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# Vapor Pressures of the Tritium Liquid Hydrogens

## Dependence of Hydrogen Vapor Pressure on Mass of the Molecule

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The Henry's law constants for HT evaporating from approximately  $10^{-9}M$  solutions in normal  $H_2$  and for DT from  $nD_2$  were determined by distillation and measuring the radioactivities of the distillate gases. On the basis of Lewis' and Hanson's data showing  $H_2$  and  $D_2$  to form nearly perfect solutions, the Henry's law constants were taken to represent the vapor pressures of the pure HT and DT liquids. A plot of vapor pressures of various kinds of hydrogen at 20.4°K led to  $45 \pm 10$  mm of Hg as the predicted vapor pressure of liquid  $nT_2$  at 20.4°K.

THE vapor pressures of the hydrogen molecules with tritium (radioactive hydrogen)<sup>1</sup> atoms should help settle certain points in the theory of liquid hydrogen involving the mass and zero-point properties of the liquid. In addition, a distillation technique may prove to be desirable for the concentration of tritium.

The method used consisted principally of the distillation under equilibrium conditions of a small volume of the liquid containing some of the tritium-containing molecules, samples of the gas being taken frequently and their specific radioactivities determined. Under such conditions of no refluxing and perfect stirring of the liquid, the Rayleigh<sup>2</sup> distillation formula applies, with a slight modification due to the large fraction of the hydrogen in the gas phase.

Suppose the vapor pressure of HT over the very dilute solutions (approximately  $10^{-9}M$ ) involved here is given by

$$P_{HT} = \beta N_{HT},$$

where  $P_{HT}$  is the pressure and  $N_{HT}$  is the mole fraction of HT, and, similarly,

$$P_{H_2} = \alpha N_{H_2} = \alpha(1 - N_{HT}).$$

Then the specific radioactivity or mole fraction of HT of the distillate gas  $\rho$  will be given by

$$\rho = \rho_0 \left( \frac{1 + (\alpha/\beta)v_0/V}{1 + (\alpha/\beta)v/V} \right)^{(\alpha-\beta)/\alpha},$$

where  $V$  is the volume of the gas space over the liquid and  $v_0$  and  $v$  are the volumes of the liquid at the beginning of the distillation and at any

subsequent point, measured in terms of the volumes of gas to which they are equivalent.

To derive this expression one notes that the total number of moles of HT in the distillation vessel is

$$t = \rho V + \rho(\alpha/\beta)v,$$

since  $\rho$  is the mole fraction of HT in the gas and is equal to  $(\beta/\alpha)N_{HT}$ .

For a small removal of gas from the distillation chamber, changing  $v$  by  $dv$ ,

$$dt = Vd\rho + (\alpha/\beta)\rho dv + (\alpha/\beta)v d\rho$$

or, after dividing by  $dv$  and replacing  $dt/dv$  by  $\rho$ ,

$$\rho = (V + (\alpha/\beta)v)d\rho/dv + \alpha/\beta\rho.$$

Rearranging gives

$$(\beta/\alpha - 1)d \ln (V + (\alpha/\beta)v) = d \ln \rho,$$

since  $V$  is essentially constant. Finally, integration gives the equation desired. Figure 1 illustrates the expected course of the specific activity

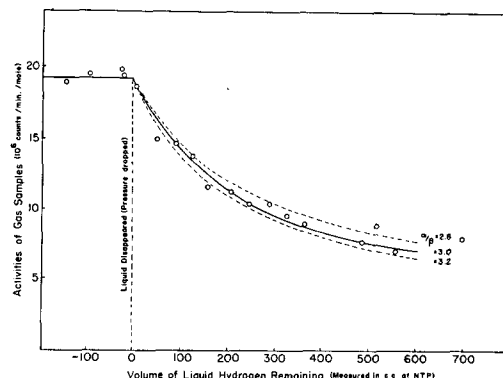


FIG. 1. Activity distillation curve for HT from  $nH_2$  (20.4°K). Solid line: calculated curve for pressure ratio of 1 to 3.0.

<sup>1</sup> Luis W. Alvarez and Robert Cornog, *Phys. Rev.* **56**, 613 (1939).

<sup>2</sup> Lord Rayleigh, *Phil. Mag.* [5] **4**, 527 (1902).

for the case where  $V$  was 500 cc (measured at 295°K and one atmosphere) and  $\alpha/\beta$  was 3.0.

The distillation bulb was immersed deeply in a bath of boiling normal  $H_2$  and the previously prepared radioactive gas introduced with a Toepler pump through several feet of small bore (1 mm) capillary glass and copper tubing. After a few minutes, gas was slowly withdrawn at equilibrium pressure into a series of bulbs which were stored for later measurement of their radioactivities. The total volume of gas used varied between one and five liters NTP and the sample bulbs were mainly of 25 cc and 100 cc capacities, the smaller bulbs being used near the point of disappearance of the last of the liquid. Obviously under the conditions outlined refluxing of the distillate is quite impossible. The second condition, that the liquid be in equilibrium with the vapor, is less easily established. Indeed, for the run shown in Fig. 1 some five liters of gas were used and only the last liter distilled under equilibrium conditions as attested by the agreement between the points and the calculated curve. The result is understandable when one realizes that the vessel in which the gas and liquid came to equilibrium was about 2

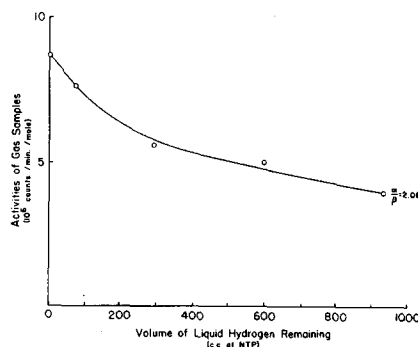


FIG. 2. Activity distillation curve for DT from  $nD_2$  (20.4°K). Solid line: calculated curve for pressure ratio of 1 to 2.08.

counter used could be filled several times to the 2 cm of Hg pressure used. The point placed just at the point of disappearance of the liquid was obtained by using the activity of the gas present after the liquid had disappeared. The gas volume  $V$  was 550 cc in this run.

The HT samples were prepared by allowing Li metal which had been irradiated for several months by the Berkeley cyclotron (the authors are indebted to the Radiation Laboratory and Dr. Robert Cornog for this irradiation) to react with  $H_2O$  after all air had been removed by pumping on the liquid-air-cooled reaction mixture. The appropriate amount of Li metal was cut from the irradiated block and placed in a liquid-air-cooled tube containing sufficient water as ice. The tube was then placed on the vacuum line and pumped. The vessel then warmed to room temperature and evolved  $H_2$ . The gas was passed through liquid-air traps for water removal. The procedure for DT was identical, except that  $D_2O$  was used instead of  $H_2O$  for reaction with the lithium. The gases were stored in large bulbs and transferred with a Toepler pump to the distillation cells. The purity of the gases must have been high because the capillary tubing immersed in liquid  $H_2$  for about two feet would have plugged immediately with any air, water vapor or any gas except the lightest rare gases. In addition the  $H_2$  and  $D_2$  samples gave the vapor pressures reported in the literature.

Two entirely separate runs were made with HT. The first one gave a value for  $\alpha/\beta$  of  $3.3 \pm .5$  considerably less accurate than the one described above, but in definite agreement with it. There seem to be only two likely sources of

TABLE I.

Molecule	Vapor pressure at 20.4°K (mm Hg)	Source
$H_2$	760	
HD	438	Reference 1.
$D_2$	256	References 2-5.
HT	$254 \pm 16$	This research.
DT	$123 \pm 6$	This research.
$T_2$	$(45 \pm 10)$	Extrapolation, Fig. 3.

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

<sup>2</sup> R. B. Scott, F. G. Brickwedde, H. C. Urey, and M. H. Wahl, J. Phys. Chem. **2**, 454 (1934).

<sup>3</sup> K. Clusius and E. Bartholomé, Zeits. f. physik. Chemie **B30**, 237 (1935).

<sup>4</sup> E. Bartholomé, Zeits. f. physik. Chemie **B33**, 387 (1936).

<sup>5</sup> H. D. Megaw and F. Simon, Nature **138**, 244 (1936).

square  $cm^2$  in cross-sectional area and about 15 cm long. Five cc of liquid hydrogen created quite a distance for diffusion to accomplish stirring. Fortunately, diffusion was sufficiently rapid when the liquid volume was reduced.

Figure 2 presents similar data for distillation of DT out of  $nD_2$ . In this case the bulb size was somewhat greater, reducing the number of points. However, the larger size of the bulbs increased the accuracy of the counting because the 500 cc

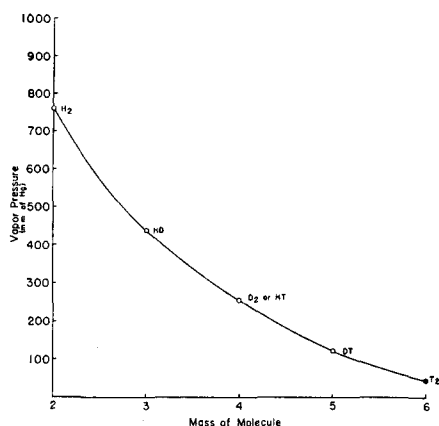


FIG. 3. Plot of vapor pressures of hydrogen molecules versus mass, at 20.4°K.

error in this type of experiment. The first is the condition that diffusion equilibrium exist and the second is that the samples of gas have their radioactivities measured properly. In connection with the first point, one notices on Fig. 1 that there remained only 600 cc of hydrogen as liquid when the data were considered to represent safely equilibrium distillation. When one realizes that this amounts to about  $\frac{1}{2}$  cc of liquid hydrogen in the distillation cell or a layer of liquid hydrogen approximately  $\frac{1}{4}$  cc thick over the 2 cm<sup>2</sup> bottom of the cell, it is difficult to imagine any but equilibrium conditions applying after 10 minutes, which was the average interval between samples.

The gaseous samples were counted by filling the counter with approximately 1.5 cm of Hg of H<sub>2</sub> or D<sub>2</sub> and 2 or 3 mm of Hg of ethyl alcohol vapor. A standard uranium sample was used to check the reproducibility of the counting apparatus. In connection with the accuracy of the counting, it was observed that air had not entered the sample bulbs and that the gas composition was uniform by noting the operating voltage for the counter when filled with the various samples. Counters are very sensitive in this respect. This being so, one could feel certain that the counter's sensitivity to tritium radiation would be reproduced if its sensitivity to uranium were reproduced.

The figures quoted for the errors in the values of the vapor pressures were obtained as shown in Fig. 1 by sketching in the curves for values of  $\alpha/\beta$  such that most of the points were included

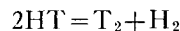
between the limits. The values for  $V$  were obtained by measurement of the cell volume and correcting to 20.4°K.

Table I summarizes the results for the vapor pressures of the hydrogen molecules at 20.4°K.

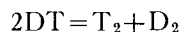
In compiling the data the Henry's law constants  $\beta$  obtained for the very dilute solutions were assumed to represent the true vapor pressure of the pure solute, i.e., the solutions were assumed to be perfect. Evidence for the essential correctness of this assumption exists in the data on the vapor pressures of H<sub>2</sub>, D<sub>2</sub> solutions.<sup>3</sup>

The first point the data emphasize is that the vapor pressure of HT is essentially the same as that for normal D<sub>2</sub>. This is rather to be expected when one realizes that the difference in moment of inertia can have little effect so long as nearly free rotation occurs in the liquid, a condition fairly well substantiated by specific heat data on H<sub>2</sub>.

The second point is shown in Fig. 3 where the vapor pressures of the various hydrogen molecules are plotted against their masses, the value for T<sub>2</sub> being obtained by extrapolation of the curve. Very evidently, the distillation technique should be successful in concentrating tritium if one were to keep the equilibria



and



well catalyzed by periodically passing the gas over a heated catalyst in the last stages of the concentration.

The complete significance of the curve in Fig. 3 must await a successful theory of liquid hydrogen. However, qualitatively it reveals the effect of translational zero-point energy on the free energy of the liquid. The van der Waals forces holding the liquids together will be nearly identical for all the liquid hydrogens. Therefore one must expect the mass effect observed to be associated very directly with the differences of the zero-point energies of the compressional vibrations of the several liquids. The effects due to rotation certainly are small compared with these mass effects. In addition they are averaged out somewhat in the data chosen for Fig. 3.

<sup>3</sup> Gilbert N. Lewis and W. T. Hanson, Jr., J. Am. Chem. Soc. **56**, 1000 (1934).