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LOW TEMPERATURE DISTILLATION OF HYDROGEN ISOTOPES

by

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INTRODUCTION

Low temperature distillation has been used successfully by several investigators to fractionate H_2 -HD- D_2 mixtures.^{1,2,3} In fact, Clusius and Starke² came to the conclusion that distillation was more economical than electrolysis for obtaining pure D_2 . The existence of low temperature facilities at this Laboratory, coupled with the interest of the Atomic Energy Commission in pure tritium, prompted the design and construction of a distillation apparatus to separate pure tritium from contaminating isotopes. Unfortunately the project had to be abandoned before a tritium mixture was distilled; however, it is felt that the design problems peculiar to tritium that were considered are worth reporting as well as the results of an initial experiment in which an H_2 -HD- D_2 mixture was fractionated with the still built for tritium distillation.

A distillation column designed for tritium must make allowance for the relatively large amount of heat generated by beta decay. Since the range of the tritium beta in the liquid is only a small fraction of a millimeter, all the beta energy will go toward raising the temperature of the still pot. The heat input in pure liquid T_2 from this source amounts to 0.091 watts/cc. Thus, a charge of 5 cc of liquid T_2 would generate 0.455 watts, which is 1.6 times the heat input used in the distillation reported here. It is clear, then, that the still pot must be designed so that any excess heat can be dissipated to prevent flooding of the column. Also, the holdup of liquid in the packing must be very small; otherwise the tendency will be to establish a uniform temperature along the column thereby drastically reducing the number of plates. The distillation apparatus described here was designed to minimize holdup and to permit removal of varying amounts of heat from the pot; the effectiveness for use with tritium remains to be tested, however.

It has been shown by Hoge and Arnold⁴ that mixtures of H_2 and D_2 form nearly perfect solutions. By assuming that Raoult's law holds for all the hydrogen isotopes, it becomes a simple matter to estimate the number

¹R. B. Scott and F. G. Brickwedde, *Phys. Rev.*, 48, 483 (1935).

²K. Clusius and K. Starke, *Z. Naturforsch.*, 4a, 549 (1949).

³A. Fookson, P. Pomerantz and E. Rich, *J. Res. NBS*, 47, No. 1, 31, (1951).

⁴H. J. Hoge and R. D. Arnold, *J. Res. NBS*, 47, No. 2, 63 (1951).

of theoretical plates necessary to separate any pair. The method of McCabe and Thiele⁵ was used to estimate the number of plates required to strip H₂ from HT (or D₂) and H₂ from T₂ so that the resulting products would be 99.5% pure. For the first pair it was found that seven plates were necessary, and for the second four plates were required. The vapor pressures for the various molecules at the boiling point of normal hydrogen are given in Table 1; a reflux ratio of 10 and a feed of 25 mole per cent H₂ were chosen for the calculation. The result indicated that a modest column would produce material of satisfactory purity.

Table 1

Molecule	Vapor Pressure at 20.39°K (mm of Hg)	Source
H ₂	760	Grilly, J. Am. Chem. Soc., <u>73</u> , No. 2 843 (1951)
HD	437	Hoge and Arnold, J. Res. NBS, <u>47</u> , No. 2, 63 (1951)
D ₂	256	Grilly, J. Am. Chem. Soc., <u>73</u> , No. 2 843 (1951)
HT	254 ± 16	Libby and Barter, J. Chem. Phys., <u>10</u> , 184 (1942)
DT	184	Friedman, White and Johnston, J. Chem. Phys., <u>19</u> , No. 1, 126 (1951)
T ₂	145	Grilly, J. Am. Chem. Soc., <u>73</u> , No. 2, 843 (1951)

APPARATUS

The apparatus consisted of a double Dewar cryostat, a glass distillation column, and a vacuum line.

The outer cryostat Dewar contained liquid nitrogen; and the inner Dewar contained liquid hydrogen. The distillation column, shown in Figure 1, was immersed in the liquid hydrogen. The 5 cc pot was surrounded by a glass jacket which was connected to the vacuum line through a small monel tube. By this means it was possible to introduce varying pressures of He into the jacket and thus regulate the heat leak from the pot to the hydrogen bath. The pot also contained an internal tungsten heater. The

⁵McCabe and Thiele, Ind. Eng. Chem., 17, 605 (1925).

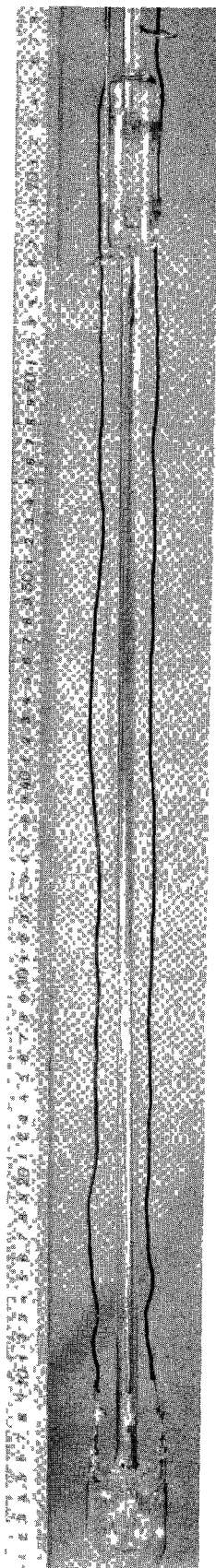
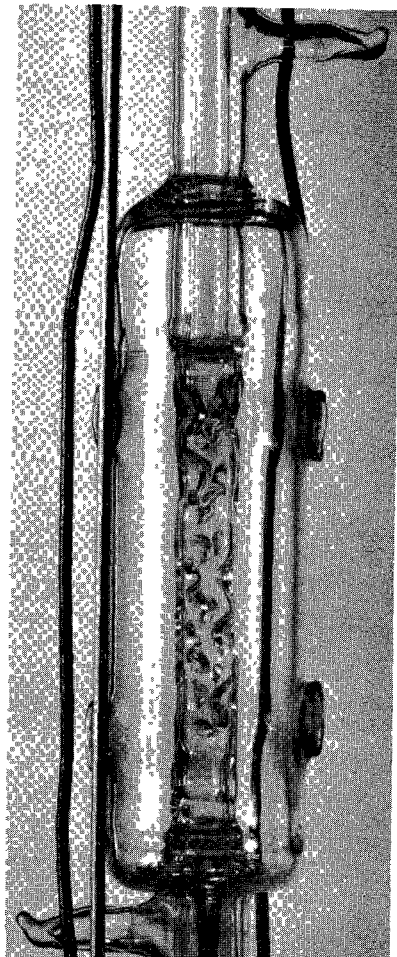
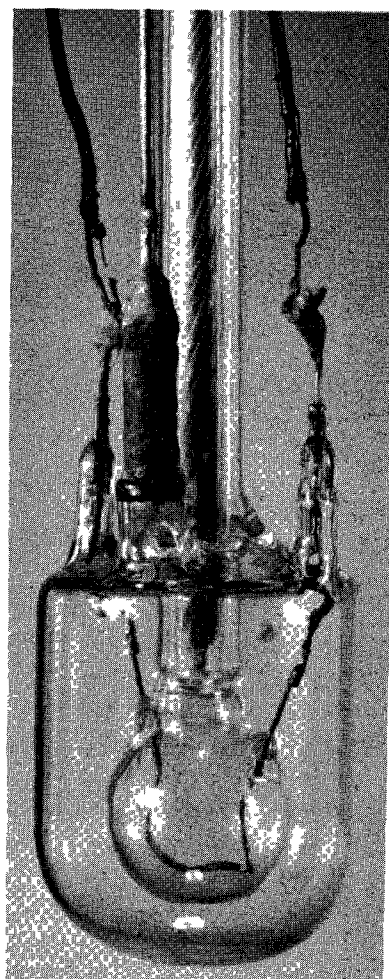


Figure 1
Distillation Column



vacuum-jacketed distillation column was fabricated from a 60 cm length of Pobdielniak "Heligrad" packing contained in a 0.4 cm i. d. glass tube. The packing was estimated to have at least 25 theoretical plates. The condenser (see Figure 1) was in direct contact with the hydrogen bath.

A mercury manometer for measuring the pressure in the still at the temperature of the condenser was connected to the take-off tube through a cold trap. The manometer was attached to the vacuum line so that measured volumes of gas could be admitted or withdrawn from the still.

EXPERIMENTAL

A mixture of H₂ and D₂ (83 atom per cent D and 17 atom per cent H) was purified and equilibrated over powdered uranium at 350° to 400°C. The Dewars were filled with liquid nitrogen and liquid hydrogen, and the gas was condensed into the distilling pot. An atmosphere of He in the jacket surrounding the pot served to transfer heat from the pot to the hydrogen bath. About one hour was required to complete the condensation of 4500 cc of gas.

The He pressure was reduced to 10 μ , and 0.200 watt of heat was supplied to boil the liquid in the pot. The charge was allowed to boil under total reflux for a period of one hour before the system came to equilibrium, as indicated by a constant pressure of 975 mm. Since the reflux ratios of all cuts were greater than 20, the observed still pressure was always approximately equal to the equilibrium pressure of the distillate at the temperature of the condenser. Therefore, a constant pressure indicated a constant isotopic composition of the distillate, and a changing pressure indicated a changing isotopic composition.

The first cut (see Table 2, sample 1) was forerun taken from the still manometer. During the second cut the pressure fell rapidly to 630 mm, since nearly all of the H₂ in the charge was distilled by the end of this cut. The pressure gradually decreased to 620 mm during the third cut. The heat input was then increased to 0.285 watt; this caused the pressure to increase to 700 mm. The pressure remained constant during the fourth cut which indicated that the distillate was high purity HD. At this point it was necessary to interrupt the run, since time did not permit the entire distillation to be completed in one day. The undistilled material was allowed to vaporize and expand into evacuated storage bulbs on the vacuum line.

The distillation was resumed on a subsequent day using the same start-up technique described above. All the previously undistilled material was transferred back into the still so that the results can be treated as if the distillation was continuous, except for a second forerun sample (see Table 2, sample 5). This second part of the distillation was carried out at

a constant heat input of 0.285 watt. The distillation was continued until the pressure indicated only high purity D₂ remained in the still. The total volume distilled was 1515 cc STP, and the residue in the pot and column was 2939 cc STP.

RESULTS AND DISCUSSION

A summary of the results is given in Table 2. N_{H₂}, N_{HD} and N_{D₂} are the mole fractions of H₂, HD, and D₂, respectively. The isotopic compositions were obtained by mass spectrometer analyses. Due to the small volume of H₂ in the charge no attempt was made to obtain a cut of high purity H₂. Samples 4, 6, 7, 8, 9, and 10 combined represent a total of 1033 cc of distillate of which 97.6% was HD, 0.2% was H₂ and 2.2% was D₂; the volume of HD in these samples was 81% of the total HD in the original charge. A total of 2964 cc of gas was isolated which contained 99.7% D₂ and 0.3% HD; the volume of this D₂ was 95% of the total D₂ in the original charge.

A plot of the pressure vs. the volume distilled for samples 6 through 12 is shown in Figure 2. Included for comparison is the atom fraction deuterium vs. the volume distilled. The fact that the pressure curve breaks at about 700 cc, whereas the atom fraction curve does not break until about 775 cc, is due mainly to hold-up of gas in the still head.

A mass balance is given in Table 3. The values in the row distilled plus residue were obtained by summation of the results given in Table 2. The analysis of the original charge was made before starting the distillation.

Although no attempt was made to operate the still under ideal conditions, the data are sufficient to show that H₂ and HD were effectively stripped from D₂.

It has been shown⁶ that at room temperature, tritium β-rays promote the equilibrium reaction H₂ + T₂ = 2HT in the gas phase. The equilibrium constant for this reaction at 20°K and 25°K was calculated from the relation:

$$- R \ln K = \Delta \left(\frac{F^0 - E_0^0}{T} \right) + \Delta \frac{E_0^0}{T}$$

The values of $-\left(\frac{F^0 - E_0^0}{T}\right)$ for H₂ were taken from the table of Woolley, Scott, and Brickwedde⁷ and the values of $-\left(\frac{F^0 - E_0^0}{T}\right)$ for HT and T₂ as well as the value of ΔE_0^0 were those calculated by Jones.⁸ Table 4 gives the calculated

⁶L. M. Dorfman and H. C. Matraw, KAPL-900, April 2, 1953.

⁷H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Res. NBS, 41, 379 (1948).

⁸W. M. Jones, J. Chem. Phys., 16, No. 11, 1077 (1948).

Table 2

SUMMARY OF RESULTS

Sample No.	N _{H₂}	N _{HD}	N _{D₂}	Volume of Sample (cc SIP)	Reflux Ratio	Take-Off Rate (cc/minute)	Remarks
1	0.324	0.439	0.237	5.6	--	--	Forerun
2	0.691	0.250	0.059	159.7	61	3.5	
3	0.056	0.906	0.038	154.5	101	3.0	
4*	0.006	0.976	0.018	174.6	42	7.3	
5	0.006	0.582	0.412	23.2	--	--	Forerun
6	0.005	0.969	0.026	177.8	78	3.9	
7	0.000	0.981	0.019	177.2	53	5.7	
8	0.000	0.985	0.015	173.6	23	13.4	
9	0.000	0.982	0.018	171.8	22	13.7	
10	0.000	0.959	0.041	154.2	52	5.8	
11	0.000	0.288	0.712	117.9	69	4.4	
12	0.000	0.004	0.996	24.7	--	--	
13	0.000	0.003	0.997	2939.0	--	--	Residue in Pot

*The distillation was interrupted after sample No. 4.

Table 3

MASS BALANCE

Sample	N _{H₂}	N _{HD}	N _{D₂}	Volume H ₂ (cc)	Volume HD (cc)	Volume D ₂ (cc)	Total Volume (cc)
Original Charge	0.033	0.273	0.694	149	1233	3135	4517
Distilled Plus Residue	0.028	0.279	0.693	125	1243	3086	4454

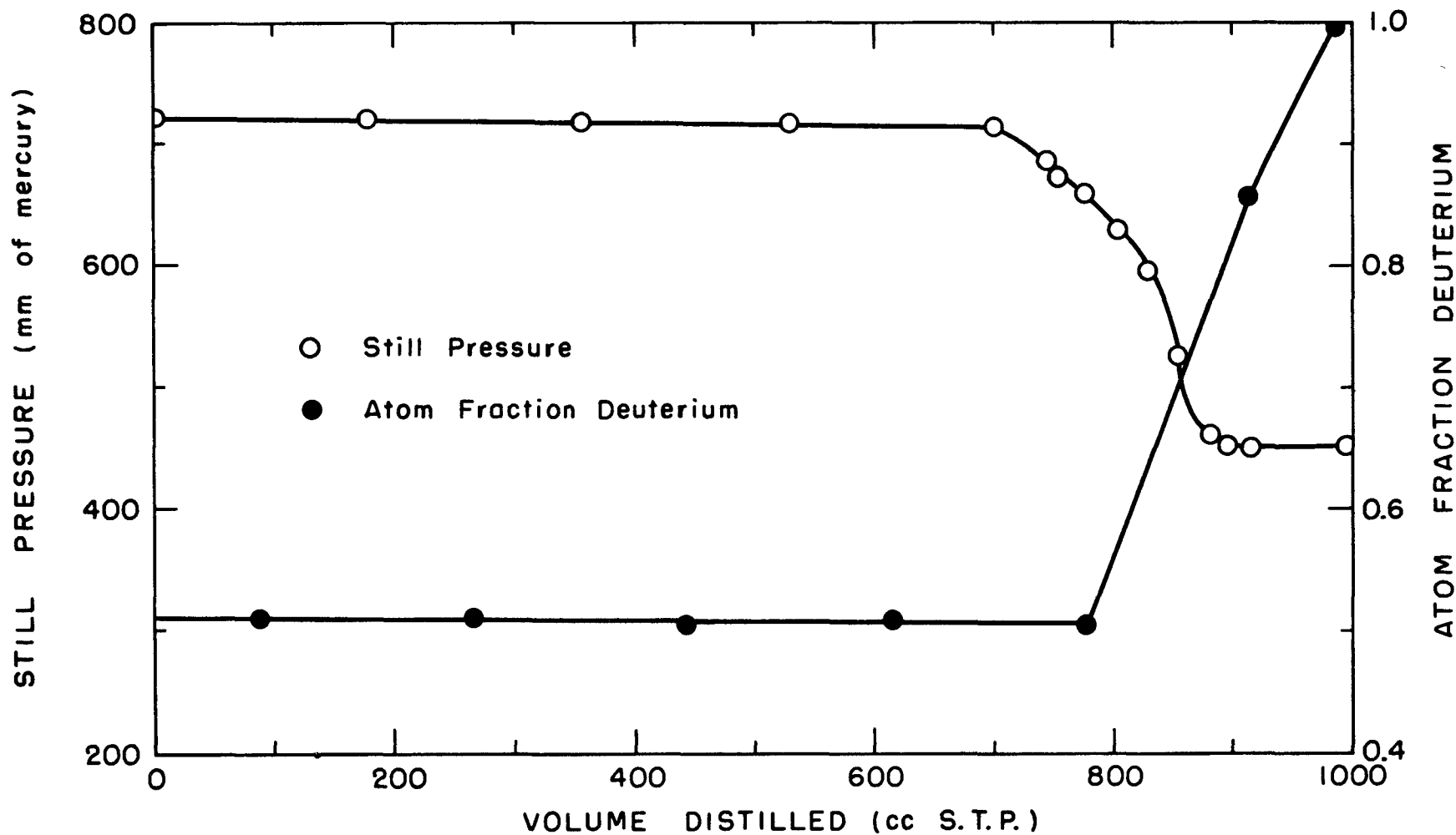


Figure 2

The still pressure and atom fraction deuterium are plotted as a function of the volume distilled for samples 6 through 12.

values of the equilibrium constant K at the low temperatures and also the value at 298.16°K reported by Jones.⁸ Also included in Table 4 are the mole fractions of H_2 , HT and T_2 in a 50 atom per cent H - 50 atom per cent T mixture.

Table 4

EQUILIBRIUM CONSTANT FOR $\text{H}_2 + \text{T}_2 = 2\text{HT}$

Mole Fractions of H_2 , HT and T_2 in a 50 Atom
Per cent H - 50 Atom Per cent T Mixture

T ($^\circ\text{K}$)	K	N_{H_2}	N_{HT}	N_{T_2}
20	0.003	0.487	0.026	0.487
25	0.012	0.471	0.058	0.471
298.16	2.57	0.274	0.452	0.274

It can be seen that low temperature equilibration favors the formation of H_2 and T_2 at the expense of HT in a tritium-hydrogen mixture. If the mixture is constantly in molecular equilibrium during distillation then the ternary system is reduced to a binary one and H_2 can be almost completely stripped in a single batch type distillation.