

Heat Capacity Curves of the Simpler Gases. VI. Rotational Heat Capacity Curves of Molecular Deuterium and of Deuterium Hydride. The Equilibrium Between the Ortho and Para Forms of Deuterium. Free Energy, Total Energy, Entropy, Heat Capacity and Dissociation of H_2H_2 and of H^1H_2 , to 3000°K

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J. Chem. Phys. **1**, 620 (1933); 10.1063/1.1749337



And again: "The fact that the logarithm of the dissociation constant varies proportional to $1/D$, and that this variation is implied in Bjerrum's picture cannot be thought to corroborate the latter." Reference to Eq. (7) of our third paper will show that the logarithm is not proportional to $1/D$ but that

$$\log K \sim \log D + A/D.$$

This formula covers a range of experimental

data to which the simple equation cited by Gross and Halpern does not apply.

In conclusion, we wish to point out that our formulation of the problem of electrolytic solutions provides a simple and consistent picture of these solutions which reproduces the experimental data over a wide range of conditions. In contrast, the theory of Halpern and Gross fails to reproduce experimental observations even in a narrow range of concentration, and in solvents of lowest dielectric constant.

Heat Capacity Curves of the Simpler Gases. VI. Rotational Heat Capacity Curves of Molecular Deuterium and of Deuterium Hydride. The Equilibrium Between the Ortho and Para Forms of Deuterium. Free Energy, Total Energy, Entropy, Heat Capacity and Dissociation of H^2H^2 and of H^1H^2 , to 3000°K^1

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(Received March 5, 1934)

Heat capacities, entropies, free energies, total energies and dissociation constants have been calculated for H^2H^2 and for H^1H^2 , to 3000°K , by reliable methods and are listed in tabular form. The ortho-para equilibrium in H^2H^2 has been considered for both the gaseous and the solid states. The solid state equilibrium has been discussed from the point of view of its bearing on the application of the third law of thermodynamics. The rotational heat capacity curves of the various forms of H^2H^2 and that of H^1H^2 are shown graphically and are compared with the rotational

heat capacity curve of ordinary hydrogen and with the hypothetical rotational specific heats of gaseous nitrogen. The heavy molecules, H^2H^2 and H^1H^2 , dissociate to only about one-half the extent of H^1H^1 below 3000°K . The three hydrogen molecules are compared with respect to the influences of molecular stretching and of anharmonic vibration in the high temperature heat capacities. We also include tables which show the distributions of molecules among the vibrational levels as a function of the temperature.

THE growing importance of deuterium and its compounds, and its increasing availability, warrant the preparation of accurate and extensive tables of its thermodynamic properties. Particular interest also attaches to the rotational heat capacity curves of molecular deuterium, which possesses ortho and para modifications, and of deuterium hydride, which exists in only one form.

We have carried out accurate calculations of this character by the summation method¹ which Davis and Johnston¹ have shown is, for the

special case of hydrogen, *more rapid* than are approximation methods.²

The discrete energies, E_i , were calculated by the equation

ibid. 55, 172, 187 (1933)], on neutral OH [Johnston and Dawson, ibid. 55, 2744 (1933)], on CO and N_2 [Johnston and Davis, ibid. 56, 271 (1934)] and on ordinary H_2 [Davis and Johnston, ibid. 56, 1045 (1934)]. The equations appropriate to the exact summation method, and the labor saving use of "corrected approximations," in obtaining sums for the excited vibrational levels, used again in this paper, are discussed in the paper by Johnston and Chapman. As we do not wish to employ space to repeat details of that treatment, the reader is referred to these earlier papers.

² Giauque and Overstreet, J. Am. Chem. Soc. 54, 1731 (1932); Johnston and Davis, ibid. 55, 271 (1934); Kassel, J. Chem. Phys. 1, 576 (1933); Gordon and Barnes, ibid. 1, 297 (1933).

* Charles A. Coffin Research Fellow, 1933-34.

¹ Previous papers in this series have been published in the Journal of the American Chemical Society. These include calculations on NO [Johnston and Chapman, J. Am. Chem. Soc. 55, 153 (1933)], on O_2 [Johnston and Walker,

$$\begin{aligned}
E_i = & \omega_e(v + \frac{1}{2}) - X_e\omega_e(v + \frac{1}{2})^2 \\
& + [B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \delta_e(v + \frac{1}{2})^3] \\
& \times J(J+1) + [D_e + \beta_e(v + \frac{1}{2})]J^2(J+1)^2 \\
& + F_eJ^3(J+1)^3. \quad (1)
\end{aligned}$$

The molecular constants which we employed are given in Table I, and were computed from those of ordinary hydrogen³ by the use of the established relationships between the constants of isotopic molecules.⁴ For this purpose we employed the mass numbers 1.00778⁵ and 2.01363⁶ for protium and deuterium, respectively.

TABLE I. *Molecular constants of the heavy hydrogens (in cm⁻¹).*

	H ² H ²	H ¹ H ²
ω_e	3125.4	3826.6
$X_e\omega_e$	65.72	98.52
B_e	30.465	45.668
α_e	1.0859	1.9931
γ_e	0.01713	0.03850
$-\delta_e$	0.00115	0.00317
$-D_e$	0.01165	0.02618
β_e	1.80×10^{-4}	4.95×10^{-4}
F_e	6.49×10^{-6}	2.19×10^{-5}

Account was also taken of the one unit⁷ of nuclear spin which is associated with the deuterium atom and which necessitates additional weight factors of 3 and 6, respectively, in the odd

³ Jeppeson, Phys. Rev. **44**, 165 (1933).

⁴ Cf. Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge University Press (1932), p. 212, for a convenient summary of these. These relationships, which have been verified to within the limits of experimental accuracy for many molecules in which the effect is much smaller than for hydrogen, have also been verified in the spectra of neutral OH (unpublished data of Johnston and Dawson) in which the isotopic shifts are greater than in hydrogen. However, we do not mean to imply that the constants listed in Table I are necessarily reliable to the full number of significant figures to which they are published since, indeed, the constants of ordinary hydrogen are not that reliable. But a reasonable estimate of the uncertainty which attaches to these constants by reason of the relationships used in deriving them indicates that the influence on the values of the various thermodynamic properties lies within the precision to which the latter are expressed.

⁵ Aston, Proc. Roy. Soc. **A115**, 487 (1927).

⁶ Bainbridge, Phys. Rev. **44**, 57 (1933).

⁷ Lewis and Ashley, Phys. Rev. **43**, 837 (1933).

TABLE II. *Low temperature heat capacities (C_P) of the heavy hydrogens (in the ideal gaseous state), in calories/mole/degree.*

T , degrees absolute	Pure ortho H ² H ²	Pure para H ² H ²	Equil. mixture of H ² H ²	Non-equil. mixture of H ² H ²	H ¹ H ²
0	0.000	0.000	0.000	0.000	0.000
10	4.970	4.970	5.009	4.970	4.970
15	4.970	4.970	5.286	4.970	5.053
20	4.972	4.970	5.696	4.970	5.371
25	5.004	4.970	6.048	4.992	5.872
30	5.107	4.970	6.277	5.061	6.376
40	5.626	4.980	6.629	5.410	6.996
50	6.425	5.034	6.943	5.961	7.149
60	7.176	5.159	7.175	6.503	7.124
70	7.663	5.353	7.295	6.893	7.076
80	7.864	5.592	7.325	7.107	7.036
90	7.859	5.844	7.295	7.187	7.012
100	7.745	6.086	7.243	7.192	6.998
120	7.447	6.472	7.132	7.122	6.984
140	7.219	6.715	7.054	7.051	6.979
160	7.090	6.848	7.010	7.010	6.976
190	7.007	6.934	6.983	6.983	6.974
220	6.982	6.961	6.975	6.975	6.975
260	6.976	6.972	6.975	6.975	6.976
300	6.977	6.977	6.977	6.977	6.978

and even rotational states of the H₂² molecule.⁸ The results of these calculations are given in the accompanying tables and figures.

THE ROTATIONAL SPECIFIC HEAT CURVES OF H²H² AND OF H¹H²

In Table II we give values of the molar heat capacity, up to 300°K, for the four possible types of gaseous deuterium and for deuterium hydride.

The results are shown graphically in Figs. 1 and 2. It is interesting to compare Fig. 1 with Fig. 4 of Johnston and Davis¹ which gives the corresponding curves for nitrogen in the ideal gaseous condition. Except for temperature, the curves for the two gases are seen to be nearly identical, which is a consequence of their iden-

TABLE III. *Equilibrium distribution of deuterium molecules in ortho and para rotation states.*

T , °K	% Ortho	T , °K	% Ortho	T , °K	% Ortho
0	100.000	50	79.193	140	66.809
10	99.972	60	74.793	160	66.716
15	99.506	70	71.779	190	66.677
20	97.973	80	69.816	220	66.669
25	95.292	90	68.579	260	66.667
30	92.065	100	67.816	300	66.667
40	85.124	120	67.074		

⁸ For the H¹H² molecule, on the other hand, there is no distinction in the weightings, as between odd and even rotational states. This is a consequence of the wave mechanics and is demonstrated, experimentally, in the spectra of O¹⁶O¹⁸ and O¹⁸O¹⁷. Giauque and Johnston, J. Am. Chem. Soc. **51**, 1436, 3528 (1929).

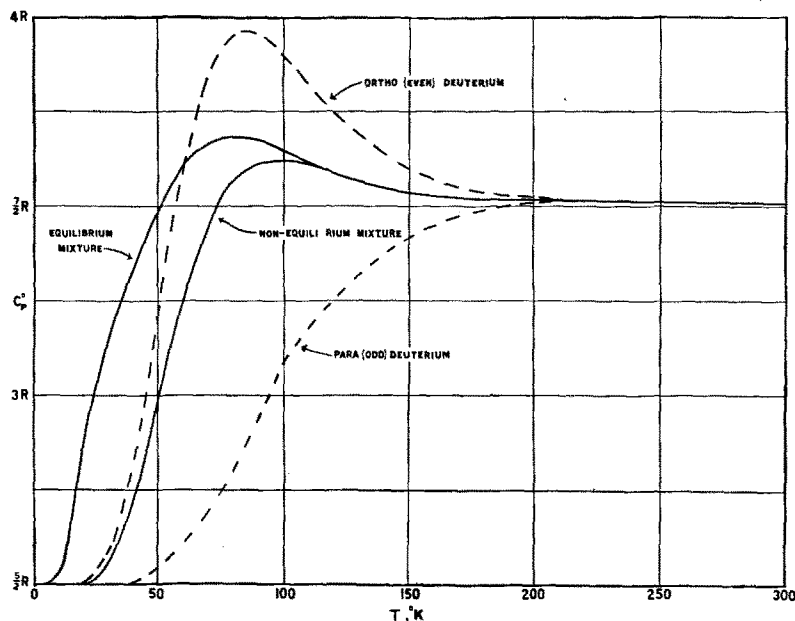


FIG. 1. Rotational portion of the heat capacity of deuterium, showing the influence of nuclear spin.

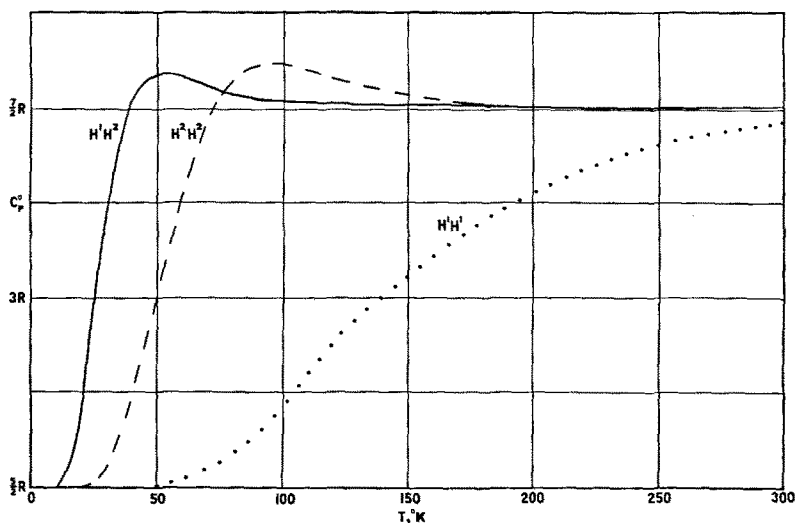


FIG. 2. Rotational portion of the heat capacity of H^1H^2 compared with the heat capacities of the normal (ortho-para) mixtures of H^2H^2 and of H^1H^1 , respectively.

tical nuclear statistics. The rotational heat capacity curves for nitrogen are, of course, hypothetical since nitrogen condenses at a temperature much above that at which its various forms attain rotational equipartition. This makes the case of deuterium the more interesting since at least three of the curves in Fig. 1 may be realized experimentally. It is also interesting to compare our Fig. 1 with the corresponding

figure for ordinary hydrogen⁹ which possesses a different nuclear statistics.

Fig. 2 shows the rotational specific heat curve for H^1H^2 (for which only one curve exists) together with the ordinary ($\frac{3}{4}$ ortho, $\frac{1}{4}$ para for

⁹ Cf. the diagram on page 193 of *Outlines of Atomic Physics*, Physics Staff of the University of Pittsburgh, John Wiley and Sons, New York, 1933, or plot the data of Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

H^1H^1 ; $\frac{2}{3}$ ortho, $\frac{1}{3}$ para for H^2H^2) non-equilibrium curves for the homonuclear gases. These latter are the curves which are measured under ordinary experimental conditions, with the gases prepared at room temperature.

The equilibrium distribution of deuterium molecules between ortho and para rotation states is given in Table III.

FREE ENERGIES, TOTAL ENERGIES, ENTROPIES AND HIGH TEMPERATURE HEAT CAPACITIES

"Free energies," "total energies," entropies and high temperature heat capacities are given in Tables IV, V and VI. These calculations all

TABLE IV. Values of $-(F^\circ - E_0^\circ)/T$ for H^2H^2 , for H^1H^2 and for atomic H^2 in the ideal gaseous state at 1 atmosphere (nuclear spin contributions included).¹⁰

$T, ^\circ\text{K}$	H^2H^2	H^1H^2	H^2 (atomic)
20	15.366	14.479	—
25	16.529	15.613	—
50	20.397	19.439	—
100	24.739	23.788	—
150	27.447	26.602	—
200	29.400	28.391	—
250	30.926	29.901	24.428
298.1	32.133	31.099	25.302
300	32.176	31.137	25.334
400	34.157	33.110	26.763
500	35.698	34.645	27.871
600	36.961	35.902	28.777
700	38.033	36.968	29.543
800	38.965	37.895	30.206
900	39.792	38.715	30.791
1000	40.536	39.451	31.314
1250	42.131	41.025	32.423
1500	43.459	42.329	33.328
2000	45.610	44.435	34.758
2500	47.335	46.119	35.866
3000	48.782	47.533	36.771

¹⁰ We have also computed many values of free energy which are omitted from the table in order to conserve space. The following empirical equations reproduce the free energy to within 0.001 or 0.002 calorie/mole/degree: between 1000° and 3000°:

For H^2H^2 ,

$$(F^\circ - E_0^\circ)/T = 7.543 - 1.5R \ln T \\ - R \ln(1 - \exp(-1862.6/T)) - 1.4000 \times 10^{-5}T + 8.1112 \\ \times 10^{-9}T^2 - 9.6668 \times 10^{-12}T^3 + 1.5556 \times 10^{-15}T^4. \quad (2)$$

For H^1H^2 ,

$$(F^\circ - E_0^\circ)/T = 8.598 - 1.5R \ln T \\ - R \ln(1 - \exp(-2257.7/T)) + 9.1667 \times 10^{-6}T - 8.5000 \\ \times 10^{-9}T^2 - 6.6667 \times 10^{-13}T^3. \quad (3)$$

These equations do not reproduce the correct values below 1000°.

TABLE V. $(E^\circ - E_0^\circ)$ for gaseous H^2H^2 and for gaseous H^1H^2 (translational energy not included), in calories per mole.

$T, ^\circ\text{K}$	H^2H^2				H^1H^2
	Pure ortho	Pure para	Equilibrium mixture	$\frac{2}{3}$ ortho $\frac{1}{3}$ para	
0	0.00	170.22	0.00	56.74	0.00
20	0.01	170.22	3.46	56.74	1.27
25	0.09	170.22	8.10	56.80	4.50
50	14.62	170.61	46.74	66.62	49.31
100	143.54	197.20	160.81	161.43	154.15
150	265.38	274.32	268.35	268.36	232.99
200	369.41	370.54	369.79	369.79	355.39
250	470.16	470.30	470.21	470.21	455.77
300	570.61	570.62	570.62	570.62	556.27
400	771.86	771.86	771.86	771.86	757.70

$T, ^\circ\text{K}$	H^2H^2	H^1H^2	$T, ^\circ\text{K}$	H^2H^2	H^1H^2
500	975.5	960.0	1250	2810	2666
600	1183.5	1164.3	1500	3581	3362
700	1399.3	1372.2	1750	4413	4129
800	1625.8	1585.5	2000	5299	4950
900	1865.1	1807.8	2500	7187	6734
1000	2118.1	2039.3	3000	9196	8658

TABLE VI. Entropies (nuclear spin included) and molar heat capacities of H^2H^2 and of H^1H^2 in the ideal gaseous state (in calories/mole/degree).

$T, ^\circ\text{K}$	S°	C_p°	S°	C_p°
298.1	38.731	6.977	37.954	6.978
400	41.054	6.985	39.972	6.985
500	42.616	7.019	41.532	6.998
600	43.901	7.081	42.810	7.025
700	44.999	—	43.896	7.072
800	45.965	7.294	44.844	7.143
1000	47.621	7.567	46.458	7.335
1250	49.346	—	48.124	7.619
1500	50.813	8.183	49.537	7.901
2000	53.227	8.600	51.877	8.357
2500	55.177	8.879	53.780	8.687
3000	56.814	9.083	55.386	8.936

refer to the ideal gaseous state at a pressure of one atmosphere and, for convenience in use at low temperatures, the tables of free energy and of entropy are given with nuclear spin contributions *included*.¹¹ In line with our usual custom, and that of Giauque and co-workers, we have employed the natural constants given in the *International Critical Tables*.^{12, 13}

¹¹ To obtain entropies or free energies with nuclear spin *excluded* the entropy or free energy values should each be decreased (numerically) by $R \ln 9$ ($= 4.366$) for H^2H^2 , $R \ln 6$ ($= 3.560$) for H^1H^2 and $R \ln 3$ ($= 2.183$) for atomic deuterium. Calculations of equilibrium with nuclear spin entropy or free energy arbitrarily excluded are not permissible in reactions involving molecular deuterium, below 150°K.

¹² Int. Crit. Tab. Vol. I, p. 16.

¹³ As a near approximation the values of thermodynamic properties computed with one set of natural constants may be converted to another set by multiplying through by the direct ratio of the values adopted for the gas constant R . This is a consequence of the fact that R enters as a factor in all of the entries in Tables II, IV, V and VI. The value of R

The values recorded in our Table VI are correct for either the equilibrium or the non-equilibrium mixtures of ortho and para deuterium. Those recorded in Table IV refer to the *equilibrium mixture* but above 100°K identical results are obtained for the non-equilibrium mixture.

We take the zero-point energy (E_0°) of each gas as that corresponding to the lowest available quantum state (here $v=0$, $J=0$) of H^2H^2 and of H^1H^2 .

Urey and Rittenberg¹⁴ have published short tables of the free energies of deuterium and of some of its compounds. When account is taken of the different set of natural constants¹³ which were employed, and also of the slightly different molecular constants, close agreement is obtained for those temperatures for which the calculations are duplicated.

It is interesting to compare the contributions of molecular stretching and of anharmonic vibration to the high temperature heat capacities, for the three hydrogens. The comparison is given in Table VII. The figures for H^1H^1 are

TABLE VII. Contributions of molecular stretching and of anharmonic vibration to the molar heat capacities of the hydrogens (calories/mole/degree).

T , °K	H^1H^1	Stretching H^1H^2	H^2H^2	Departure from Hooke's law H^1H^1	H^1H^2	H^2H^2
1000	0.072	0.072	0.072	0.010	0.009	0.025
2000	0.135	0.136	0.135	0.097	0.101	0.138
3000	0.174	0.178	0.175	0.223	0.248	0.273

TABLE VIII. Distribution of H^2H^2 molecules among the vibrational levels as a function of the temperature (°K).

v	400°	600°	800°	1000°
0	99.998	99.92	99.51	98.57
1	0.002	0.08	0.48	1.40
2	0.000	0.00	0.01	0.02
3	0.000	0.00	0.00	0.00
v	1500°	2000°	3000°	
0	93.98	87.66	74.53	
1	5.59	10.66	18.54	
2	0.38	1.43	4.92	
3	0.05	0.21	1.39	
4	0.00	0.03	0.42	
Higher	0.00	0.01	0.10	

given in the International Critical Tables, and used in these calculations, is 1.9869.

¹⁴ Urey and Rittenberg, J. Chem. Phys. 1, 137 (1933).

TABLE IX. Distribution of H^1H^2 molecules among the vibrational levels as a function of the temperature (°K).

v	600°	800°	1000°
0	99.982	99.85	99.43
1	0.018	0.15	0.56
2	0.000	0.00	0.01
3	0.000	0.00	0.00
v	1500°	2000°	3000°
0	96.78	92.28	81.31
1	3.09	7.01	14.69
2	0.12	0.65	3.08
3	0.01	0.06	0.70
4	0.00	0.00	0.16
Higher	0.00	0.00	0.06

taken from Davis and Johnston.¹ Those for H^2H^2 and for H^1H^2 were calculated in the manner described in the same paper.

Tables VIII and IX show the distributions of molecules among the vibrational levels as a function of the temperature.

THE DISSOCIATION OF THE HYDROGENS

We have calculated dissociation constants, and percentage dissociations at a total pressure of 1 atmosphere, for H^2H^2 and for H^1H^2 by the relationships:

$$-R \ln K + \Delta F^\circ/T = \left(\frac{F^\circ - E_0^\circ}{T} \right)_{\text{atoms}} - \left(\frac{F^\circ - E_0^\circ}{T} \right)_{\text{molecule}} + \frac{\Delta E_0^\circ}{T} \quad (4)$$

and

$$100\alpha = 100[K/(K+4P)]^{\frac{1}{2}}, \quad (5)$$

where 100α is the percentage dissociation. The values of $(F^\circ - E_0^\circ)/T$ are taken from our Table IV and from Table VII of Giauque.⁹ ΔE_0° was taken to be $104,593 \pm 1000$ cal. for the dissociation of H^2H^2 , and $103,618 \pm 1000$ cal. for the dissociation of H^1H^2 .¹⁵

¹⁵ These values are greater than that for H^1H^1 ($102,800 \pm 1000$) by the difference in the zero-point energies of vibration (1793 calories/mole and 818 cal./mole for H^2H^2 and H^1H^2 , respectively, relative to H^1H^1) and rest on the assumption that there is a negligible isotope effect on the electronic terms of hydrogen. We are informed by Professor R. T. Birge (personal communication) that Dr. C. R. Jeppesen has found an electronic isotope effect of approximately 135 wave numbers in the A-C band system of H^1H^2 . If, as Professor Birge suggests, this can be accounted

TABLE X. *Dissociation constants and percentage dissociations of hydrogen.*

T , °K	H^1H^1	$\frac{K}{\text{H}^1\text{H}^2}$	H^2H^2
1000	64.49×10^{-19}	12.39×10^{-19}	9.27×10^{-19}
1500	36.00×10^{-11}	7.831×10^{-11}	6.747×10^{-11}
2000	29.60×10^{-7}	6.811×10^{-7}	6.227×10^{-7}
2500	6.915×10^{-4}	1.638×10^{-4}	1.542×10^{-4}
3000	26.87×10^{-3}	6.474×10^{-3}	6.187×10^{-3}

T , °K	H^1H^1	Percent Dissociation (1 atmosphere) H^1H^2	H^2H^2
1000	13×10^{-3}	5.6×10^{-3}	4.8×10^{-3}
1500	9.5×10^{-4}	4.4×10^{-4}	4.1×10^{-4}
2000	8.6×10^{-2}	4.1×10^{-2}	3.9×10^{-2}
2500	1.31	0.64	0.62
3000	8.1	4.0	3.9

The results of our calculations at five temperatures are given in Table X, in which we also include figures for the dissociation of H^1H^1 , published by Giauque.⁹

It is interesting to note the nearly equal dissociation constants for the two heavier molecules and the fact that *both* of these molecules are considerably less dissociated than is the usual hydrogen. These relationships are not those that one would expect from classical considerations. Indeed, it is possible to show by the present method of treatment that at sufficiently high temperatures (temperatures at which $\Delta E_0^\circ/T$ becomes negligible) the two homonuclear molecules will have equal dissociation constants while K for H^1H^2 will be one-half of the K for either of the others. The relationships exhibited in Table IX are a consequence, primarily, of the difference in the zero-point energies of vibration and the nearly equal constants for the two heavier molecules over this range of temperature are a fortuitous consequence of the magnitude of the isotopic vibrational effects. If account is taken of the electronic isotope shifts referred to by Birge¹⁵ the small differences that exist in the K 's for H^1H^2 and for H^2H^2 will be somewhat increased.

for in terms of the electronic interaction discussed by Hughes and Eckert [Phys. Rev. **36**, 694 (1930)] and if account is also taken of the isotope effect on the zero-point energy of the *atom* (the zero-point energy of the H^2 atom is 84.4 cal./g atom less than for H^1), ΔE_0° for H^1H^2 will be some 50 calories larger than the value which we are using. A corresponding effect would be applicable to ΔE_0° for H^2H^2 . The influence of these changes would be to further *decrease* the dissociation both of H^1H^2 and of H^2H^2 , the decrease being the greater for the heavier molecule.

Urey and Rittenberg¹⁴ have considered the reaction $\text{H}^1\text{H}^1 + \text{H}^2\text{H}^2 = 2\text{H}^1\text{H}^2$, which is especially interesting at low temperatures. They found that, even at 700°K, the equilibrium constant for this reaction failed to attain the classical value of 4 by some 5 percent. We have calculated the constant at higher temperatures by the relationship

$$K = K_{11}K_{22}/(K_{12})^2, \quad (6)$$

in which the K 's with sub-numerals refer to H^1H^1 , H^2H^2 and H^1H^2 , respectively, and were taken from Table X. The results indicate that the constant for this reaction lies under 4 by about 3 percent at 1000°, 1 percent at 1500° and by about 0.5 of 1 percent at 3000°.

THE ENTROPY OF SOLID DEUTERIUM

Measurements of the heat capacities of solid and of liquid deuterium, together with the heats of fusion and of vaporization, are of interest in connection with the proper usage of the third law of thermodynamics. Four examples¹⁶ are now known for which the correct values of entropy for use in thermodynamic calculations are not given by the $\int C_p dT$'s in conjunction with the ordinary application of the third law. One of these is ordinary hydrogen for which a correction amounting to $(R \ln 4 + \frac{3}{4}R \ln 3)$ must be applied to the calorimetric value to obtain the absolute entropy. Of this amount, $R \ln 4$ is contributed by nuclear spin and at temperatures comparable to room temperature and above may be disregarded in the conventional usage of the third law, provided nuclear spin effects are excluded consistently for the other reactants and products as well. The remaining term, $\frac{3}{4}R \ln 3$, is a consequence of the rotational non-degeneracy of ortho hydrogen which goes into the solid state with one unit of rotational angular momentum which it holds down to about 2°K.¹⁷

There are four possibilities regarding the behavior of solid deuterium as a consequence of

¹⁶ (a) H_2 , Giauque and Johnston, J. Am. Chem. Soc. **50**, 3221 (1928); Phys. Rev. **36**, 1592 (1930); (b) NO, Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929); (c) CO, Clusius and Teske, Zeits. f. physik. Chemie **B6**, 135 (1929); Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932); (d), N_2O , Clusius, Nature **130**, 775 (1932).

¹⁷ Simon, Mendelssohn and Ruhemann, Naturwiss. **18**, 34 (1930).

its nuclear statistics. (1) H^2H^2 may completely lose its nuclear spin entropy, amounting to $R \ln 9$ entropy units, in the process of freezing. This corresponds, physically, to the formation of a molecular crystal lattice in which the component molecules are composed of atoms whose respective spin momentum vectors are antiparallel to one another. In this event the values of entropy based on calorimetric measurements should be identical with those recorded in our Table VI, which include nuclear spin. (2) Para molecules may undergo transformation, at low temperatures, into the stable ortho form with its nuclear spin weighting of six. The entropy values obtained calorimetrically should then be lower than those given in Table VI by an amount $R \ln 6$. (3) The para molecules may lose the one unit of rotation which they possess in their ground state without, however, losing their identity. This would correspond to a molecular crystal lattice in which the para molecules (constituting $\frac{1}{3}$ of the total) would perform weak angular oscillations about fixed positions without making complete rotations.¹⁸ In this event the calorimetric determinations of entropy should be lower than those given in Table VI by $R \ln 9$. This corresponds to the case actually observed for nitrogen¹⁹ which possesses the same nuclear statistics as does deuterium. The formation of an atomic crystal lattice would lead to the same results. (4) The para molecules may retain their one unit of rotation in the crystal lattice while both para and ortho molecules retain their full spin multiplicity. This situation would lead to calorimetric values of entropy lower than those in Table VI by an amount $(R \ln 9 + \frac{1}{3}R \ln 3)$. This is analogous to the case of H^1H^1 although the numerical corrections are different.

Of these four possibilities, (1) and (2) are improbable and (4) is more probable than (3). Experimental heat capacity measurements would clearly distinguish between the several possi-

bilities. It is also probable, assuming case (4) to be the actual situation, that H^2H^2 in the solid state would begin to lose the entropy associated with the rotation of its para molecules at a temperature somewhat above that at which the effect occurs for H^1H^1 . This would bring the investigation of the effect into a more suitable experimental region than the one necessary for the investigation of ordinary hydrogen.

The calorimetric entropy of solid H^1H^2 , in the pure state, is also of interest since it does not possess the possibilities of ortho-para influences which are responsible for the observed behavior of ordinary hydrogen and for the anticipated behavior of pure deuterium. We would expect the calorimetrically determined entropy of H^1H^2 to lie $R \ln 6$ entropy units below the values recorded in Table VI. We would not expect thermal effects similar to those observed at 2°K by Simon and co-workers to appear in solid H^1H^2 at temperatures above some very small fraction of a degree absolute.

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Note added in proof.—An experimental paper by Jeppeson²⁰ on the spectrum of H^1H^2 , which has appeared since the manuscript was submitted, gives molecular constants for H^1H^2 which are in excellent agreement with our Table I except for the value of β_e . Although we do not understand the discrepancy, since this constant depends on others in the list, the influence of the disagreement is negligible for even the precision to which the tables in this paper are given. An experimental paper by Farkas and Farkas²¹ has also appeared with measurements of the ortho-para distributions at equilibrium in almost exact agreement with our Table III.

¹⁸ Cf. Pauling, Phys. Rev. **36**, 430 (1930).

¹⁹ Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

²⁰ Jeppeson, Phys. Rev. **45**, 480 (1934).

²¹ Farkas and Farkas, Science **79**, 204 (1934); Proc. Roy. Soc. **A144**, 481 (1934).