, Reinhold Publishing Corp, New York, 1951.



Preparation of the feed consists of cooling by heat exchange with the HD depleted low temperature gas stream from the absorber and providing a small amount of auxiliary refrigeration. The primary heat exchanger removes the bulk of the sensible heat from the feed and also serves to condense a small portion of the nitrogen. The secondary heat exchanger, along with the auxiliary refrigeration, cools the feed down to the operating temperature of 78° K and condenses sufficient nitrogen to provide a feed saturated with nitrogen at 78° K and 25 atmospheres. The nitrogen which is condensed from the feed stream is throttled to 0.9 atmospheres to provide a coolant at 76° K in the secondary heat exchanger. The vapor from this exchanger is fed to the primary heat exchanger to provide further cooling. The primary heat exchanger consists of three channels: (1) the incoming feed gas, (2) the one atmosphere N₂ stream, and (3) the 25 atmosphere depleted gas stream. The one atmosphere N₂ stream is then recompressed to 25 atmospheres, mixed with the depleted gas, and returned to the ammonia process.

Since the rectified absorption process involves a high liquid-to-vapor flow ratio, a quadruple-weired column is proposed to allow reasonable apparatus size. With this arrangement, a flow of about 2000 GPM in a six foot diameter column can be realized. Several designs which provide a high weir length to diameter ratio are presently being considered.

The contacting apparatus may be considered in two sections, the upper or absorbing section which provides the necessary recovery of HD, and the lower or enriching section which provides the required purity. The absorbing section consists of 50 actual plates and the enriching section 100

actual plates, based on an assumed plate efficiency of 40 percent. Plate efficiencies must be determined experimentally for this system, because no suitable correlation for a reliable prediction is available.

The phase data may not be very reliable; so only one set of operating conditions was investigated. For the same reason, only an isothermal multiple flash stripping system has been studied (See Figure 2). When reliable data are available, a more thorough investigation will be made to find the optimum operating conditions.

To provide the necessary auxiliary refrigeration for the process, a propane-ethane-methane-nitrogen cascade system is proposed. This system comprises 60 percent of the capital cost. Since 50 percent of the refrigeration system is required to remove the energy of recycle pumping from the liquid nitrogen, a constant pressure stripping system will be studied to determine whether this process might be more economic.

The following cost tabulation (Table 1) is based primarily on Chilton's article in Chem. Engr., June, 1949. Materials of construction are carbon steel at temperatures above 165° K and austenitic stainless steel at lower temperatures.

Table 1
Detailed Cost Analysis

Capital Costs

I. Feed Preparation

1. Heat Exchangers

(a) 308° to 165° K, 40,400 ft ² , 11.6 M ² Btu/hr, carbon steel	\$ 40,500
(b) 165° to 76° K, 21,800 ft ² , 6.31 M ² Btu/hr, stainless steel	150,000
(c) 76° K, 6,500 ft ² , 0.29 M ² Btu/hr stainless steel	72,000
(d) Auxiliary cooler, 76° K, 4330 ft ² , 0.49 M ² Btu/hr, stainless steel	48,000
2. N ₂ compressor, 0.9 to 25 atm, 308° K, 2420 B.H.P., 80% efficient	<u>181,400</u>
Sub total	\$ 491,900

II. Columns and Strippers

1. 6 absorber sections, 6'D., 50 plates each	300,000
2. 6 enriching sections, 6'D., 100 plates each	600,000
3. 24 flash chambers, 6'D, 6' high	<u>288,000</u>
Sub total	1,188,000

III. Stripper Auxiliaries

1. 30 intercoolers and boilers, 30,000 ft ²	180,000
2. 6 primary liquid N ₂ pumps, 3640 B.H.P. total	50,000
3. 6 secondary liquid N ₂ pumps, 310 B.H.P. total	11,000
4. Heat exchanger to remove pumping energy, 26,500 ft ²	180,000
5. 36 interstage compressors, 2610 B.H.P.	<u>367,000</u>
Sub total	788,000

IV. Refrigeration, central unit to perform all cooling jobs.

1. Heat exchangers

(a) CH ₄ cycle, 34,900 ft ² , 34.9 M ² Btu/hr, stainless steel,	200,000
(b) C ₂ H ₆ cycle, 66,600 ft ² , 66.6 M ² Btu/hr, stainless steel	290,000
(c) C ₃ H ₈ cycle, 108,000 ft ² , 108 M ² Btu/hr, carbon steel	72,000
(d) H ₂ O cooling, 162,000 ft ² , 162 M ² Btu/hr, carbon steel	80,000

2. Compressors

(a) CH ₄ cycle, 7,070 HP, stainless steel	920,000
(b) C ₂ H ₆ cycle, 11,950 HP, stainless steel	1,560,000
(c) C ₃ H ₈ cycle, 16,370 HP, carbon steel	820,000
(d) H ₂ O cycle, 21,100 HP, carbon steel	<u>1,000,000</u>

Sub total 5,407,500

Total 7,874,000

Add:

30% for Piping

2% for Instrumentation

5% for Buildings

10% for Auxiliaries

3% for Outside Lines
50%

Total physical cost 11,820,000

Add:

25% for engineering and construction 14,790,000

Amortize at five years, Annual Capital Cost 2,958,000

V. Annual Operating Cost

1. Total power, 46,600 K.W., at 2 mils/kwh	1,810,000
2. Labor, 120 man hours/day	<u>72,000</u>
Subtotal operation cost	1,882,000
Subtotal annual cost	4,840,000
Add 10% for maintenance and miscellaneous overhead	484,000
Total annual cost	5,324,000
Cost/ton D ₂ O	<u><u>185,000</u></u>

DISCUSSION

On the basis of the particular process design which has been analyzed in this report, the use of rectified absorption for the recovery and purification of deuterium from hydrogen rich gas appears to hold some promise. The cost data shown in the previous section indicate a figure of approximately \$185,000 per ton of D₂O, to be compared with costs of \$132,000/ton for distillation of hydrogen and \$153,000/ton for the H₂S - H₂O exchange process. However, these latter costs were based on equipment costs levels of the period 1942-45 while the costs reported for the rectified absorption process were based on 1949 levels.

The present process design is undoubtedly not the most economic which could be devised for the rectified absorption method. The major costs of the process obviously lie in the external cascade refrigeration system and are governed by the mechanical energy introduced into the low temperature process by the liquid nitrogen recycle pump and by the compressors for recompressing the flash vapors. The largest item here is the energy input of the liquid nitrogen pump, and this can be eliminated almost completely in the constant pressure process or can be materially reduced by operation of the constant temperature process at the same pressure but at a higher temperature level than the 78° K level chosen here. On the other hand, the energy input of the heat pump compressors can also be expected to undergo considerable change with these variations. Without detailed calculation the effect on the total cost is impossible to predict.

Several possibilities do exist for reducing the costs of the process. The temperature level of the operation may be increased to such a point

(at 25 atm, approximately 90° K) that the saturated vapor is $3\text{H}_2 - \text{N}_2$, so as to reduce the cost of feed preparation. Also an increase in recovery of deuterium from 50 percent, as used here, to nearly 100 percent would again reduce these feed processing cost, while not affecting significantly the other costs of the process. The constant pressure process, while requiring a large amount of heat exchange between the "rich" nitrogen and "lean" nitrogen streams and perhaps a larger capital investment would reduce the operating costs by approximately half. Lastly, increase in process temperature level very rapidly lowers the horsepower requirements of the external refrigeration system for the same amount of heat pumping. In view of these possibilities and of the large number of processes which could be devised, the ultimate reduction of costs by a sizeable amount seems a certainty.

Despite the importance of the process design, however, the major influence on cost is the value of the relative volatility (α') between H_2 and HD. The costs reported in this report have been calculated on a relative volatility of 1.25. Since the total cost is roughly inversely proportional to $\alpha - 1$, an α of 1.10 would increase the costs by a factor of about 2.5 and would place the process in a distinctly unfavorable economic position unless the process design could be changed to affect very substantial savings. This factor is of such importance that an experimental program for determination of the vapor-liquid equilibrium data for the system $\text{H}_2 - \text{HD} - \text{N}_2$ has been undertaken. The apparatus for these determinations has been designed and is now being constructed.

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The possibility of employing absorbents other than liquid nitrogen is also being considered. The light hydrocarbons and fluorocarbons appear to have promise and could be used at temperatures up to cooling water levels with obvious advantage. Experimental work is presently being done on the solubilities of H_2 and D_2 in a series of prospective solvents in order to determine the relative volatility.

Rectified absorption appears to be a feasible process for the recovery of deuterium from hydrogen streams. The economics of such a process, in comparison with low temperature distillation and with exchange processes, are considerably in doubt because of the uncertainties in the basic physical data. However, the process may be economically and operationally competitive. The process does offer advantages, since it can use directly $3H_2 - N_2$ streams from ammonia plants, and does not involve any wide departure from existing engineering practice.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

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