

The Difference in Vapor Pressures of Ortho and Para Deuterium

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The Difference in Vapor Pressures of Ortho and Para Deuterium^{1, 2}

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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 D₂ 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 approximately 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 one mm

of Hg in 200 hours, whereas the vapor pressure of liquid normal hydrogen increases one mm in 4 hours. This large difference in rates is attributable to the difference in magnetic moments of the proton and deuteron. 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.

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 I are listed properties of molecular hydrogen and deuterium that are useful in the interpretation of the differences between 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 $p\text{-H}_2$ and $o\text{-D}_2$, the molecules with lowest rotational energy, $J=0$, increase as we proceed to lower temperatures.

The ortho-para deuterium vapor pressure differences were calculated from the measured vapor pressures of the normal mixture, $n\text{-D}_2$, and the 20.4°K temperature equilibrium mixture, $e\text{-D}_2$. The $e\text{-D}_2$ mixture was established by means of a zinc chromite catalyst, ZnCrO₂, 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 ammonium and the

¹ Published with the approval of the Director of the National Bureau of Standards of the Department of Commerce.

² 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.

used in the previous paper.⁶

$$\log_{10} P(\text{mm of Hg}) = 4.6633$$

$$-44.7291/T + 0.02023T. \quad (1)$$

Since the vapor pressure of normal hydrogen increases with time the measured vapor pressures were corrected by using the relation previously determined.⁶ 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 air, as it flowed from a cylinder, was passed over copper gauze at 600°C and then through a liquid air trap.

The $e\text{-D}_2$ mixture was established by pumping the deuterium several times in and out of its vapor pressure tube containing the ZnCrO_3 at 20.4°K. Pumping was continued until the vapor pressure was not changed by further adsorption and desorption from the catalyst.

EXPERIMENTAL AND CALCULATED RESULTS

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:

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

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

TABLE II.

1 AGE OF CONDENSED STATES (hrs.)	2 OBSERVED VAPOR PRESSURE OF HYDROGEN (mm Hg)	3 VAPOR PRESSURE OF NORMAL HYDROGEN (calc.) (mm Hg)	4 VAPOR PRESSURE OF NORMAL DEUTERIUM (obs.) (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
.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

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)).

⁶ Scott, Brickwedde, Urey and Wahl, J. Chem. Phys. 2, 454 (1934).

TABLE III. Calculated boiling points and triple points.

	VAPOR PRESSURE (mm Hg)	
	$n\text{-H}_2$	$n\text{-D}_2$
23.59°K (Boiling point of $n\text{-D}_2$)	1753	760
20.38 (Boiling point of $n\text{-H}_2$)	760	256.2
18.71 (Triple point of $n\text{-D}_2$)	448	128.7
13.92 (Triple point of $n\text{-H}_2$)	54	5.2

With Eq. (1), these become

$$\log_{10} P(n\text{-D}_2 \text{ liquid}) = 4.7266$$

$$-58.1657/T + 0.02630T, \quad (4)$$

$$\log_{10} P(n\text{-D}_2 \text{ solid}) = 5.1572$$

$$-67.7333/T + 0.03063T. \quad (5)$$

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

In Table II 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 change⁶ with time of the vapor pressure of the hydrogen resulting from the conversion of ortho to para hydrogen.

In Table III 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 $n\text{-D}_2$ at 20.38°K reported here is 1.3 mm lower and the triple point temperature 0.13° higher than the previous values.⁶

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

In Table IV are recorded observed differences between the vapor pressures of $e\text{-D}_2$ and $n\text{-D}_2$. These are plotted⁷ in Fig. 2. The measurements

⁷ Fig. 2 does not imply that the vapor pressures of the liquid and solid phases of $e\text{-D}_2$ at its triple point are not equal. At the high temperature end of the lower temperature curve is the triple point of $e\text{-D}_2$ and at the low temperature end of the higher temperature curve is the triple point of $n\text{-D}_2$. Between these two points the curve is continuous but the interval between the triple-point temperatures (Table V) is too small to represent on Fig. 2.

Separate lines were drawn through the observations for the liquid and solid phases because there is no reason for

TABLE IV. Experimental observations of $\Delta P(e\text{-}D_2 - n\text{-}D_2)$ (mm Hg).

Dec. 13, 1934		Dec. 14, 1934		Dec. 15, 1934	
SERIES #1	SERIES #2	SERIES #3	SERIES #4	SERIES #5	
$P(n\text{-}D_2)$	ΔP	$P(n\text{-}D_2)$	ΔP	$P(n\text{-}D_2)$	ΔP
247.17	3.66	35.76	0.74	247.80	3.69
208.86	2.92	75.74	1.48	203.37	3.35
178.63	2.41	140.60	1.98	178.76	2.80
157.46	2.18	179.44	2.69	150.60	2.38
122.10	1.71	245.67	3.44	102.29	1.85
103.21	1.61			80.02	1.44
75.56	1.36			60.58	0.97
62.20	1.10			38.65	0.67
37.77	0.76			18.08	0.37
19.40	0.73			252.34	3.38
				251.56	3.62
				253.01	3.58
				204.98	2.76
				180.82	2.46
				153.34	2.23
				125.20	2.50
				91.78	1.77
				74.60	1.33
				60.65	0.99
				41.18	0.76
				24.65	0.55

of series No. 1 and No. 2 were made on $e\text{-}D_2$ in a vapor pressure tube without catalyst, after D_2 had been converted to the equilibrium mixture in the tube containing the $ZnCrO_2$. 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 $ZnCrO_2$ produced no appreciable change in the vapor pressure.

To prove that the observed ΔP '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 next 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 $n\text{-}D_2$.

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:

$$\log_{10} P(e_{20.4^\circ}\text{-}D_2 \text{ liquid}) = -1.3302 + 1.3000 \log_{10} P(n\text{-}H_2), \quad (6)$$

$$\log_{10} P(e_{20.4^\circ}\text{-}D_2 \text{ solid}) = -1.8873 + 1.5106 \log_{10} P(n\text{-}H_2). \quad (7)$$

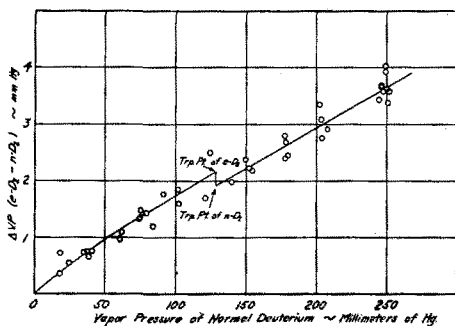


FIG. 2. The vapor pressure difference of 20.4°K temperature equilibrium deuterium ($e\text{-}D_2$) and normal deuterium ($n\text{-}D_2$).

a single line. The meeting of the lines of Fig. 2 would imply that $e\text{-}D_2$ and $n\text{-}D_2$ have the same triple-point temperatures. The ortho-para vapor pressure difference of solid hydrogen has not been investigated, but $e\text{-}H_2$ has a lower triple-point temperature than $n\text{-}H_2$ (Table V). Therefore, the ΔP curve for hydrogen must be similar to that for deuterium (Fig. 2).

TABLE V. Triple-point temperatures and pressures.

	$n\text{-}D_2$	$e\text{-}D_2$	$n\text{-}H_2$	$e\text{-}H_2^*$
$T^\circ K$	18.71	18.67	13.92	13.79
P (mm Hg)	128.7	128.4	54.	53.

* Bonhoeffer and Harteck, Zeits. f. physik. Chemie **B4**, 113 (1929).

TABLE VI.

T°K	HYDROGEN (mm Hg)				DEUTERIUM (mm Hg)			
	$P(n \cdot H_2)$	$\Delta P(e \cdot H_2 - n \cdot H_2)$	$\Delta P(p \cdot H_2 - o \cdot H_2)$	$\frac{\Delta P(p \cdot H_2 - o \cdot H_2)}{P(n \cdot H_2)}$	$P(n \cdot D_2)$	$\Delta P(e \cdot D_2 - n \cdot D_2)$	$\Delta P(o \cdot D_2 - p \cdot D_2)$	$\frac{\Delta P(o \cdot D_2 - p \cdot D_2)}{P(n \cdot D_2)}$
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 ^a	442.5	18.1	24.2	.055	126.5	2.2	6.7	.053
18.71 ^b	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

^a Triple point of $e-D_2$.^b Triple point of $n-D_2$.

With Eq. (1), these become

$$\log_{10} P(e_{20.4^\circ} - D_2 \text{ liquid}) = 4.7321$$

$$-58.1478/T + 0.02630T, \quad (8)$$

$$\log_{10} P(e_{20.4^\circ} - D_2 \text{ solid}) = 5.1571$$

$$-67.5678/T + 0.03056T. \quad (9)$$

In Table V are listed the triple point temperatures and pressures of $n-D_2$, $e-D_2$, $n-H_2$ and $e-H_2$.

In Table VI values for deuterium based on the curves of Fig. 2 are compared with corresponding values for hydrogen derived from the observations of Keesom, Bijl and van der Horst.⁸ $\Delta P(o \cdot D_2 - p \cdot D_2)$ and $\Delta P(p \cdot H_2 - o \cdot H_2)$ were calculated from $\Delta P(e - n)$ on the assumption of Raoult's law. The smaller difference between the vapor pressures of $e-D_2$ and $n-D_2$ 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 $p-H_2$ and $o-H_2$, $\Delta P(p \cdot H_2 - o \cdot H_2)$, is about 3 times the corresponding difference $\Delta P(o \cdot D_2 - p \cdot D_2)$ 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 VI.)

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

⁸ Keesom, Bijl and van der Horst, Royal Academy of Sciences, Amsterdam 34, 1223 (1931); also Leiden Communication No. 217a.

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:

$$pV(\text{liters per mole}) = RT$$

$$-0.0381(1 + 1150/T^2)p. \quad (10)$$

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:

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

Here v is the molecular volume of the condensed state. For liquid hydrogen⁹ it is 28.43 cm³, for solid deuterium¹⁰ 23.15 cm³ and for liquid deuterium it was assumed to be 25.2 cm³ or 11.5 percent smaller than that of liquid hydrogen. For liquid hydrogen the observations of Keesom, Bijl and van der Horst¹¹ were used. The two derivatives of Eq. (11) were determined graphically.

⁹ International Critical Tables, Vol. I, p. 102.

¹⁰ Clusius and Bartholomé, Zeits. f. tech. Physik 15, 545 (1934).

¹¹ Keesom, Bijl and van der Horst, Proc. Amst. Acad. Sci. 34, 1229 (1931).

TABLE VII. Differences between heats of vaporization.

	TEMP. RANGE	$\Delta L(n-e)$	$\Delta L(p-o)$
Solid D ₂	16°-18.71°K	0.6±0.5	1.8±1.5
Liquid D ₂	18.71°-20.4°K	0.0±0.5	0.0±1.5
Liquid H ₂	16°-20.4°K	2.3±0.5	-3.1±0.7

The results are tabulated in Table VII 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 H₂ and D₂ 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.

It is interesting that $\Delta L(p-o)$ for liquid D₂ 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 VII. Since $\Delta P v(p-o)$ for the condensed phases is negligibly small, the ΔL values of Table VII are also the differences between the internal energies of the condensed states.

ON THE UNCATALYZED CHANGE OF THE VAPOR PRESSURE OF LIQUID DEUTERIUM WITH TIME

Scott, Brickwedde, Urey and Wahl⁸ 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 one mm of Hg in 4 hours, whereas the change for deuterium is less than one mm in 200 hours. The vapor pressure increase of liquid hydrogen follows the law of a bimolecular reaction, which Cremer and Polanyi¹² found to fit their thermal conductivity measurements of the increase of p -H₂ in liquid hydrogen. Since the p -H₂ 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 -H₂ molecules having a nuclear magnetic moment of 5.8 Bohr nuclear magnetons (BNM)¹³ 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 -D₂ to o -D₂ in liquid deuterium will follow the simple bimolecular change of hydrogen. Five-sixths of the o -D₂ molecules have a nuclear magnetic moment of 1.5 BNM¹³ and the remaining sixth has a zero moment; there is no rotational moment. The p -D₂ molecules have a nuclear magnetic moment of 0.75 and a rotational moment of 0.42 BNM.¹⁴ The resultant moments of p -D₂ are 1.2, 0.9, and 0.3, averaging 0.8 BNM. It is seen, therefore, that not only does the para to ortho deuterium 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.

Wigner¹⁵ 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 H₂ molecules, the magnetic moments μ_1 and μ_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

$$W(J=1 \rightarrow J=0) \propto I_H \mu_1^2 \mu_2^2 ((2i+1)/i) \quad (12)$$

resulting from collisions with paramagnetic o -H₂ in liquid H₂, substituting for μ_1 , the magnetic

¹³ J. Estermann and O. Stern, *Nature* **132**, 169 (1933); **133**, 911 (1934); J. I. Rabi, J. M. B. Kellogg and J. R. Zacharias, *Phys. Rev.* **46**, 157, 163 (1934).

¹⁴ The value 0.42 is based upon the assumption that the rotational moments are proportional to the angular velocities of rotation.

¹⁵ Wigner, *Zeits. f. physik. Chemie* **B23**, 31 (1933).

¹² Cremer and Polanyi, *Zeits. f. physik. Chemie* **B12**, 231 (1921).

moment of $o-H_2$. The velocity constant, 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 Eq. (12), we obtain

$$K_H = CI_H \left[\frac{1}{3} ((6.6)^2 + (5.9)^2 + (5.0)^2) \right] (2.9)^2 4 \\ = 1.2 \times 10^3 C'.$$

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

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

The different statistics applicable to H and D require different spin factors in Eqs. (12) and (13)

$$K_{p,p} = C(2I_H) \left[\frac{1}{3} ((1.2)^2 + (0.9)^2 + (0.3)^2) \right] \\ \times (0.75)^2 6 = 5.3 C'.$$

For the para to ortho conversion resulting from collisions of $o-D_2$ and $p-D_2$ molecules

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

and

$$K_{o,p} = C \times (5/12) (2I_H) (1.5)^2 (0.75)^2 6 = 6.3 C'.$$

The factors 5/6 and 1/2 were introduced to take account of the fact that (1) only 5/6 of the $o-D_2$ 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 $[o-H_2]$ and $[p-D_2]$ are the concentrations of $o-H_2$ and $p-D_2$ in liquid hydrogen and liquid deuterium, respectively

$$d[o-H_2]/dt = K_H [o-H_2]^2 = 1.2 \times 10^3 C' [o-H_2]^2$$

and

$$d[p-D_2]/dt = K_{p,p} [p-D_2]^2 \\ + K_{o,p} (1 - [p-D_2]) [p-D_2] \\ = \{6.3[p-D_2] - [p-D_2]^2\} C'.$$

The ratio of the rate of $o-H_2 \rightarrow p-H_2$ in liquid normal hydrogen, to the rate of $p-D_2 \rightarrow o-D_2$ in normal deuterium is

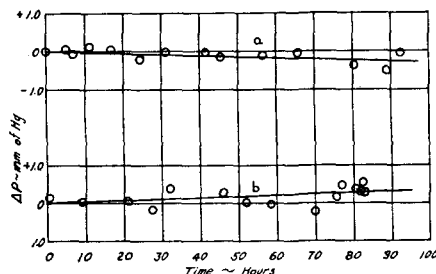


FIG. 3. The uncatalyzed change in the vapor pressure of liquid normal deuterium at 20.4°K.

$$(d[o-H_2]/dt)_{n.H_2} / (d[p-D_2]/dt)_{n.D_2} = 3.4 \times 10^2.$$

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

$$(dP/dt)_{n.H_2} / (dP/dt)_{n.D_2} = 1 \times 10^3.$$

Although this calculation is not to be regarded as rigorous, it shows that the rate of conversion of para to ortho deuterium is approximately proportional to the concentration of $p-D_2$ 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.

Fig. 3a and b are graphs of observations of the vapor pressure of normal deuterium at 20.38°K plotted against the age of the condensed state. Fig. 3a is a reproduction of previously reported data obtained February 1934. The data of Fig. 3b were observed December 1934 with purer deuterium. ΔP 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 the method of least squares, with each point given equal weight.¹⁵ 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

¹⁵ We are indebted to W. E. and L. S. Deming of the Bureau of Chemistry and Soils, Department of Agriculture for the statistical analysis of our data.

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 ± 0.27 mm at 100 hours.

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.¹⁷ 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.

¹⁷ Johnston and Long, J. Chem. Phys. 2, 389 (1934).

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The Infrared Spectrum of Heavy Water

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Samples of water vapor containing 90 and 40 percent of deuterium have been examined in the infrared, and the absorption bands ν_2 and ν_3 for D_2O and ν_2 and ν_1 for HDO have been located. The position of ν_1 for D_2O is known from Raman scattering. Of the nine fundamental frequencies for the three varieties of water, eight have now been observed. The ninth, ν_3 for HDO , should lie very close to the corresponding band for H_2O and is apparently completely masked. Computed values of these frequencies already

available agree very well with the measured ones. A fair degree of resolution is obtained in the bands ν_3 . The fine structure observed agrees approximately with that predicted by using the molecular dimensions obtained by Mecke, *viz.*, OH distance $\sim 0.95 \times 10^{-8}$ cm and apex angle $\sim 105^\circ$. The magnitude of the interactions is so great, however, that precise determinations of these constants must await a more complete solution of the mechanical problem.

ALL available evidence indicates that the three atoms of the water molecule form an isosceles triangle. Hence there should be three active fundamental vibrations, and the bands should be of two types, involving changes in electric moment parallel to or perpendicular to the bisector of the apex angle. If this angle were smaller than 86.5° two of the fundamental bands should have zero branches and the other should not since the moment of inertia (B) about an axis bisecting the apex angle would then be less than the one (A) about a perpendicular axis lying in the plane. A larger angle ($A < B$) would require

one band with and two without zero branches. Only two fundamental bands have been identified however, and one is of each type. The fact that the one of lower frequency at 6.26μ (ν_2) has no zero branch strongly suggests the obtuse form. The fundamental ν_1 has not been observed in the infrared. It must be weak, and is apparently masked by ν_3 , the intense band at 2.67μ . In this region it would be exceedingly difficult to locate if no zero branch occurs. Its small intensity suggests that the associated motion must be nearly symmetrical (hence the designation ν_1) and consequently that it should yield the strong-