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## THE DIFFERENCE IN VAPOR PRESSURES OF ORTHO- AND PARADEUTERIUM<sup>1</sup>

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### ABSTRACT

The difference between the vapor pressures,  $\Delta P(e-n)$ , of the 20.4° K equilibrium mixture and the normal mixture of the ortho and para varieties of D<sub>2</sub> were determined from 15 to 20.4° K.  $\Delta P(e-n)$  varied from 0.3 mm of Hg at 15° K to 3.8 mm at 20.4°.  $\Delta P(e-n)$  for deuterium is small as compared with  $\Delta P(e-n)$  hydrogen, but  $[\Delta P(\text{ortho-para})/P_n]$  for deuterium is about equal to  $[\Delta P(\text{para-ortho})/P_n]$  for hydrogen at the same temperature.

Further measurements were made on the uncatalyzed change with time of the vapor pressure of liquid normal deuterium. The change for deuterium is less than 1 mm of Hg in 200 hours, whereas the vapor pressure of liquid normal hydrogen increases 1 mm in 4 hours. This large difference in rates is attributable to the difference in magnetic moments of the proton and deuterium. If Wigner's theory of the ortho-para conversion by paramagnetic molecules in the gaseous phase is extended to the liquid phase to calculate the relative rates of change of the vapor pressures of liquid normal deuterium and liquid normal hydrogen, a ratio of 1/1000 is obtained for the ratio of the rate of change for deuterium to the rate of change for hydrogen.

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### I. INTRODUCTION

The difference between the vapor pressures of ortho- and para-deuterium in relation to the corresponding difference for hydrogen is in itself interesting, but it also seems important because the physical basis of the vapor pressure difference, even for hydrogen, has not been made clear. Moreover vapor pressures of the ortho and para varieties have not been reported for any solid.

In table 1 are listed properties of molecular hydrogen and deuterium that are useful in the interpretation of the differences between

<sup>1</sup> The results contained in this paper were reported in part at the symposium on Heavy Hydrogen and Its Compounds, before a joint session of Section C of the American Association for the Advancement of Science and the American Physical Society, in Pittsburgh, December 28, 1934.

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the vapor pressures of ortho and para varieties of these isotopes. The arrows indicate the relative orientations of the spins of the protons and the deuterons, the spins being  $\frac{1}{2}$  and 1, respectively. The equilibrium concentrations of *p*-H<sub>2</sub> and *o*-D<sub>2</sub>, the molecules with lowest rotational energy,  $J=0$ , increase as we proceed to lower temperatures.

TABLE 1.—Concentration of ortho and para varieties of hydrogen and deuterium

<u>HYDROGEN</u>	ORTHO	PARA
FERMI-DIRAC STATISTICS	$\uparrow \uparrow$	$\uparrow \downarrow$
J (ROTATIONAL QUANTUM NUMBER)	ODD	EVEN
CONCENTRATION <sup>1</sup>		
at 300°K ( <i>n</i> -H <sub>2</sub> )	0.75	0.25
at 20°K ( <i>e</i> -H <sub>2</sub> )	0.002	0.998
<u>DEUTERIUM</u>	ORTHO	PARA
BOSE-EINSTEIN STATISTICS	$\uparrow \uparrow$   $\uparrow \downarrow$	$\uparrow \downarrow$ $\swarrow \searrow$ 120°
J (ROTATIONAL QUANTUM NUMBER)	EVEN	ODD
CONCENTRATION <sup>2</sup>		
at 300°K ( <i>n</i> -D <sub>2</sub> )	0.667	0.333
at 20°K ( <i>e</i> -D <sub>2</sub> )	0.978	0.022

<sup>1</sup> Harkness and Deming, *J. Am. Chem. Soc.* 54, 2850 (1932).<sup>2</sup> Johnston and Long, *J. Chem. Phys.* 2, 389 (1934).

The ortho-para deuterium vapor-pressure differences were calculated from the measured vapor pressures of the normal mixture, *n*-D<sub>2</sub>, and the 20.4° K temperature equilibrium mixture, *e*-D<sub>2</sub>. The *e*-D<sub>2</sub> mixture was established by means of a zinc chromite catalyst, ZnCrO<sub>2</sub>, placed in the bottom of a vapor-pressure tube in which deuterium was condensed. The zinc chromite catalyst was prepared from zinc ammonium chromate, which was obtained by mixing equimolecular proportions of dilute solutions of zinc nitrate and ammonium chromate. The solution was made slightly alkaline with ammonia and the resulting precipitate washed, filtered, and dried. The product was heated for 5 hours at 450° C and was then reduced by hydrogen at 400° C for 24 hours. The final product was a pale-green powder which, by evacuation at 400° C, could be largely freed from traces of water which might interact with deuterium and thus contaminate it with hydrogen. Before use, it received a high-temperature treatment with deuterium to convert any residual water to deuterium oxide. Zinc chromite, thus prepared, is strongly para-

magnetic and has been found to be an excellent agent for conversion of *o*-H<sub>2</sub> to *p*-H<sub>2</sub> at liquid-air temperatures.<sup>2</sup> Although not so efficient as chromium oxide gel<sup>3</sup> in the conversion process, it is superior to the latter in the present work owing to its small residual water content.

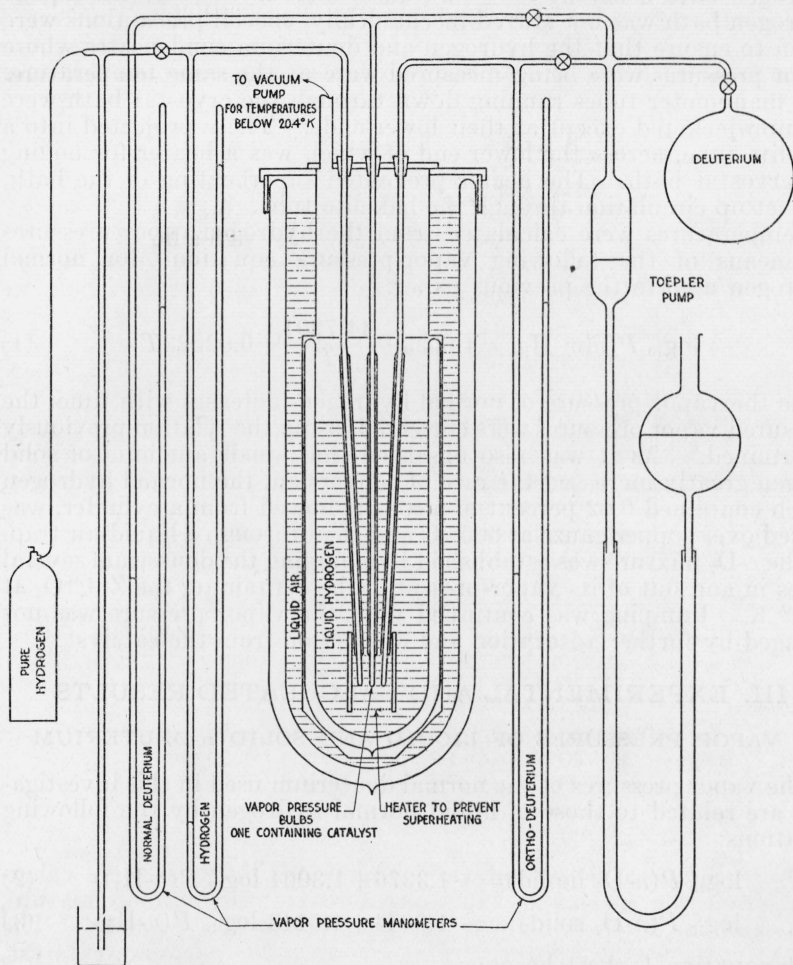


FIGURE 1.—Apparatus used in the measurement of the vapor pressures of deuterium.

## II. DESCRIPTION OF APPARATUS

Figure 1 represents diagrammatically the apparatus used in making the vapor-pressure measurements. In a liquid-hydrogen cryostat were immersed three vapor-pressure tubes connected with oil-lubricated (*n*-butyl phthalate) mercury manometers. Normal hydrogen was condensed in one tube and normal deuterium in the other two, one of which contained the ZnCrO<sub>2</sub> catalyst.

<sup>2</sup> H. Diamond, Thesis, Princeton University (1935).

<sup>3</sup> Howard, Trans. Faraday Soc. **30**, 278 (1934).

The temperature of the liquid-hydrogen bath in the inner dewar vessel was varied by means of a vacuum pump. With the aid of a fine-adjustment valve and an oil-filled differential manometer it was possible to maintain the pressure in the vapor space over the liquid-hydrogen bath constant to  $\pm 0.2$  mm of mercury. Since the liquid-hydrogen bath was not stirred mechanically, special precautions were taken to ensure that the hydrogen and deuterium condensates whose vapor pressures were being measured were at the same temperature. The manometer tubes running down through the cryostat bath were vacuum-jacketed except at their lower ends. These projected into a bakelite tube, across the lower end of which was a heater for boiling the cryostat bath. The heater prevented superheating of the bath, and set up circulation through the bakelite tube.

Temperatures were calculated from the hydrogen vapor pressures by means of the following vapor-pressure equation<sup>4</sup> for normal hydrogen used in the previous paper:<sup>5</sup>

$$\log_{10} P(\text{mm Hg}) = 4.6633 - \frac{44.7291}{T} + 0.02023T \quad (1)$$

Since the vapor pressure of normal hydrogen increases with time, the measured vapor pressures were corrected, using the relation previously determined.<sup>6</sup> As it was also observed that small amounts of solid oxygen greatly increased the rate of conversion, the normal hydrogen which contained 0.02 percent of air, as it flowed from a cylinder, was passed over copper gauze at 600° C and then through a liquid-air trap.

The *e*-D<sub>2</sub> mixture was established by pumping the deuterium several times in and out of its vapor-pressure tube containing the ZnCrO<sub>2</sub> at 20.4° K. Pumping was continued until the vapor pressure was not changed by further adsorption and desorption from the catalyst.

### III. EXPERIMENTAL AND CALCULATED RESULTS

#### 1. VAPOR PRESSURES OF LIQUID AND SOLID *n*-DEUTERIUM

The vapor pressures of the normal deuterium used in this investigation are related to those of liquid normal hydrogen by the following equations:

$$\log_{10} P(n\text{-D}_2 \text{ liquid}) = -1.3376 + 1.3004 \log_{10} P(n\text{-H}_2), \quad (2)$$

$$\log_{10} P(n\text{-D}_2 \text{ solid}) = -1.9044 + 1.5143 \log_{10} P(n\text{-H}_2). \quad (3)$$

With equation 1, these become:

$$\log_{10} P(n\text{-D}_2 \text{ liquid}) = 4.7266 - \frac{58.1657}{T} + 0.02630T, \quad (4)$$

$$\log_{10} P(n\text{-D}_2 \text{ solid}) = 5.1572 - \frac{67.7333}{T} + 0.03063T. \quad (5)$$

These equations represent the lowest vapor-pressure data yet obtained for deuterium and fit three of our samples prepared at different times.

<sup>4</sup> This equation was deduced as the best fit for the experimental data on (1) the vapor pressure of liquid hydrogen, (2) the latent heat of vaporization, and (3) deviations of the molecular volume of the vapor from that of an ideal gas. All published vapor-pressure measurements were considered, but this equation agrees best with the most recent Leiden measurements (van Agt and Onnes, Leiden Comm. no. 176b (1925)).

<sup>5</sup> Scott, Brickwedde, Urey, and Wahl, *J. Chem. Phys.* 2, 454 (1934).

<sup>6</sup> See footnote 5.



In table 2 are recorded two series of determinations of the vapor pressures of normal hydrogen and deuterium. The observed vapor pressures are given in columns 2 and 4. Column 3 is obtained from column 2 by correcting for the change (see footnote 5) with time of the vapor pressure of the hydrogen resulting from the conversion of ortho- to parahydrogen.

TABLE 2.—Two typical series of observations of the vapor pressure of normal deuterium

1	2	3	4
Age of condensed states	Observed vapor pressure of hydrogen	Vapor pressure of normal hydrogen (calculated)	Vapor pressure of normal deuterium (observed)
Hours	mm Hg	mm Hg	mm Hg
1.75	751.9	751.4	252.4
2.33	654.2	653.5	210.7
2.70	557.1	556.5	170.9
3.5	364.2	363.7	93.9
3.8	278.8	278.3	39.8
0.9	741.9	741.6	248.1
1.5	549.9	549.6	168.2
1.8	489.7	489.4	144.4
2.2	414.3	414.0	114.4
2.7	385.7	385.3	102.6

In table 3 are listed the vapor pressures of normal hydrogen and deuterium at their boiling and triple points calculated from these equations. The values differ slightly from those of the earlier paper because the later measurements were made of purer deuterium. The vapor pressure of *n*-D<sub>2</sub> at 20.38° K reported here is 1.3 mm lower and the triple-point temperature 0.13° higher than the previous values.<sup>7</sup>

TABLE 3.—Calculated boiling points and triple points

Temperatures	Vapor pressures	
	<i>n</i> -H <sub>2</sub>	<i>n</i> -D <sub>2</sub>
	mm Hg	mm Hg
23.59° K (boiling point of <i>n</i> -D <sub>2</sub> ).....	1,753	760
20.38° K (boiling point of <i>n</i> -H <sub>2</sub> ).....	760	256.2
18.71° K (triple point of <i>n</i> -D <sub>2</sub> ).....	448	128.7
13.92° K (triple point of <i>n</i> -H <sub>2</sub> ).....	54	5.2

## 2. VAPOR PRESSURE DIFFERENCES FOR NORMAL AND TEMPERATURE (20.4° K) EQUILIBRIUM DEUTERIUM

In table 4 are recorded observed differences between the vapor pressures of *e*-D<sub>2</sub> and *n*-D<sub>2</sub>. These are plotted in figure 2.<sup>8</sup> The

<sup>7</sup> Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. 2, 454 (1934).

<sup>8</sup> Figure 2 does not imply that the vapor pressures of the liquid and solid phases of *e*-D<sub>2</sub> at its triple point are not equal. At the high-temperature end of the lower-temperature curve is the triple point of *e*-D<sub>2</sub> and at the low-temperature end of the higher-temperature curve is the triple point of *n*-D<sub>2</sub>. Between these two points the curve is continuous, but the interval between the triple-point temperatures (table 5) is too small to represent on figure 2.

Separate lines were drawn through the observations for the liquid and solid phases because there is no reason for a single line. The meeting of the lines of figure 2 would imply that *e*-D<sub>2</sub> and *n*-D<sub>2</sub> have the same triple-point temperatures. The ortho-para vapor-pressure difference of solid hydrogen has not been investigated, but *e*-H<sub>2</sub> has a lower triple-point temperature than *n*-H<sub>2</sub> (table 5). Therefore, the  $\Delta P$  curve for hydrogen must be similar to that for deuterium (fig. 2).

measurements of series 1 and 2 were made on  $e\text{-D}_2$  in a vapor-pressure tube without catalyst, after the  $\text{D}_2$  had been converted to the equilibrium mixture in the tube containing the  $\text{ZnCrO}_2$ . The observations of the other series were made with  $e\text{-D}_2$  in the presence of the catalyst. It was found that the presence of the  $\text{ZnCrO}_2$  produced no appreciable change in the vapor pressure.

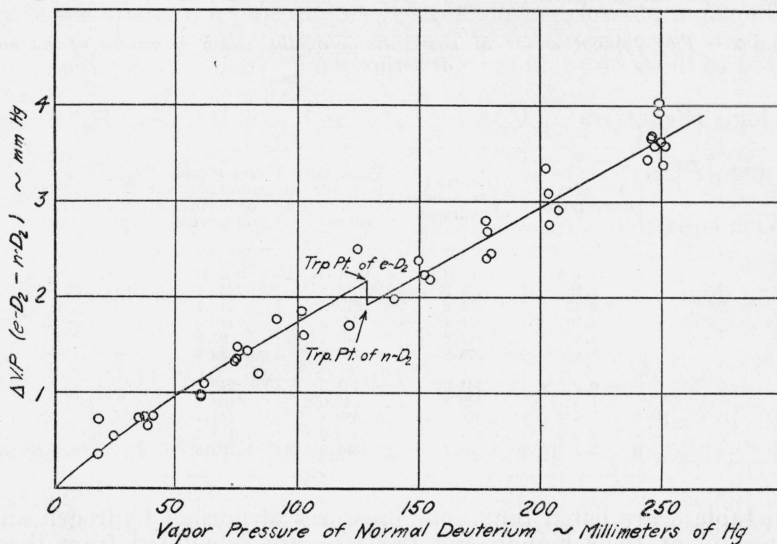


FIGURE 2.—Vapor-pressure difference of  $20.4^\circ$  K temperature equilibrium deuterium ( $e\text{-D}_2$ ) and normal deuterium ( $n\text{-D}_2$ ).

To prove that the observed  $\Delta P$ 's are to be attributed to a change in the ortho-para concentration and are not in error due to a contamination of the  $e\text{-D}_2$  with hydrogen, the  $e\text{-D}_2$  was pumped from its vapor-pressure tube into a flask in which it was converted to  $n\text{-D}_2$  by a hot platinum filament, at the end of each day's observations, and the vapor pressure of the converted  $n\text{-D}_2$  was compared the following day with a sample of unconverted  $n\text{-D}_2$ . The differences between the vapor pressures of the converted  $n\text{-D}_2$  and the unconverted  $n\text{-D}_2$  scattered to positive and negative values without any definite indication of a hydrogen contamination even after a second conversion to  $e\text{-D}_2$  and reconversion to  $n\text{-D}_2$ .

TABLE 4.—Experimental observations of  $\Delta P(e\text{-D}_2 - n\text{-D}_2)$  (mm Hg)

December 13, 1934				December 14, 1934		December 15, 1934			
Series 1		Series 2		Series 3		Series 4		Series 5	
$P(n\text{-D}_2)$	$\Delta P$	$P(n\text{-D}_2)$	$\Delta P$	$P(n\text{-D}_2)$	$\Delta P$	$P(n\text{-D}_2)$	$\Delta P$	$P(n\text{-D}_2)$	$\Delta P$
247.17	3.66	35.76	0.74	247.80	3.69	253.01	3.58	84.38	1.20
208.86	2.92	75.74	1.48	203.37	3.35	204.98	2.76	205.11	3.09
178.63	2.41	140.60	1.98	178.76	2.80	180.82	2.46	250.52	3.93
157.46	2.18	179.44	2.69	150.60	2.38	153.34	2.23	250.43	4.03
122.10	1.71	245.67	3.44	102.29	1.85	125.20	2.50	248.99	3.58
103.21	1.61	-----	-----	80.02	1.44	91.78	1.77	-----	-----
75.56	1.36	-----	-----	60.58	0.97	74.60	1.33	-----	-----
62.20	1.10	-----	-----	38.65	0.67	60.65	0.99	-----	-----
37.77	0.76	-----	-----	18.08	0.37	41.18	0.76	-----	-----
19.40	0.73	-----	-----	252.34	3.38	24.65	0.55	-----	-----
-----	-----	-----	-----	251.56	3.62	-----	-----	-----	-----

Although the  $D_2$  used for this investigation probably was purer than any other previously used for vapor-pressure determinations, it may have contained a small but constant HD impurity. Since HD does not have ortho and para varieties, it should not have affected our results to any greater extent than in proportion to its concentration.

The vapor pressures of the 20.4° K equilibrium mixture of the ortho and para varieties of the deuterium used in this investigation are related to those of liquid normal hydrogen by the following equations:

$$\log_{10} P(e_{20.4^\circ}\text{-D}_2 \text{ liquid}) = -1.3302 + 1.3000 \log_{10} P(n\text{-H}_2) \quad (6)$$

$$\log_{10} P(e_{20.4^\circ}\text{-D}_2 \text{ solid}) = -1.8873 + 1.5106 \log_{10} P(n\text{-H}_2). \quad (7)$$

With equation 1, these become:

$$\log_{10} P(e_{20.4^\circ}\text{-D}_2 \text{ liquid}) = 4.7321 - \frac{58.1478}{T} + 0.02630T \quad (8)$$

$$\log_{10} P(e_{20.4^\circ}\text{-D}_2 \text{ solid}) = 5.1571 - \frac{67.5678}{T} + 0.03056T. \quad (9)$$

In table 5 are listed the triple-point temperatures and pressures of  $n\text{-D}_2$ ,  $e\text{-D}_2$ ,  $n\text{-H}_2$ , and  $e\text{-H}_2$ .

In table 6 values for deuterium, based on the curves of figure 2, are compared with corresponding values for hydrogen derived from the observations of Keesom, Bijl, and van der Horst.<sup>9</sup>

TABLE 5.—Triple-point temperatures and pressures

<i>T</i> and <i>P</i>	<i>n</i> -D <sub>2</sub>	<i>e</i> -D <sub>2</sub>	<i>n</i> -H <sub>2</sub>	<i>e</i> -H <sub>2</sub> <sup>a</sup>
Temperature, °K.....	18.71	18.67	13.92	13.79
Pressure, mm Hg.....	128.7	128.4	54	53

<sup>a</sup> Bonhoeffer and Harteck, Z. physik. Chem. [B] 4, 113, (1929).

$\Delta P(o\text{-D}_2 - p\text{-D}_2)$  and  $\Delta P(p\text{-H}_2 - o\text{-H}_2)$  were calculated from  $\Delta P(e - n)$  on the assumption of Raoult's law. The smaller difference between the vapor pressures of  $e\text{-D}_2$  and  $n\text{-D}_2$  as compared with the corresponding difference for hydrogen is accounted for by the smaller percentage change in concentration and by a smaller difference between the vapor pressures of the ortho and para varieties. The difference between the vapor pressures of  $p\text{-H}_2$  and  $o\text{-H}_2$ ,  $\Delta P(p\text{-H}_2 - o\text{-H}_2)$ , is about 3 times the corresponding difference  $\Delta P(o\text{-D}_2 - p\text{-D}_2)$  at 20.4° K and 5.7 times at 15° K. However, the ratio  $\Delta P/P(n)$  is approximately the same for hydrogen and deuterium at the same temperature. (See table 6.)

<sup>9</sup> Roy. Acad. Sci., Amsterdam 342, 1,223 (1931); also Leiden Comm. no. 217a.

TABLE 6.—Comparison of  $\Delta P$ 's (mm Hg) for hydrogen and deuterium

Temperature	Hydrogen				Deuterium				
	$P(n\cdot H_2)$	$\Delta P(e\cdot H_2 - n\cdot H_2)$	$\Delta P(p\cdot H_2 - o\cdot H_2)$	$\frac{\Delta P(p\cdot H_2 - n\cdot H_2)}{P(n\cdot H_2)}$	$P(n\cdot D_2)$	$\Delta P(e\cdot D_2 - n\cdot D_2)$	$\Delta P(o\cdot D_2 - p\cdot D_2)$	$\frac{\Delta P(o\cdot D_2 - p\cdot D_2)}{P(n\cdot D_2)}$	
°K									
15.....	96.6	5.1	6.8	0.070	12.6	0.3	0.8	0.063	
16.....	155.4	7.6	10.2	.066	25.9	0.5	1.7	.065	
17.....	237.7	10.8	14.4	.061	49.4	0.9	2.9	.060	
18.....	348.7	14.8	19.8	.057	88.2	1.6	4.9	.055	
18.67 <sup>a</sup> .....	442.5	18.1	24.2	.055	126.5	2.2	6.7	.053	
18.71 <sup>b</sup> .....	447.5	18.3	24.5	.055	128.7	1.9	6.2	.048	
19.....	493.7	19.7	26.3	.053	146.3	2.2	6.9	.047	
20.....	678.3	25.0	33.4	.049	221.0	3.2	10.4	.047	
20.38.....	760.0	27.1	36.2	.048	256.2	3.8	12.1	.047	

<sup>a</sup> Triple point of  $e\cdot D_2$ .<sup>b</sup> Triple point of  $n\cdot D_2$ .

## 3. HEATS OF VAPORIZATION

As it is customary to use vapor-pressure data with the Clausius-Clapeyron equation to calculate latent heats, we have attempted to use our data to calculate the difference between the latent heats  $\Delta L(n-e)$  of the normal and equilibrium mixtures of ortho and para varieties. In this calculation use was made of the following equation of state of hydrogen, which is very closely that used in the previous paper:

$$pV(\text{liters per mole}) = RT - 0.0381 \left( 1 + \frac{1150}{T^2} \right) p \quad (10)$$

In the absence of any data on the equation of state of deuterium at liquid-hydrogen temperatures, this same equation was used for deuterium as well. Substituting in the Clausius-Clapeyron equation for the volume of the saturated vapor from the above equation, the following relation for the difference between the latent heats  $\Delta L(n-e)$  of the normal and equilibrium mixtures was obtained:

$$\Delta L(n-e) = R \frac{d \ln_e P_e / P_n}{d(1/T)} + T \left[ v + 0.0381 \left( 1 + \frac{1150}{T^2} \right) \right] \frac{d P(e-n)}{dT} \quad (11)$$

Here  $v$  is the molecular volume of the condensed state. For liquid hydrogen<sup>10</sup> it is 28.43 cm<sup>3</sup>, for solid deuterium<sup>11</sup> 23.15 cm<sup>3</sup>, and for liquid deuterium it was assumed to be 25.2 cm<sup>3</sup> or 11.5 percent smaller than that of liquid hydrogen. For liquid hydrogen the observations of Keesom, Bijl, and van der Horst<sup>12</sup> were used. The two derivatives of equation 11 were determined graphically.

The results are tabulated in table 7 together with values of  $\Delta L(p-o)$  calculated from  $\Delta L(n-e)$  upon the assumption that ortho and para varieties form ideal solutions. The difference in signs of  $\Delta L(p-o)$  for H<sub>2</sub> and D<sub>2</sub> arises from the interchange of the terms ortho and para to designate the rotating and nonrotating varieties of hydrogen and deuterium. The  $\pm$  values are estimated probable errors.

TABLE 7.—Differences between heats of vaporization

Material	Temperature range	$L(n-e_{20.4^\circ})$	$L(p-o)$
	°K		
Solid D <sub>2</sub> .....	16 to 18.71..	0.6 ± 0.5	1.8 ± 1.5
Liquid D <sub>2</sub> .....	18.71 to 20.4..	0.0 ± 0.5	0.0 ± 1.5
Liquid H <sub>2</sub> .....	16 to 20.4..	2.3 ± 0.5	-3.1 ± 0.7

It is interesting that  $\Delta L(p-o)$  for liquid D<sub>2</sub> is not more nearly equal to  $\Delta L(o-p)$  for liquid hydrogen.

The differences between the external latent heats of vaporization are small as compared with the values of table 7. Since  $\Delta P v(p-o)$  for the condensed phases is negligibly small, the  $\Delta L$  values of table 7 are also the differences between the internal energies of the condensed states.

<sup>10</sup> Int. Crit. Tables 1, 102 (1926).<sup>11</sup> Clusius and Bartholomé, Z. tech. Physik 15, 545 (1934).<sup>12</sup> Proc. Amsterdam Acad. Sci. 34, 1229 (1931).



## 4. ON THE UNCATALYZED CHANGE OF THE VAPOR PRESSURE OF LIQUID DEUTERIUM WITH TIME

Scott, Brickwedde, Urey, and Wahl<sup>13</sup> investigated the uncatalyzed change with time of the vapor pressures of liquid hydrogen and liquid deuterium resulting from the ortho-para conversion in the liquid state. The vapor pressure of normal hydrogen at 20.38° K increases at the rate of 1 mm of Hg in 4 hours, whereas the change for deuterium is less than 1 mm in 200 hours. The vapor pressure increase of liquid hydrogen follows the law of a bimolecular reaction, which Cremer and Polanyi<sup>14</sup> found to fit their thermal-conductivity measurements of the increase of  $p\text{-H}_2$  in liquid hydrogen. Since the  $p\text{-H}_2$  molecules have neither nuclear nor rotational magnetic moments, they have no magnetic field to effect a realignment of the nuclei of the ortho molecules with which they collide. Conversion in liquid hydrogen, therefore, results only from collisions of two ortho molecules. The  $o\text{-H}_2$  molecules having a nuclear magnetic moment of 5.8 Bohr nuclear magnetons (BNM)<sup>15</sup> and a rotational magnetic moment of 0.85 BNM have resultant moments of 6.6, 5.9, and 5.0, averaging 5.8 BNM.

It is not to be expected that the conversion of  $p\text{-D}_2$  to  $o\text{-D}_2$  in liquid deuterium will follow the simple bimolecular change of hydrogen. Five-sixths of the  $o\text{-D}_2$  molecules have a nuclear magnetic moment of 1.5 BNM<sup>16</sup> and the remaining sixth has a zero moment; there is no rotational moment. The  $p\text{-D}_2$  molecules have a nuclear magnetic moment of 0.75 and a rotational moment of 0.42 BNM.<sup>17</sup> The resultant moments of  $p\text{-D}_2$  are 1.2, 0.9, and 0.3, averaging 0.8 BNM. It is seen, therefore, that not only does the para- to orthodeuterium conversion result from collisions of para and ortho molecules as well as collisions of para molecules, with each other, but that actually the para-ortho collisions are more effective since the magnetic moments of the ortho molecules are greater than those of para molecules.

Wigner<sup>18</sup> developed a theory for the ortho-para conversion in gaseous hydrogen resulting from collisions with paramagnetic oxygen molecules. This theory is not directly applicable to liquids, but it does seem justifiable to use it to calculate the order of magnitude of the relative rates of conversion in liquid hydrogen and deuterium.

For the ortho to para conversion in gaseous hydrogen resulting from collisions with paramagnetic oxygen, the probability,  $W$ , of a transition from  $J=1$  to  $J=0$  is related to the moment of inertia  $I_H$  of the  $\text{H}_2$  molecules, the magnetic moments  $\mu_1$  and  $\mu_2$  of the oxygen molecule and the proton, and the spin,  $i$ , of the proton. We apply this relation to the ortho to para conversion

$$W(J=1 \rightarrow J=0) \propto I_H \mu_1^2 \mu_2^2 \left( \frac{2i+1}{i} \right) \quad (12)$$

resulting from collisions with paramagnetic  $o\text{-H}_2$  in liquid  $\text{H}_2$ , substituting for  $\mu_1$ , the magnetic moment of  $o\text{-H}_2$ . The velocity constant,

<sup>13</sup> Scott, Brickwedde, Urey, and Wahl, *J. Chem. Phys.* **2**, 454 (1934).

<sup>14</sup> *Z. physik. Chem. [B]* **12**, 231 (1921).

<sup>15</sup> I. Estermann and O. Stern, *Nature* **132**, 169 (1933); **133**, 911 (1934). I. I. Rabi, J. M. B. Kellogg, and J. R. Zacharias, *Phys. Rev.* **46**, 157 and 163 (1934).

<sup>16</sup> See footnote 15.

<sup>17</sup> The value 0.42 is based upon the assumption that the rotational moments are proportional to the angular velocities of rotation.

<sup>18</sup> *Z. physik. Chem. [B]* **23**, 31 (1933).

$K_H$ , of the ortho to para conversion in liquid hydrogen is proportional to  $W(J=1 \rightarrow J=0)$ . Substituting numerical values for the symbols in equation 12, we obtain:

$$K_H = CI_H \left[ \frac{(6.6)^2 + (5.9)^2 + (5.0)^2}{3} \right] (2.9)^2 = 1.2 \times 10^3 C'.$$

For the para to ortho conversion in liquid deuterium resulting from the collision of two para molecules

$$W_{p,p}(J=1 \rightarrow J=0) \propto I_D \mu_1^2 \mu_2^2 \frac{(i+1)(2i+1)}{i^2}. \quad (13)$$

The different statistics applicable to H and D require different spin factors in equations 12 and 13.

$$K_{p,p} = C(2I_H) \left[ \frac{(1.2)^2 + (0.9)^2 + (0.3)^2}{3} \right] (0.75)^2 = 5.3 C'.$$

For the para to ortho conversion resulting from collisions of *o*-D<sub>2</sub> and *p*-D<sub>2</sub> molecules

$$W_{o,p}(J=1 \rightarrow J=0) \propto \frac{5}{6} \times \frac{1}{2} I_D \mu_1^2 \mu_2^2 \frac{(i+1)(2i+1)}{i^2} \quad (14)$$

and

$$K_{o,p} = C \times \frac{5}{12} (2I_H) (1.5)^2 (0.75)^2 = 6.3 C'.$$

The factors  $\frac{5}{6}$  and  $\frac{1}{2}$  were introduced to take account of the fact that (1) only  $\frac{5}{6}$  of the *o*-D<sub>2</sub> molecules have a magnetic moment, and (2) the *a priori* probability of a para to ortho conversion for the collision of an ortho and a para molecule is only half of that for the collision of two para molecules.

If  $[o\text{-H}_2]$  and  $[p\text{-D}_2]$  are the concentrations of *o*-H<sub>2</sub> and *p*-D<sub>2</sub> in liquid hydrogen and liquid deuterium, respectively,

$$\frac{-[o\text{-H}_2]}{dt} = K_H [o\text{-H}_2]^2 = 1.2 \times 10^3 C' [o\text{-H}_2]^2$$

and

$$\begin{aligned} \frac{d[p\text{-D}_2]}{dt} &= K_{p,p} [p\text{-D}_2]^2 + K_{o,p} (1 - [p\text{-D}_2]) [p\text{-D}_2] \\ &= \{6.3 [p\text{-D}_2] - [p\text{-D}_2]^2\} C'. \end{aligned}$$

The ratio of the rate of *o*-H<sub>2</sub>  $\rightarrow$  *p*-H<sub>2</sub> in liquid normal hydrogen, to the rate of *p*-D<sub>2</sub>  $\rightarrow$  *o*-D<sub>2</sub> in normal deuterium is

$$\left( \frac{d[o\text{-H}_2]}{dt} \right)_{n\text{-H}_2} / \left( \frac{d[p\text{-D}_2]}{dt} \right)_{n\text{-D}_2} = 3.4 \times 10^2.$$

For the ratio of the rates of change of the vapor pressures we have:

$$\left( \frac{dP}{dt} \right)_{n\text{-H}_2} / \left( \frac{dP}{dt} \right)_{n\text{-D}_2} = 1 \times 10^3.$$

Although this calculation is not to be regarded as rigorous, it shows that the rate of conversion of para- to orthodeuterium is approximately proportional to the concentration of  $p\text{-D}_2$  instead of to the square of the concentration as it is for the corresponding change in liquid hydrogen. It also shows that the rate of the para to ortho conversion in liquid deuterium must be very much smaller than for the ortho to para conversion in liquid hydrogen.

Figure 3 (A and B) are graphs of observations of the vapor pressure of normal deuterium at  $20.38^\circ\text{K}$  plotted against the age of the condensed state. Figure 3 (A) is a reproduction of previously reported data obtained February 1934. The data of figure 3 (B) were observed December 1934, using purer deuterium.  $\Delta P$  is the difference between the observed vapor pressure and the intercept with the axis of vapor pressures of a line through the observations determined by

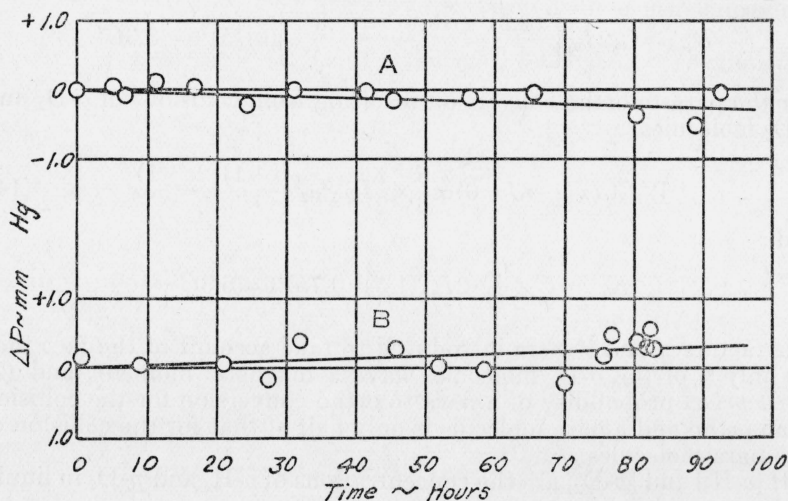


FIGURE 3.—Uncatalyzed change in the vapor pressure of liquid normal deuterium at  $20.4^\circ\text{K}$ .

A. Observations of February 1934.  
B. Observations of December 1934.

the method of least squares, with each point given equal weight.<sup>19</sup> These are the lines drawn through the observations in the two figures. The observations of February indicate a slow decrease in vapor pressure with time, whereas those of December indicate an increase about equal to the decrease of the February observations. When the two series of observations are thrown together and treated statistically as a single set, the line through the observations, determined by the method of least squares, indicates a decrease in vapor pressure of 0.027 mm of Hg in 100 hours. We conclude that the vapor pressure of liquid normal deuterium over a period of 100 hours is constant to within the accuracy of our measurements. The *estimated probable error* calculated from our observations is  $\pm 0.27$  mm at 100 hours.

<sup>19</sup> We are indebted to W. E. and L. S. Deming of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for the statistical analysis of our data.

## IV. ROTATION IN THE CONDENSED STATES

Although it was surmised that there would be *free* rotation of deuterium molecules in the liquid and solid states just as in the case of hydrogen, we now have definite evidence from the ortho-para vapor pressures that this is so. The latent heats of vaporization of solid and liquid deuterium are 355 and 305 calories per mole, respectively, and the rotational energy ( $J=1$ ) of  $p\text{-D}_2$  in the vapor phase at liquid-hydrogen temperatures is 170 calories per mole.<sup>20</sup> If there were no rotation in the condensed states, the heats of vaporization of  $p\text{-D}_2$  would be about 170 calories per mole greater than the corresponding values for  $o\text{-D}_2$ . Actually there may be a small difference in the heats of vaporization of  $p\text{-D}_2$  and  $o\text{-D}_2$ , but it is less than for liquid hydrogen, in which the difference is 3 calories per mole. We conclude, therefore, that there is free rotation in condensed states of deuterium just as in the case of hydrogen.

WASHINGTON, August 13, 1935.

<sup>20</sup> Johnston and Long, J. Chem. Phys. 2, 389 (1934).