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Citation: [The Journal of Chemical Physics](#) **2**, 454 (1934); doi: 10.1063/1.1749509

View online: <http://dx.doi.org/10.1063/1.1749509>

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The Vapor Pressures and Derived Thermal Properties of Hydrogen and Deuterium^{1, 2, 3}

R. B. SCOTT, F. G. BRICKWEDDE, HAROLD C. UREY AND M. H. WAHL, *National Bureau of Standards and Columbia University*

(Received June 15, 1934)

(1) The vapor pressure equations of liquid and solid, normal deuterium were determined by comparison of the vapor pressure of deuterium with that of liquid, normal hydrogen between 13.9° and 20.40°K. The triple and boiling points of deuterium were found to be 18.58° and 23.5°K, respectively. (2) The changes with time in the vapor pressures of liquid hydrogen and liquid deuterium at 20.4°K, resulting from ortho-para conversions, were investigated. The rate of change of the vapor pressure of liquid deuterium resulting from its natural, self-conversion was found to be less than 1/40th of the natural rate of conversion for liquid hydrogen. (3) From the vapor pressure equations of deuterium and an equation of state, its latent heats were deduced by the use of the Clausius-Clapeyron equation. Two equations of state for deuterium were used: (a) the empirically determined equation for hydrogen, and (b) an equation deduced from an equation of state of hydrogen of a form required by the Bose-Einstein statistics by including the effect of mass in such

an equation. The first of these is believed to be the better approximation though the latter might be used with little change in results. The vapor pressure equation required by the third law of thermodynamics has been derived and by the use of the Debye theory values of the zero point energies and Debye Θ 's are secured. These Θ 's which are used to calculate the heat capacities of solid and liquid deuterium at constant pressure are calculated from the vapor pressure data. The difference between C_p and C_v is much greater for solid hydrogen than for solid deuterium indicating a larger coefficient of expansion in the case of hydrogen. This is to be expected because of the larger zero point energy of hydrogen. The heat capacity under saturation pressure of liquid deuterium is considerably less than that of hydrogen. A recalculation of the distillation data of Urey, Brickwedde and Murphy on the natural mixture of H_2 and HD shows that they secured approximately the enrichment to be expected from the theory and experimental conditions.

SINCE it was by the fractional distillation of liquid hydrogen that we first concentrated deuterium,³ we were naturally interested in determining the difference in the vapor pressures of the hydrogens responsible for the partial separation effected. Although in the initial stages of the separation one is concerned with the molecules HD and H_2 , the investigation reported here has to do with the molecules D_2 and H_2 . The difference between the vapor pressures of these isotopic molecules was found experimentally to be much larger than we had calculated³ upon the basis of accepted theories of the

vapor pressures of crystals. At the triple point of ordinary hydrogen (13.92°K), the calculated ratio of the vapor pressure of H_2 to that of D_2 at the same temperature is 3.35, whereas now it is found experimentally to be 10.8. The zero point energies were deduced, however, from the heat capacity of hydrogen under the saturation pressure instead of from the heat capacity at constant volume, data on which are not available. It appears that the difference between our previously calculated ratio of vapor pressures and that found here is due to larger zero point energies than those previously calculated. It appears further that the difference, $C_p - C_v$, is smaller for deuterium than for hydrogen, a situation which seems reasonable in view of the very large difference in the zero point energies of the solids, as will be shown later.

The deuterium used in this experiment was prepared by the electrolysis of a sample of heavy water of high concentration. Calculations using the usual fractionation factors for such an electrolytic process showed that it should be approximately 99.9 percent deuterium. It is, of course, difficult to be certain that a small

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

² The results contained in this paper were reported at the February and April, 1934 meetings of the American Physical Society in New York and Washington, respectively (Phys. Rev. **45**, 565 and 762 (1934)), and at the symposium on deuterium during the meeting of the American Chemical Society in St. Petersburg, March, 1934. The more theoretical aspects of the problem were presented by one of us as the Willard Gibbs Medal Award address in Chicago, April 28, 1934.

³ Urey, Brickwedde and Murphy: *A Hydrogen Isotope of Mass 2 and Its Concentration*, Phys. Rev. **40**, 1 (1932).

hydrogen impurity did not get into this sample. However, this sample of deuterium has the lowest vapor pressure of any we have investigated.

DESCRIPTION OF THE APPARATUS

Fig. 1 represents diagrammatically the apparatus used in making the vapor pressure measurements. The glass flask *F* which contained the sample of deuterium was connected with a capsule-shaped glass bulb, at the end of a

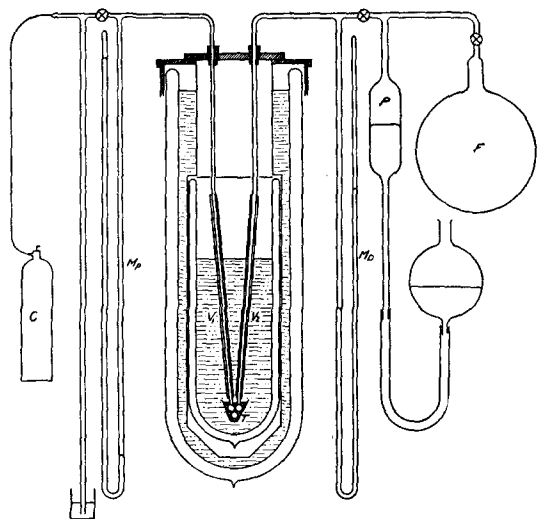


FIG. 1. The cryostat.

vacuum jacketed tube *V*₂, in the inner Dewar flask of a liquid hydrogen cryostat. The vapor pressure of the solid or liquid deuterium condensed in the capsule, when this inner Dewar flask was filled with liquid hydrogen, was measured on an oil (*n*-butyl phthalate) lubricated mercury manometer, *M*_D. By means of a hand operated mercury pump *P*, the deuterium sample was pumped from the flask *F* and afterwards returned to it.

Normal hydrogen, from a small cylinder *C*, was condensed in a glass capsule at the end of the tube *V*₁, and its vapor pressure was measured on the manometer *M*_P. The hydrogen as it flowed from the cylinder contained air as an impurity, the molecular concentration of which was not greater than 0.02 percent. Since the effect of solid oxygen on the vapor pressure of

the liquid hydrogen had not been investigated, the hydrogen as it flowed from the cylinder was passed over hot copper at 600°C, and then through a liquid air trap.

Temperatures were determined with a four lead, pure platinum, resistance thermometer, *T*, whose resistance at 0°C was 28.8 ohms. The platinum coil, wound on a mica cross,⁴ was sealed in a platinum case filled with helium, the four leads, current and potential, being brought out through a soft glass seal. The outside diameter of the platinum case was 0.5 cm and the overall length of the thermometer 5 cm. It was calibrated by comparison with the vapor pressure of freshly condensed normal hydrogen, using the vapor pressure equation discussed later for the determination of temperatures.

The temperature of the liquid hydrogen bath in the inner Dewar vessel was varied by means of a large capacity vacuum pump and a series of hand operated valves interposed between the pump and the vacuum connection at the top of the cryostat. With the aid of a fine adjustment valve and an oil filled manometer, especially designed for the purpose, it was possible to hold the pressure in the vapor space over the liquid hydrogen bath constant to within ± 0.2 mm of mercury.

Since the liquid hydrogen bath was not stirred, special precautions were taken to insure that the thermometer, and the hydrogen and deuterium condensates whose vapor pressures were to be investigated, were all at the same temperature. The manometer tubes, leading down to the capsules through the liquid hydrogen bath, were vacuum-jacketed, and the thermometer and two glass capsules were cast in a low melting point alloy metal block, as indicated in Fig. (1).

EXPERIMENTAL AND CALCULATED RESULTS

Vapor pressure of deuterium

In Table I are recorded a series of determinations of the vapor pressures of normal hydrogen and deuterium. The observed vapor pressures are given in columns 3 and 5. Column 4 is obtained from column 3 by correcting for the change with time of the vapor pressure of the

⁴For the method of winding these coils, see C. H. Meyers, Bur. Standards J. Research 9, 807 (1932).

TABLE I.

1	2	3	4	5
Age of condensed states hrs.	Temperature °K	Observed vapor pressure of hydrogen mm of Hg	Vapor pressure of normal hydrogen (calculated) mm of Hg	Vapor pressure of normal deuterium (observed) mm of Hg
0	20.334	749.8	749.8	252.0
0.5	19.969	672.0	672.0	218.5
1.2	19.330	550.3	550.0	168.5
1.5	19.167	522.0	521.7	157.1
2.4	18.953	486.5	486.0	143.2
2.8	18.945	485.3	484.9	142.4
3.0	18.182	372.8	372.4	97.7
3.6	17.479	287.3	287.0	65.5
4.0	16.463	190.6	190.3	35.0
4.5	15.188	106.2	106.1	14.2

hydrogen resulting from the conversion of ortho- to para-hydrogen. The ages of the condensed state at the time of the observations are recorded in column 1. The results of an investigation of the change of the vapor pressures of hydrogen and deuterium with time are presented below. The temperatures were calculated from the vapor pressures of normal hydrogen recorded in column 4, with the equation,

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

This 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 the ideal gas. All published vapor pressure measurements were considered, but this equation agrees best with the latest Leiden determinations.⁵

We have tried the use of two equations of state in our calculations. The following equation was deduced from the latest experimental determinations of the virial coefficients^{5a} for hydrogen:

$$PV = RT(1 - 0.0381/V(1 + 1150/T^2)), \quad (2)$$

where the volume is measured in liters. The latent heat at the boiling point calculated from these equations agrees exactly with Simon and Lange's⁶ experimental value and differs by only 0.3 percent at the triple point.

⁵ Keesom, Bijl and van der Horst, *Proc. Amst. Acad.* **34**, 1223 (1931).

^{5a} van Agh and Onnes, *Leiden Comm.* No. 176b (1925).

⁶ Simon and Lange, *Zeits. f. Physik* **15**, 312 (1923), see footnote 8.

It may be expected that deuterium will not have exactly the same equation of state as hydrogen. If the entire imperfection of these gases could be accounted for by the Bose-Einstein gas theory, the equation of state should be of the form,

$$PV = RTf(V^3T).$$

The equation,

$$PV = RT(1 - 13.192/VT^3) \quad (3)$$

agrees with the experimental data on hydrogen about as well as Eq. (2), though the value of the constant is much larger than that required by the theory for an ideal gas. The correction terms in the Bose-Einstein theory contain the mass to the same power as the temperature, and hence the maximum difference to be expected in the equations of state of hydrogen and deuterium can be estimated. The equation of state of deuterium would then be

$$PV = RT(1 - 4.6707/VT^3). \quad (4)$$

This equation of state for deuterium makes the maximum correction possible for the difference between the equations of state for hydrogen and deuterium, though it seems probable that the equation of state of deuterium will be more nearly the same as hydrogen. The use of either of the equations of state (2) or (4) for deuterium makes but little difference in the derived data, but Eq. (2) does fit the experimental and calculated results better than Eq. (4) does.

Fig. 2 is a graph of the logarithm of the vapor pressure of normal hydrogen against that of deuterium (columns 4 and 5 of Table I). The lines fitting the lower and upper ranges of pressures are the vapor pressure curves of solid and liquid D₂, respectively; their point of intersection (18.5°K) is the triple point of D₂. It is interesting to note that the observations plotted as in Fig. 2 fall along straight lines to within the precision of the results, whereas there is noticeable curvature of the graphs of the logarithms of the vapor pressures plotted against 1/T.

The experimental data can be represented by the empirical equations,

$$\log_{10} P(\text{D}_2 \text{ liquid}) = -1.363 + 1.310 \log P(\text{H}_2 \text{ liquid}), \quad (5)$$

$$\log_{10} P(\text{D}_2 \text{ solid}) = -1.954 + 1.534 \log P(\text{H}_2 \text{ liquid}). \quad (6)$$

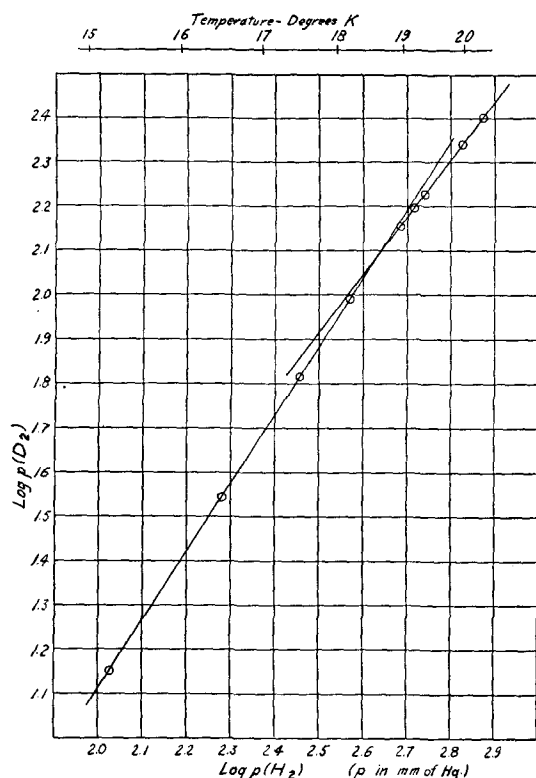


FIG. 2.

With Eq. (1), these become

$$\log_{10} P(\text{D}_2 \text{ liquid}) = 4.7459 - 58.5951/T + 0.02650T, \quad (7)$$

$$\log_{10} P(\text{D}_2 \text{ solid}) = 5.1995 - 68.6144/T + 0.03103T. \quad (8)$$

Since the vapor pressures of hydrogen and deuterium were compared directly, Eqs. (5) and (6) are independent of the temperature scale, whereas Eqs. (7) and (8) are not.

In Table II are listed the vapor pressures of normal hydrogen and deuterium at their boiling points, and triple points, calculated from these equations.

Although the values given by these equations and in Table II are accurate for the sample investigated, they may be subject to revision when purer deuterium is secured. As stated above, there are reasons for believing that the deuterium used here was of very high purity. The results reported here are not in good agreement with those of Lewis and Hanson,⁷ who

⁷ G. N. Lewis and W. T. Hanson, Jr., J. Am. Chem. Soc. 56, 1001 (1934).

TABLE II.

	Vapor pressure in mm of Hg	
	H ₂	D ₂
23.5°K (Boiling point of normal D ₂)	1740	760
20.38 (Boiling point of normal H ₂)	760	257
18.58 (Triple point of normal D ₂)	429	121
13.92 (Triple point of normal H ₂)	54	5

compared the vapor pressure of a supposedly "pure" sample of deuterium with that of para-hydrogen. For the same temperatures the vapor pressure values of Table II are lower than those of Lewis and Hanson, indicating that the sample of deuterium used for the investigations reported here was purer than theirs by about 0.5 percent. It is possible that the conversion of their reference sample of hydrogen to para-hydrogen was not as complete as they supposed, the error resulting, thereby, being in the direction to make their values for the vapor pressure of deuterium too high.

Latent heats of deuterium

Table III is a table of latent heats of hydrogen and deuterium. The values for hydrogen are the results of calorimetric determinations,⁸ those for deuterium were obtained by calculation from the slopes of the vapor pressure curves using the Clausius-Clapeyron equation. In the absence of experimental data, it was assumed that the molecular volumes of the liquid and solid deuterium between 13.92° and 20.38° are equal to those of liquid hydrogen at the same temperature.* The volumes of liquid hydrogen were taken from the *International Critical Tables*, Vol. I. Under $\Delta H(\text{ideal})$ are given the heats of vaporization to a gas at zero pressure, using

⁸ Simon and Lange, Zeits. f. Physik 15, 312 (1923). The equation of Simon and Lange was modified to allow for the difference in the temperature scales. This modified equation yields the same latent heats at the same thermal states as does the original equation, $Lv = 219.7 - 0.27(T - 16.63)^2$.

* Keesom and Lisman, Proc. Roy. Acad. Amst. 35, 607 (1932) have given the fusion curve of hydrogen. From these values it is possible to deduce with the aid of the equation

$$dP/dT = \Delta H_f / T \Delta V$$

the values of ΔV , and assuming that the molecular volume

TABLE III.

T	H ₂		D ₂		
	ΔH	$\frac{\Delta H}{\text{Ideal}}$	$^*\Delta H$	$^*\frac{\Delta H}{\text{Ideal}}$	$^\dagger\Delta H$
13.92	245.7	247.7			
	(28.0)	(28.0) [†]			
13.92	217.7	219.7	340.8	340.9	341.1
15.188			345.4	345.7	345.8
16.43			349.6	350.2	350.0
17.479			352.7	353.7	353.7
18.182			354.5	355.9	355.9
18.58	218.7	224.8	355.4	357.1	357.2
			(52.3)	(52.3)	(52.4) [†]
18.58			303.1	304.8	
18.945			304.0	305.9	
18.953			304.0	305.9	
19.167			304.4	306.5	
19.330			304.8	306.9	
19.969			306.0	308.6	
20.334			306.6	309.6	
20.38	215.9	225.3			

* The values given in these columns were calculated from the empirical vapor pressure equation.

† The values given here were calculated from the equation, $\Delta H = \Delta H_0 + (5/2)RT - H_s$, from values given in a following paragraph, where H_s is taken as a Debye energy with $\Theta_2' = 100$.

‡ The quantities in parentheses are the latent heats of fusion per mole. At the triple points latent heats of vaporization and sublimation are given.

Eq. (2) for both gases. The heat content of the gas is then given by the equation,

$$H = H_0 + (5/2)RT - (RT/V)0.0381(1 + 3450/T^2), \quad (9)$$

and it is only necessary to add the values of the last term to the values in column 4 to secure those in column 5 of Table III. If Eq. (4) is used for diplogen, the value of $\Delta H(\text{ideal})$ for deuterium at 20.334° is decreased by 4.15 cal., and other values in the table are decreased by small amounts. The heat of fusion is changed from 52.3 cal. to 53.1 cal.

of liquid hydrogen as given in the literature is correct, the molecular volume and density of solid hydrogen at the triple point can easily be calculated. When calculated in this way, the density is found to be larger than any values recorded. This would indicate that the values for the density of solid hydrogen are very inaccurately known. The correction for the volume of the solid is small in any case, amounting to only 1.8 cal. as a maximum. The error introduced by using the volumes of liquid protium is only about 10 percent of this, or about 0.2 cal. For this reason, we have not attempted to estimate the volume of solid deuterium any more accurately.

On the change of the vapor pressure of deuterium with time

Figs. 3 and 5 are graphs of determinations of the vapor pressures (reduced to 20.38°K) of liquid hydrogen and liquid deuterium plotted against the age of the liquid state.

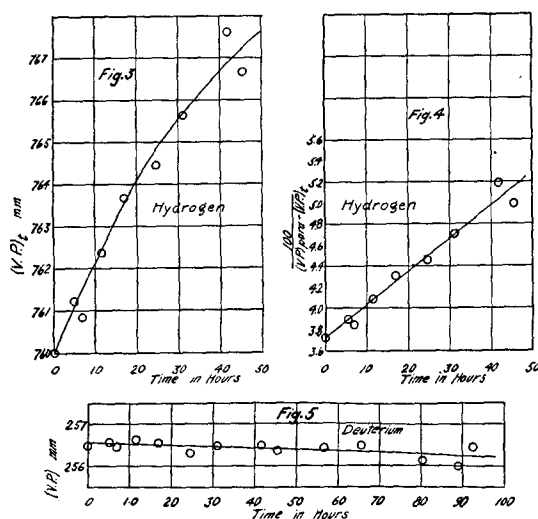


FIG. 3. The change of vapor pressure of hydrogen with time.

FIG. 4. The ortho-para conversion of hydrogen.

FIG. 5. The para-ortho conversion of deuterium.

Fig. 4 is a plot of one hundred times the reciprocal of the difference between the vapor pressure of para-hydrogen and the vapor pressure of the liquid hydrogen, originally normal, the age of whose condensed state is the abscissa. That the observations plotted in Fig. 4 fall along a straight line is a consequence of the conversion of ortho- to para-hydrogen in the liquid phase being a bimolecular change.⁹ For such a change, the rate of decrease of the ortho-hydrogen concentration ($-dx/dt$) is proportional to the square of the concentration,

$$-dx/dt = kx^2. \quad (10)$$

The slope of the line is $k/[(v.p.)_{\text{para}} - (v.p.)_{\text{ortho}}]$. The velocity constant k of the conversion change in the liquid phase was calculated using 786.86 mm of Hg for the vapor pressure of para-hydrogen and 751.00 mm for ortho-hydrogen at the temperature at which the vapor pressure of

⁹ Cremer and Polanyi, *Zeits. f. physik. Chemie* **B21**, 459 (1933).

freshly condensed normal hydrogen is 760.00 mm (20.38°K).¹⁰ The value obtained for k was 0.0114 per hour when concentrations are expressed in terms of mol fractions. This is in agreement with the value obtained by Cremer and Polanyi⁹ using the thermal conductivity method of analysis to follow the change in concentration of ortho-hydrogen. Their values range from 0.010 to 0.013, averaging 0.0118. The agreement is better than the accuracy of the work reported here and that of Cremer and Polanyi as well.

It is interesting to note that a small amount of solid oxygen in the liquid hydrogen markedly increased the rate of conversion, as was made manifest by a proportionately greater rate of increase of vapor pressure. The rate of increase for a sample containing about 0.01 percent O₂ was greater by a factor of 3 than the rate after the oxygen had been removed by passing the hydrogen over copper at 600°C.

Referring to Fig. 5, the straight line which is the best fit for the observations, reduced to 20.38°K, of the vapor pressure of originally normal deuterium plotted as a function of the age of the condensed state indicates a decrease of the vapor pressure of deuterium with time. However, F. G. Brickwedde, R. B. Scott and H. S. Taylor¹¹ have measured the vapor pressure of deuterium passed over a conversion catalyst at liquid hydrogen temperatures and find that at 20.38°K the vapor pressure of the "converted" deuterium is about 5 mm of Hg greater than the vapor pressure of normal deuterium. It was concluded that the uncatalyzed change of the vapor pressure of liquid normal deuterium with time is too small for measurement with the apparatus used in this investigation. The observations reported here show that the rate of change of the vapor pressure of normal deuterium with time is less than 1/40th of the rate of change of the vapor pressure of normal hydrogen.

¹⁰ Considering all the published determinations of the vapor pressure of para-hydrogen at the boiling point of normal hydrogen, 786.86 mm of Hg was selected as the most probable value for the vapor pressure of para-hydrogen. The vapor pressure of ortho-hydrogen (751.00 mm) was calculated from the vapor pressures of para- and normal hydrogen.

¹¹ F. G. Brickwedde, R. B. Scott and H. S. Taylor, *The Vapor Pressure of Ortho- and Para-Deuterium* to be published in this Journal.

CALCULATION OF THE VAPOR PRESSURE EQUATION WITH THE THIRD LAW AND THE DEBYE THEORY OF THE SOLID STATE

Simon and Lange found that the heat capacity of solid hydrogen under saturation pressure could be described by the use of a Debye function using a Θ_1' of 91. It is assumed here that it is also possible to describe the heat capacity of solid deuterium at zero pressure in a similar way. The Θ 's which are used for the thermodynamic functions at constant pressure will be indicated by primes. The subscripts 1 and 2 will be used to designate the values of the quantities for hydrogen and deuterium, respectively.

In the paper by Urey, Brickwedde and Murphy,³ an approximate theory for the ratio of vapor pressures of solid H₂ and solid D₂ was developed, assuming (1) that the vapor pressure could be calculated using the third law of thermodynamics, (2) that the zero point energies were given by the Debye theory of the solid state, namely $(9/8)R\Theta$, and moreover, (3) that the Θ 's for the two hydrogens varied inversely as the square roots of the molecular weights. The ratio of vapor pressures calculated for molecules of masses 2 and 4 was 3.354 at the triple point of hydrogen, which is in marked disagreement with the experimental results reported in this paper. For hydrogen the value of Θ_1' derived by Simon and Lange⁶ from the heat capacity under the saturation pressure was used. This cannot give the correct Θ_1 for it would be necessary to derive this from the heat capacity at constant volume, and since the heat capacity at constant volume must be less than the heat capacity at constant or saturation pressure, the true Θ_1 must be greater than the value used, namely 91. With values for the coefficients of expansion and of compressibility of hydrogen from the *International Critical Tables*, the difference $C_p - C_v$ is calculated to be about 37 cal., where in fact the heat capacity of hydrogen under saturation pressure is about 1.2 cal. It is obvious that these coefficients of expansion and compressibility are very inaccurately known. Moreover, the assumption that the internal rotational and vibrational energies in the solid and gaseous states are the same will be discussed later. Also, it was assumed that the gases

followed the ideal gas laws. This, of course, is only approximately true, but the corrections necessitated by this approximation are small.

The free energy of the gaseous hydrogen at a pressure P can be set equal to the free energy at a very low pressure P^* approaching zero $+\int_{P^*}^P VdP$. The free energy of the gas at pressure P^* is given accurately by the Sackur-Tetrode equation,

$$F = H_0 + (5/2)RT - RT(\ln M^{3/2}T^{5/2}P^*) + CT. \quad (11)$$

The free energy of the solid is equal to its free energy under pressure $P^* + \int_{P^*}^P V_s dP$, and if the volume of the solid can be regarded as constant with changing pressure, this additional term is equal to $V_s P$. At equilibrium these free energies must be equal. Equating them and introducing the equation of state (2), we secure for the vapor pressure equation,

$$\ln P = -\frac{\Delta H_0}{RT} + \frac{5}{2} \ln T + \frac{3}{2} \ln M + 2.30259i + \frac{V_s P}{RT} + \frac{F_s}{RT} + \ln \left(1 - \frac{0.0381}{V} \left(1 + \frac{1150}{T^2}\right) + \frac{2 \times 0.0381}{V} \left(1 + \frac{1150}{T^2}\right)\right), \quad (12)$$

where ΔH_0 is the heat of vaporization at absolute zero, i is the chemical constant equal to -1.5882 according to Birge,¹² and F_s is the free energy of the solid at zero pressure. The correction term due to the imperfection of the gas has been calculated by calculating the volume from the equation of state at the pressures given by the empirical vapor pressure Eq. (8). As before, we have taken the volume of the solid deuterium as equal to the volume of liquid hydrogen as given by the *International Critical Tables*. These correction terms for deuterium are small.

As stated above, it is assumed that F_s can be described by the use of a Debye Θ_2' . By trial and error it is found that constant values for ΔH_0 can be secured if Θ_2' is taken as equal to 100.¹³

The values of ΔH_0 calculated in this way for

¹² Birge, Rev. Mod. Phys. 1, 65 (1929).

¹³ The values of F_s as a function of Θ_2' are given in the Handbuch d. Physik, Volume 10, page 369.

the four temperatures for which measurements have been made give the values in Table IV.

TABLE IV.

T	15.188	16.463	17.479	18.182	
ΔH_0	276.11	275.97	276.09	276.08	Av. 276.06

The average value of ΔH_0 determined in this way is 276.0 cal./gram mole. By using equation of state (4) and by making a similar calculation, ΔH_0 equals 276.2 cal./gram mole and $\Theta_2' = 105$. Thus it seems to be impossible to change the value of ΔH_0 except by small amounts and that Θ_2' is correct within about ± 5 units.

This Θ_2' is one which will describe the thermodynamic functions for solid deuterium in this range of temperature at zero pressure, though with the small vapor pressures involved, no observable difference can be expected if the thermodynamic functions are those under the saturation pressures. The heats of vaporization recorded in the last column of Table III for solid deuterium have been calculated using the constants derived here. The agreement between the heats of vaporization calculated from the empirical equation (column 5) and the equation given in this section is very good and indicates that Eqs. (12) and (8) give the vapor pressures equally well.

Simon and Lange⁶ have determined the heat of vaporization and the heat of fusion of the solid hydrogen. They found that the heat of sublimation of solid hydrogen at the triple point is 245.8 cal./mole. This is equal to the heat content of the vapor at a pressure of 5.38 cm mercury minus the heat content of solid deuterium at the triple point. With our equation of state and Eq. (9),

$$\Delta H = \Delta H_0 + (5/2)RT - (RT/V)0.0381(1 + 3450/T^2) - H_s \quad (\Theta = 91).$$

Substituting the numerical values, we find that $\Delta H_0 = 182.9$ instead of 183.4 as given by Simon.

CALCULATION OF THE ZERO POINT ENERGIES

If it is assumed as it was by Urey, Brickwedde and Murphy that the heat of vaporization of the vibrationless solid to the motionless gas at

absolute zero, represented by χ , is the same for hydrogen and deuterium, and that the ratio of the zero point energies of the two solids is inversely proportional to the square root of the molecular weights, it is possible to calculate the value of χ and of the zero point energies. Thus

$$\chi = E_0(\text{H}_2) + 182.9 = E_0(\text{D}_2) + 276.0$$

and

$$E_0(\text{H}_2)/E_0(\text{D}_2) = (4.0273/2.0156)^{\frac{1}{2}}.$$

From these equations, $\chi = 501.2$, $E_0(\text{H}_2) = 318.3$ and $E_0(\text{D}_2) = 225.2$. The corresponding Θ 's are given by the equation $\Theta = 8/9 E_0/R$, and thus we find that $\Theta_1 = 142.4$ and $\Theta_2 = 100.7$. These should be used to calculate the heat capacity and other thermodynamic properties at constant volume. The Θ_1 is greater than the Θ_1' and hence the heat capacity of hydrogen at constant pressure is greater than that at constant volume. The difference between Θ_2 and Θ_2' is so small that we cannot be certain that this is not altogether due to the nature of the calculation, and thus we may say that these quantities would indicate that the heat capacity at constant pressure and at constant volume for deuterium are equal. With the well-known thermodynamic relation $C_p - C_v = \alpha^2 VT/\beta$, where α and β are the coefficients of thermal expansion and compressibility respectively, it is seen that the coefficient of thermal expansion for deuterium must be very small. This is surprising and leads us to question the assumption upon which this calculation is based.

EFFECT OF ROTATIONAL AND VIBRATIONAL ENERGY CHANGES

In the calculations which we have made, it is assumed that there is no change in the rotational and internal vibrational energies of the molecules in going from the solid to the gaseous state. The Raman spectra data on liquid hydrogen show that energy differences of the rotational states are within experimental error (approximately 1 wave number) equal to the differences in the gaseous state, and that the vibrational frequency in the liquid state differs from its value in the gaseous state¹⁴ by about 10 cm^{-1} .

¹⁴ J. C. McLennan and J. H. McLeod, Roy. Soc. Canada, Trans. **23**, Section 3, 19-20 (1929); McLennan, Smith and Wilhelm, *ibid.* 279-282 (1929).

This difference is not much greater than the experimental error as nearly as we can judge. It may be expected that the difference may be even larger in the solid state. Recent work by Salant, Sandow and Callahan¹⁵ on the Raman spectra of the hydrogen halides show very appreciable differences in the vibrational frequencies in the gaseous, liquid and solid states, and that the frequencies are uniformly less in the condensed phases. This would affect the heat of vaporization since it would be necessary to supply energy to the internal degrees of freedom in the process of vaporization. If the change in vibrational frequency for hydrogen is 10 cm^{-1} and if the percent change in the vibrational frequencies of deuterium is the same as that for hydrogen, the heats of vaporization would be increased by approximately 14 and 10 cal., respectively, for hydrogen and deuterium. In order to secure the contribution to the heats of vaporization at 0°K due to the potential energies between the molecules the previously calculated ΔH_0 's must be decreased by 14 and 10 cal., respectively. If there is such a difference between the internal vibrational energies for the solid and vapor states, these reduced ΔH_0 's should be introduced into Eq. (13) for the calculations of the E_0 's. The Θ 's would be increased, thus making $\Theta_2' = 106.4$ and hence somewhat larger than Θ_2 .

Such a correction would still leave the heat capacity at constant pressure for deuterium very nearly equal to its heat capacity at constant volume. However, any such correction would change the values of the Θ_1 and Θ_2 by the same percentage, and thus the heat capacity of deuterium at constant volume will always be larger than that of hydrogen, as is to be expected. This means that the difference between the heat capacities at constant pressure and constant volume will always be less for deuterium than for hydrogen, and hence the ratio of the square of the coefficient of expansion to the coefficient of compressibility will be less for deuterium than for hydrogen. One might expect the coefficient of compressibility of hydrogen to be larger than this coefficient for deuterium, and hence, in order

¹⁵ Salant and Sandow, Phys. Rev. **37**, 373 (1931). Salant and Callihan, Phys. Rev. **43**, 590 (1933).

to account for the difference in the ratio, it must be assumed that the coefficient of thermal expansion of deuterium is less than that for hydrogen. This conclusion seems reasonable because the zero point energy of hydrogen amounts to about 64 percent of the value of χ , while for deuterium it is only 46 percent of this quantity. As energy is acquired by the vibrating solid, the oscillators become more anharmonic and hence the volume of the solid increases. The high energy oscillators of hydrogen should be more anharmonic in character than the high energy oscillators of deuterium, and hence it is reasonable to expect that hydrogen should expand more rapidly which would be in accordance with our conclusions.

It follows, of course, that the ratio of the zero point lattice energies will not be exactly proportional to the square root of the molecular weights if this anharmonic character is considered, and in fact that the ratio of the zero point energies of hydrogen to that of deuterium will be less than that assumed. The zero point energy of both hydrogen and deuterium are increased over that calculated above, and thus, their Θ 's are larger and the heat capacity at constant volume calculated in this way is decreased, again bringing the whole calculation to a more understandable situation.

Pauling¹⁶ has considered the rotational energy of hydrogen molecules in the solid state, for the special case of free rotation or an oscillatory rotation in a plane. He gives reasons for believing that the height of the potential energy hill corresponding to a rotation of the molecule through 180° is about 112 cal./mole. This theory cannot be used for a rotator in space, but the application of the perturbation theory to this problem, if the height of the potential energy hill is small, as compared with the energy difference of the lowest rotational states, can be made by well-known methods. In this way the energies of the lowest rotational states of the perturbed rotator in space are found to be those of the third column of Table V. The potential energy curve is assumed to be of the same form as that used by Pauling, namely, $V = V_0(1 - \cos 2\theta)$. If we use Pauling's value for V_0 ,

TABLE V.

J	M	ΔE	ΔE (cals./mole)
0	0	$4/3 V_0$	20
1	0	$4/5 V_0$	12
1	± 1	$8/5 V_0$	24

namely 56, it is immediately evident that there is a very large difference in energy between the 1, 0 and the 1, ± 1 states, and thus, the ortho-hydrogen in the solid phase would be in the lower of these two states. Thus the entropy of hydrogen as determined from the heat capacity curve would not agree with the observed value.¹⁷ This is due to the fact that part of the degeneracy of the first rotational state would have disappeared at these temperatures. Hence, the height of the potential energy hill must be very much smaller than was assumed by Pauling. If V_0 is smaller, say 28 cal./mole, a maximum would occur in the heat capacity in the region of about 10° absolute, which again is not in agreement with experiment. It must be concluded that the value of V_0 is small, something like 15 cal./mole, or less. Taking this value, one secures for the change in energy states in the solid the values given in the last column of Table V.

At the absolute zero, all the molecules in the first rotational state would occupy the level, $J, M=1, 0$. Since ΔH_0 was deduced by extrapolation from higher temperatures where very nearly statistical distribution between the states exists, in proportion to the *a priori* probabilities, and since at higher temperatures the mean energies of the states $J=0$ and $J=1$ do not depend on the temperature, a value for ΔH_0 was obtained which does not depend upon the differences in rotational energy of Table V. Hence, our extrapolation to absolute zero does not include any rotational effect of this kind. Moreover, since it is necessary to assume a very low value of the potential energy hill in solid hydrogen, it follows that the calculated values also hold for deuterium, and hence, that there is practically free rotation in the case of solid deuterium.

Throughout this discussion it is assumed χ to be the same for solid hydrogen and deuterium

¹⁶ L. Pauling, Phys. Rev. **36**, 430 (1930).

¹⁷ Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

and this assumption may not be correct. Bernal¹⁸ has shown that the molecular volume of solid deuterium oxide is less than that of ice and similarly the molecular volumes of solid hydrogen and deuterium may not be identical. If this were the case, the values of χ and the restoring forces would hardly be the same in the two cases. Hence the ratio of the zero point energies would not be the inverse of the square roots of the molecular weights. Both of these assumptions may need revision later.

We can conclude that the zero point energies and the χ for solid hydrogen and deuterium are greater than those recorded above, and that $C_p - C_v$ is considerably greater for hydrogen than for deuterium and hence that the coefficient of expansion of hydrogen is greater than that of deuterium.

HEAT CAPACITIES OF HYDROGEN AND DEUTERIUM

The heat capacities of the solids were calculated using the Θ 's and Θ 's derived in the preceding sections assuming as before that they follow the Debye functions. The values thus calculated are listed in Table VI.

The heat capacities of the liquids can be secured from the relation,

$$d\Delta H_{(\text{ideal})}/dT = \Delta C = (5/2)R - C_{s(\text{liquid})}.$$

It is found that C_s is approximately equal to a constant $\times T$ both for hydrogen and deuterium. The heat capacity of liquid hydrogen derived from the vapor pressure equation and the equation of state used here is equal to $0.2314T$. The values calculated in this way are listed in Table VI together with the values calculated from Simon and Lange's empirical equation based on their calorimetric measurements. The agreement between the two sets of values indicates the reliability of heat capacity data calculated from vapor pressure data and the equation of state.

In the same way, the heat capacities of liquid deuterium have been calculated and listed in Table VI. The results indicate that the heat capacity of liquid deuterium is considerably less than that of liquid hydrogen and that there is less difference in the heat capacities of liquid

TABLE VI.

<i>T</i>	<i>Solid</i>			<i>D₂</i>
	<i>H₂</i>	<i>C_v</i>	<i>C_{p=0}(C_s)</i>	<i>C_v</i>
	$\Theta_1' = 91$	$\Theta_1 = 142.4$	$\Theta_2' = 100$	$\Theta_2 = 100.7$
10	0.59	0.16	0.45	0.44
11	0.76	0.21	0.59	0.58
12	0.94	0.28	0.74	0.73
13.92	1.32	0.42	1.07	1.06
16	—	—	1.46	1.43
18	—	—	1.84	1.82
18.58	—	—	1.96	1.92

<i>Liquid</i>			
	<i>C_s</i> (S. & L.)	<i>C_s</i> (this paper)	<i>C_s</i>
13.92	3.19	3.22	—
16	3.62	3.70	—
18	4.02	4.17	—
18.58	4.15	4.30	2.20
19	4.24	4.40	2.26
19.5	4.34	4.51	2.32
20	4.44	4.63	2.38
20.38	4.53	4.72	2.42

and solid deuterium at its triple point and under its saturation pressure than of liquid and solid hydrogen at its triple point and under its saturation pressure.

THE VAPOR PRESSURE OF SOLID HYDROGEN-DEUTERIUM

Urey, Brickwedde and Murphy gave an approximate calculation of the ratio of vapor pressures of the solid hydrogen and the solid hydrogen-deuterium.* The results of this paper make possible a better estimate of this ratio. If it is assumed that the Θ 's are inversely proportional to the square roots of the molecular weights, the calculated Θ_{12} for the hydrogen-deuterium solid equals $\sqrt{\frac{2}{3}}\Theta_1$ and is 125. If further it is assumed that the Θ_{12}' is between the Θ 's of the hydrogen and deuterium, i.e., about 97, the ratio of the vapor pressures of hydrogen and hydrogen-deuterium at 13.92°K should be 2.42. With this in the Rayleigh distillation formula, it is possible to calculate the enrichment which should have been secured

* The ratio of the vapor pressures calculated for these two was given as 2.698. This is unfortunately in error. We neglected the factor $3/2$ in the last term of our Eq. (6), Phys. Rev. **40**, 4 (1932). The correct value should have been 2.23.

¹⁸ Bernal, Proc. Roy. Soc. **A144**, 24 (1934).

in the original distillations made by simple evaporation 2 mm of Hg above the triple point pressure. The hydrogen used in these experiments was prepared electrolytically from cells which had been freshly filled with ordinary water. The hydrogen discharged from these cells, as is now known, should contain considerably less deuterium than natural hydrogen. It seems reasonable to assume that the hydrogen used in these experiments contained about 1 part deuterium in 25,000. The ratio of the original volume of liquid hydrogen to the final volume was approximately 4000. Substituting in the Rayleigh equation,³ it is found that the final sample

should have contained approximately 1 part in 200 of deuterium instead of 1 part in 1100 as found by the mass-spectrograph analysis. Or, if the observed fractionation factor is calculated using 1 part in 25,000 for the original concentration, and one part in 1100 for the final concentration, one obtains 2.1 for the ratio of the vapor pressure of hydrogen to that of hydrogen-deuterium at 13.92°K. Because of its low surface tension and density, boiling liquid hydrogen readily forms a spray which is carried along with the vapor in a distillation. It appears, therefore, that the enrichment secured was about what should be expected from the theory.

The Raman Spectrum of Heavy Water Vapor

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(Received May 29, 1934)

The Raman spectrum of heavy water vapor was obtained by using water having a $d_{20}^{20} = 1.073$, at two atmospheres pressure. A line $\Delta\nu = 2666 \text{ cm}^{-1}$ was found for D_2O and $\Delta\nu = 2718 \text{ cm}^{-1}$ for HDO . The other line expected from the work of Wood on liquid heavy water in the region $\Delta\nu = 3700 \text{ cm}^{-1}$ was not found. The line $\Delta\nu = 3650 \text{ cm}^{-1}$ of H_2O was resolved into a doublet $\Delta\nu = 3646.1 \text{ cm}^{-1}$ and $\Delta\nu = 3653.9 \text{ cm}^{-1}$. An attempt has been made to explain the Raman spectrum of H_2O empirically by using the data of Mecke on the infrared absorption spectrum of H_2O .

EXPERIMENTAL

THE apparatus used in the present investigation was essentially the same as that employed by one of us¹ previously in obtaining the Raman spectrum of ordinary water.

In order to utilize a long scattering tube to the best advantage it is necessary to make the distance from the condensing lens to the scattering tube large compared to the distance from the lens to the slit of the spectrograph. Necessarily the fulfillment of this condition produces a very small image, which must be accurately focussed on the slit of the spectrograph. This adjustment can be made quite accurately in the following manner. After the scattering tube has been lined up, the achromatic condensing lens is put in the proper position to focus the image on the slit of the spectrograph. The prisms are then removed from the spectrograph and an auxiliary telescope is aimed down the collimator

and the slit brought into sharp focus. The condensing lens is then adjusted until the two tiny arcs of light caused by the light diffracted by the diaphragm in the scattering tube come into sharp focus. The necessity for a critical focus of this small image is best appreciated when one considers the fact that in the present case the actual useful length of the spectral lines on the photographic plate was only 0.25 mm.

From a sample of heavy water $d_{20}^{20} = 1.048$ the Raman spectrum of the liquid was obtained. A reproduction of this spectrogram is shown in Fig. 1b. This sample had been purified by a distillation from alkaline KMnO_4 . However, in spite of this treatment it fluoresced so badly that the spectrum was only obtainable by the use of strong filters. We were unable to obtain any results from this sample in the vapor phase because of the strong fluorescence.

The second sample of heavy water which we used had a $d_{20}^{20} = 1.073$, which should contain on a basis of pure probability approximately 11.5 percent H_2O , 45.0 percent HDO and 43.5 percent D_2O . This sample was much better than

* Presented by K. D. Larsen in partial fulfillment of the requirements for the degree of Ph.D. at the Pennsylvania State College.

¹ D. H. Rank, *J. Chem. Phys.* **1**, 504 (1933).