

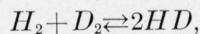
Preparation and Purification of Hydrogen Deuteride

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In an investigation of the physical properties of hydrogen isotopes it was necessary to prepare 10 liters of high-purity hydrogen deuteride. This was done by reacting lithium aluminum hydride with deuterium oxide, giving hydrogen deuteride, in two batches, of 98.1- and 97.0-percent purity, respectively. This material was then fractionated at liquid hydrogen temperature in three batches, yielding the desired amount of hydrogen deuteride in a purity of 99.8 percent.

I. Introduction

In connection with a project on the measurement of precise physical properties of hydrogen isotopes, it was found necessary to prepare about 10 liters of high-purity hydrogen deuteride. This substance had been prepared for the first time by Scott and Brickwedde [2, 6]¹ by passing a mixture of hydrogen and deuterium over a heated metal filament, followed by fractionation at liquid hydrogen temperature. The equilibrium mixture after conversion contained about 50 mole percent hydrogen deuteride, as would be anticipated from the equation



for which the equilibrium constant is about 4 [5].

Mixtures containing a high percentage of hydrogen deuteride have also been prepared by the action of deuterium oxide or water on various hydrides or deuterides, respectively. These methods give, in general, higher yields of hydrogen deuteride than is obtainable by equilibrating hydrogen and deuterium. Thus, Norton [5] treated boron hydride, B_2H_6 , with deuterium gas to obtain the deuterated product, B_2D_6 . The latter, when treated with 83-percent sulfuric acid, reacted with the water present to yield a mixture of hydrogen isotopes containing 85-percent hydrogen deuteride.

Similarly, lithium hydride with deuterium oxide has been used to prepare enriched hydrogen deuteride [1]. With sodium hydride, 87-percent hydrogen deuteride is obtainable [7], and with lithium aluminum hydride and deuterium oxide at 0° C, 99-percent hydrogen deuteride has been prepared [7].

For the purpose at hand, which requires hydrogen deuteride containing no more than several tenths percent of impurities, the last-mentioned reaction suggested itself as the most appropriate. In addition, to further purify the material obtained from this reaction, the fractionation technique of Scott and Brickwedde was employed.

II. Apparatus

The "crude" hydrogen deuteride was prepared in the apparatus described by Dibeler [4], shown in

figure 1, except for the method employed for adding deuterium oxide. This reagent was added by means of a hypodermic syringe through a neoprene septum held in a fitting attached to the tapered joint, *C*. It was found that the septum could be punctured several times without danger of admitting air to the system. This rendered it possible to add the deuterium oxide in several portions, thereby diminishing the vigor of the reaction.

In addition to the method for adding deuterium oxide, the apparatus of Dibeler was further modified by the inclusion of a magnetic stirrer in the flask, *D*; this was operated by a rotating magnetic field outside the flask.

The crude hydrogen deuteride was distilled in the apparatus shown in figure 2. This is, with minor modifications, the apparatus used by Scott and Brickwedde [2, 6] in their work; this technique has not heretofore been published.² The still, *A*, consisted of a jacketed boiler of about 5-ml capacity and monel helix rectifying section, *B*, a re-entrant portion, *C*, which served as a cold-finger dephlegmating condenser, and a take-off tube, *E*, which was connected to the top of the still by means of a U-tube, *D*. The liquid was boiled by means of an electric heater, *F*, of constantan wire, the leads of which ran up the still and emerged through a vacuum-tight wax seal, *G*. The still was immersed in a Dewar flask of liquid hydrogen, the level of which was maintained at about the position indicated in the drawing. This Dewar was in turn immersed in another Dewar containing liquid nitrogen (not shown in the drawing).

The still was connected through a ground glass joint to a regulator valve, *H*, thence to a graduated Toepler pump, *J*, of 500-ml capacity. The regulator valve consisted of a length of thin drill rod brazed to an iron core. The drill rod fit with little clearance into a length of heavy-walled capillary tubing, and was movable within this capillary by means of the solenoid, *K*. By thereby varying the length of annular space between the drill rod and tube wall, the rate of flow of gas from the still to the Toepler pump was easily controlled. The pressure in the still was indicated by a manometer; by adjusting the levels in the Toepler pump by means of the mercury reservoir, *M*, to a pressure less than that shown on the manometer, gas could be caused to flow from

² Clusius and Starke [3] have recently described a similar procedure. This was developed subsequent to, and independent of, Scott and Brickwedde.

¹ Figures in brackets indicate the literature references at the end of this paper.

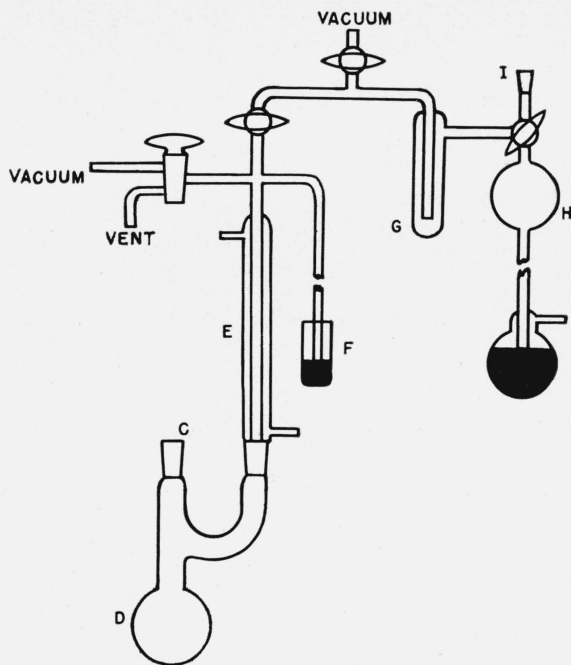


FIGURE 1. Apparatus used in preparation of hydrogen deuteride.

This drawing is identical with that reproduced in V. H. Dibelers paper [4].

the still to the Toepler pump at a rate determined by the pressure difference and the setting of the regulator valve.

The Toepler pump was connected to a manifold, *N*, and from there to a mercury diffusion pump. The manifold was fitted with a number of ground glass joints, to which sample tubes, receiver bulbs, or bulbs containing charging stock could be attached. The general practice was to use the charging bulbs as receivers, after the material they contained had been added to the still and the residual gas removed by the vacuum pump.

III. Preparation of Hydrogen Deuteride

Since 10 liters of high-purity hydrogen deuteride were required, this could readily be obtained by distillation from 15 liters of crude prepared by the method of Wender, Friedel, and Orchin [7] (lithium aluminum hydride and deuterium oxide at 0° C). Generous allowance could then be made for losses incurred during handling and distillation.

Accordingly, 15 liters of hydrogen deuteride were prepared in two runs, of 5 and 10 liters, respectively, of 98.1- and 97.0 percent purity. Since both batches were prepared in the same manner, only one will be described.

Into the Claisen flask, *D* (letters in this section refer to fig. 1), there was distilled about 150 ml of *n*-butyl ether, which had been previously dried and distilled from sodium. This was followed by 5.75 g of lithium aluminum hydride, the addition of this reagent being carried out in a nitrogen atmosphere. This quantity of lithium aluminum hydride was 40 percent in excess of that required to prepare 10 liters of gas, as calculated from the equation

The rubber septum-retaining device was fitted to the flask, at *C*, and the latter attached to the condenser, *E*.

The reaction mixture was frozen by means of a liquid nitrogen bath, the system evacuated, and the reaction mixture heated until it boiled under its own vapor pressure. After 1½ hours, the flask was again cooled with liquid nitrogen, and the system re-evacuated. By means of a hypodermic syringe, 5 ml of deuterium oxide (99.5-percent purity) was added to the solid reaction mixture. The latter was permitted to melt, and the gas evolved as a consequence of the ensuing reaction was collected in two 5-liter collecting bulbs attached to a manifold at *I*. During this operation, the mixture was being stirred continuously. Due to its low temperature, the outside of the flask quickly accumulated a layer of frost. Whenever this began to melt, the liquid nitrogen bath was applied; in this manner, the reaction temperature was kept at 0° C or lower.

During the course of the reaction, deuterium oxide was added two more times, to make a total of 18 ml of this reagent added. This quantity was about 150 percent excess over that required to make 10 liters of gas as calculated from the above equation. It was found desirable to use this excess in order to prevent the reaction from becoming too sluggish as the reagents were consumed.

After each run was completed, a sample was withdrawn from the collecting bulb by means of the Toepler pump, and added to an evacuated sample tube. These samples were subsequently analyzed mass spectrographically to determine purity of the hydrogen deuteride. This was found to be 98.1 and 97.0 percent, respectively, for the two batches prepared.

IV. Distillation of Hydrogen Deuteride

Since about 935 ml of hydrogen deuteride gas at 20° C is equivalent to 1 ml of liquid at the boiling point of hydrogen, 20.34° K, one 5-liter bulbfull of the crude as prepared was used as a convenient charge for each distillation. The entire 15 liters was therefore distilled in three batches, of which only one will be described in detail.

The collecting bulb, *S* (letters in this section refer to fig. 2) containing the charge at atmospheric pressure was attached to the manifold, as shown, and the entire system evacuated by means of a mercury diffusion pump. The Dewar flasks surrounding the still were filled with liquid hydrogen and liquid nitrogen, stopcock *R* was closed, and stopcocks *U*, *O*, *P*, and *Q* opened; the regulator valve, *H*, was also opened wide by means of solenoid *K*. The contents of *S* were thereby permitted to flow into the still, where condensation occurred on the condenser surface, *C*. After about 1 hour, the jacketed portions of the still had cooled sufficiently to permit liquid to begin accumulating in the boiler. The Toepler pump was then used to withdraw the remain-

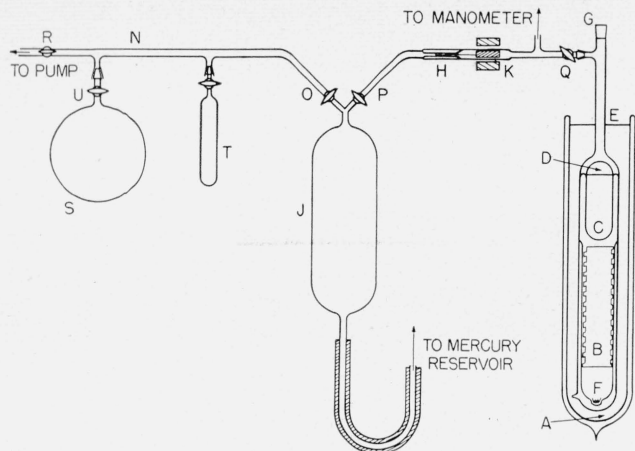


FIGURE 2. Apparatus used for purification of hydrogen deuteride by fractional distillation.

ing gas from *S* and to force it into the still; this last operation was continued until the pressure in the bulb as read on the manometer (stopcock *Q* closed), was 50 mm. It was not considered practical, with regard to the amount pumped for the time consumed, to attempt to reduce the pressure any lower.

Stopcock *P* was then closed, and a current of 71 ma permitted to flow through the heater, *F*. This current was controlled by means of a variable transformer; since the heater had a resistance of 27 ohms, it was equivalent to a heat input of 0.136 watt, or 0.033 cal/sec. The charge was thus caused to boil under total reflux, and, as the hydrogen present in the still was concentrated in the head as a consequence of fractionation, the pressure indicated on the manometer rose from an initial value of 447 to 531 mm. This rise occurred in about 45 min and did not increase thereafter. (Had there been sufficient hydrogen in the charge, the pressure at equilibrium should have been about atmospheric, or somewhat greater due to the fact that heat was being introduced.)

During this time, stopcocks *R*, *U*, and *O* were open, evacuating the Toepler pump and the bulb, *S*, for use as a receiver. Other, smaller, bulbs were also on the manifold, to be used as forerun and residue receivers; these are not shown in figure 2.

When equilibrium had been reached, as indicated by constancy of pressure, the regulator valve was adjusted to about half-open, stopcock *O* was closed, and stopcock *P* opened. The mercury levels in *J* and *M* were adjusted so that the pressure in the Toepler pump was about 160 mm less than that in the still. Take-off of distillate was thereby begun.

Each time the bulb *J* filled, stopcock *P* was closed, stopcock *O* was opened, and the contents of the Toepler pump were discharged into the appropriate receiver. The points at which fractions were to be cut were determined by the pressure indicated on the manometer. This pressure was approximately the equilibrium pressure of the distillate at the condenser temperature. Its absolute value was of little

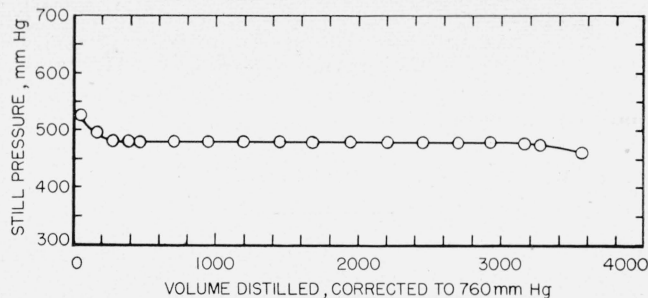


FIGURE 3. Distillation curve of hydrogen deuteride.

concern; what was of interest during the distillation was its variation. As can be seen from figure 3, the pressure-volume distilled curve for this distillation, the bulk of the distillate was removed at 478 to 480 mm. The pressure at any time was influenced by the level, *E*, of liquid hydrogen, the take-off rate at that moment, the ambient temperature, and the rate of boiling.

During the course of the distillation it was necessary to adjust the regulator valve several times and to determine the proper pressure in the Toepler pump, in order to achieve the desired reflux ratio. The heat of vaporization of hydrogen deuteride is 257 cal mole⁻¹ at its boiling point, 22.54° K [8]. Since the heat input was 0.033 cal sec⁻¹, the boil-up rate was 185 ml min⁻¹, at 20° C and 760 mm. The take-off rate was observed by noting the amount withdrawn in the Toepler pump, and the time taken to withdraw it. From these figures, the reflux ratio was calculated. Because of the nature of the adjustments necessary to the operation of the still (as the mercury level in *J* fell, the leveling bulb, *M*, had to be periodically lowered to maintain approximately the same head), the reflux ratio was variable. During the withdrawal of the pure hydrogen deuteride fraction, this quantity ranged from 9.3:1 to 26.5:1, with an average of 13.7:1.

In the distillation described above, the charge was equivalent to 4,600 ml of gas, at 20° and 1 atm. There was distilled 3,580 ml, of which 390 ml was forerun, 2,850 ml pure hydrogen deuteride, and the rest holdup. The volumes of the fractions were obtained by summing the volumes of gas discharged from the Toepler pump and correcting to 20° C and 1 atm; these values are plotted on the distillation curve, figure 3. Upon completion of the distillation, the pressure in the bulb containing the pure hydrogen deuteride was measured on the manometer. The corrected volume as calculated from this figure was 3,080 ml. It is believed that this value is more reliable than that obtained by summing the Toepler pump fractions, since the latter undoubtedly contain cumulative errors.

The distillation was continued until the boiler and the lower coils of the fractionating section were dry. This left a holdup of about 1 liter of gas, since with such a small amount of material fractionation was impossible in this still. The forerun and holdup of the distillation were discarded.

A sample of the main fraction was analyzed by means of the mass spectrometer, and was shown to have a purity of 99.8-percent hydrogen deuteride, disregarding a small percentage of nitrogen. The remainder of the crude hydrogen deuteride was distilled in the manner described herein, and yielded material of about the same purity.

The authors express their appreciation to V. H. Dibeler, whose apparatus was used in the preparation of the crude hydrogen deuteride, and who performed the mass spectrographic analyses reported in this work. Thanks are also due R. B. Scott and W. E. Gifford, who assisted in the distillation described in this paper.

V. References

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